

Electronic Supplementary Information

Solvent induced reversible single-crystal-to-single-crystal structural transformation in dynamic metal organic frameworks: A case of enhanced hydrogen sorption in polycatenated framework

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Experimental section

Chemicals

Immensely fresh $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, imidazole, dichloromethane, tetrabutylammonium chloride have been acquired from the Sigma-Aldrich Chemical Co. All other reagents and solvents have been bought from commercial sources and used except further clarification. di(1H-imidazol-1-yl)methane¹ have been synthesized by a reaction between dichloromethane and imidazole in presence potassium hydroxide and tetrabutyl aluminium bromide (TBAB) at 40°C in inert atmosphere condition. Na_2 -fum had been synthesized by the sluggish collation of solid NaOH to the analogous acids (H_2 -fum) in water in a 2:1 ratio and allowed to evaporate until dryness.

Physical measurements

Elemental analyses (C, H, N) have been performed using a PerkinElmer 240C elemental analyzer. FT-IR spectra have been obtained on a PerkinElmer spectrometer (Spectrum II) with the samples. PerkinElmer STA8000 thermal analyzer has been used for thermogravimetric analysis (TGA) with a ramp rate of 10 °C/min from room temperature to 600 °C under nitrogen flow. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Discover instrument with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 40 mA. UV-vis spectra are collected in PerkinElmer Lambda 35 instrument with integrating sphere attachment. Fluorescence measurements were done using HoribaFluoroMax 4 spectrofluorimeter.

Sorption measurements

Quantachrome Autosorb– iQ adsorption instrument have been used to measured adsorption isotherms N₂ (77 K), CO₂ (195 K) and H₂ (77 K) for the dehydrated frameworks of **1a** and **2''**. Very pure N₂ gas (99.999% purity), CO₂ gas (99.95%) and H₂ gas (99.999%) have been used for this measurement. The N₂ (at 77 K, liquid nitrogen bath), CO₂ (at 195 K, dry ice-acetone bath) and H₂ (at 77 K, liquid nitrogen bath) sorption measurements have been carried out in the pressure range 0–1 bar using dehydrated samples of **1a** and **2''**. Before measurements, all the as-synthesized complexes (40 mg for each) have been dehydrated in the sample tube at 413 K for 3 h under a 1×10^{-1} Pa vacuum. By controlled introducing ultra pure helium gas (99.999% purity) into the sample tube and allowing it to diffuse into the sample, the dead volume has been measured. The gas adsorption volume for each and every measurement has been calculated from the difference of pressure ($P_{\text{cal}} - P_{\text{e}}$), where P_{cal} signifies the calculated pressure without any gas adsorption and P_{e} indicates the observed pressure at equilibrium. The pressure change has been monitored by taking the adsorbent in the sample tube, and the degree of adsorption was calculated by observing the decrease in pressure at equilibrium.

Synthesis

{{Zn₂(fum)₂(dim)₂}(H₂O)(MeOH)}_n (1). After deprotonation of H₂-fumarate in aqueous solution by NaOH (2 mmol, 80 mg), the resulting 20 ml solution of Na₂-fum (1 mmol, 160 mg) was slowly mixed with a methanolic solution (20 mL) of di(1H-imidazol-1-yl)methane (1 mmol, 148 mg) and stirred for 20 min to mix well. slowly and carefully, 4ml aqueous solution of Zn(II) from 20 mL aqueous solution of Zn(NO₃)₂·6H₂O (1 mmol, 0.297 g) was layered with 6 mL of the aforesaid mixed-ligand solution by using 5 mL of buffer (1:1 water/ MeOH mixture). At the juncture of the solution colourless block-shaped single crystals appropriate for X-ray diffraction analysis were form in the layer tube after 4 days. The crystals were collected, washed with MeOH, and dried under air to separate for experiments. Yield: 82%. Elemental analysis, calculated for C₂₃H₂₆N₈O₁₀Zn₂ (705.29): C 39.13; H 3.68; N 15.87. Found: C 39.08; H 3.55; N 15.70. IR spectra (KBr pellet, 4000–400 cm⁻¹): $\nu(\text{O-H})$, 3479 (stretch, H-bonded); $\nu(\text{C-H, imidazole})$, 3007 (stretch); $\nu(\text{C-H, alkane})$, 2816 (stretch) and 1359 (bending); $\nu(\text{C-C, imidazole})$, 1613–1516 (stretch); and $\nu(\text{C-O})$, 1231 (stretch).

{{Zn₂(fum)₂(dim)₂}(H₂O)} (1a). Complex **1** undergoes selective solvent (methanol) elimination and structural transformation to complex **1a** at room temperature. Elemental analysis, calculated for C₁₁H₁₂N₄O₅Zn (345.62): C 38.19; H 3.47; N 16.20. Found: C 38.06; H 3.40; N 16.15. IR spectra (KBr pellet, 4000–400 cm⁻¹): ν(O–H), 3445 (stretch, H-bonded); ν(C–H, imidazole), 3027 (stretch); ν(C–H, alkane), 2819 (stretch) and 1359 (bending); ν(C–C, imidazole), 1615–1506 (stretch); and ν(C–O), 1232 (stretch).

{{Zn₂(fum)₂(dim)₂}(H₂O)(MeOH)}_n (1'). Complex **1a** added to methanol solution for 30 minutes, resulting a new complex, which is complex **1**, denoted as **1'**. Elemental analysis, calculated for C₂₃H₂₆N₈O₁₀Zn₂ (705.19): C 39.13; H 3.68; N 15.87. Found: C 39.06; H 3.52; N 15.68. IR spectra (KBr pellet, 4000–400 cm⁻¹): ν(O–H), 3479 (stretch, H-bonded); ν(C–H, imidazole), 3007 (stretch); ν(C–H, alkane), 2816 (stretch) and 1359 (bending); ν(C–C, imidazole), 1613–1506 (stretch); and ν(C–O), 1231 (stretch).

{{Cd₂(fum)₂(dim)₂}(H₂O)}_n (2). By following the same procedure, instead of Zn(NO₃)₂·6H₂O, Cd(NO₃)₂·4H₂O has been used. Suitable colorless crystals obtain at the juncture of the solution after 1 week for X-ray diffraction analysis. The crystals were collected, washed with MeOH, and dried under air to separate for experiments. Yield 78%. Elemental analysis, calculated for C₂₃H₂₄N₈O₁₀Cd₂, (797.29): C 34.62; H 3.01; N 14.05. Found: C 34.58; H 2.94; N 14.01. IR spectra (KBr pellet, 4000–400 cm⁻¹): ν(O–H), 3417 (stretch, H-bonded); ν(C–H, imidazole), 3011 (stretch); ν(C–H, alkane), 1396 (bending); ν(C–C, imidazole), 1582 (stretch); and ν(C–O), 1230 (stretch).

{{Cd₂(fum)₂(dim)₂}(H₂O)} (2a). After elimination of solvent (methanol) molecules in open air from the reaction mixture of **2**, dissolution–recrystallization structural transformation has been happened, formed complex **2a**. Elemental analysis, calculated for C₁₈H₂₀N₈O₇Cd (587.81): C 34.75; H 3.40; N 19.05. Found: C 34.68; H 3.35; N 19.01. Anal. Cal. for, IR spectra (KBr pellet, 4000–400 cm⁻¹): ν(O–H), 3180 (stretch, H-bonded); ν(C–H, imidazole), 3006 (stretch); ν(C–H, alkane), 2824 (stretch) and 1338 (bending); ν(C–C, imidazole), 1529 (stretch); and ν(C–O), 1238 (stretch).

{{Cd₂(fum)₂(dim)₂}(H₂O)}_n (2'). Immersing the complex **2a** in methanol-water solvents for 6 days, converts to a similar structure of **2**, denoting as **2'**. Elemental analysis, calculated for C₂₃H₂₄N₈O₁₀Cd₂, (797.29): C 34.62; H 3.01; N 14.05. Found: C 34.58; H 2.94; N

14.01. IR spectra (KBr pellet, 4000–400 cm^{-1}): $\nu(\text{O-H})$, 3417 (stretch, H-bonded); $\nu(\text{C-H}$, imidazole), 3011 (stretch); $\nu(\text{C-H}$, alkane), 1396 (bending); $\nu(\text{C-C}$, imidazole), 1582 (stretch); and $\nu(\text{C-O})$, 1230 (stretch).

Structural transformation

The single crystal to single crystal (SCSC) structural transformation and dissolution–recrystallization structural transformation (DRST) have been studied by single crystal x-ray diffraction, luminescence and powder crystal x-ray diffraction studies. The colourless block crystals of complex **1** have been collected by washing with MeOH:H₂O (1:1) solution from the layer tubes. The dry crystals of complex **1** have been placed in open air for seven days, after that single crystal X-ray diffraction studies has been performed, formed a new crystal, denoted as **1a**. Also, the powder x-ray diffraction studies have been done for these two complexes, exhibit exactly similar peak position matching with their simulated patterns (Fig. S23). Complex **1a** has been revert back to complex **1** by immersing it in methanol for 30 minutes, confirmed by single crystal x-ray diffraction and luminescence studies. Single crystal x-ray diffraction studies have been done for complex **2** after formation of 30 days at the layer tube, showed a different crystal due to the slow evaporation of methanol molecules from the tube, which denoted as **2a**. The complex **2a** reverses back to complex **2**, after immersing it in equal ratio of methanol-water solution for six days, which has been confirm by single crystal x-ray diffraction studies.

Crystallographic data collection and refinement

The X-ray single-crystal data for complexes **1**, **1a**, **1'**, **2**, **2a** and **2'** have been collected at room temperature in a Bruker made APEX III diffractometer. At first, single crystals of both the compounds have been isolated and then mounted on the glass fiber tip using commercial super glue. Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a sealed tube X-ray source has been used. The raw data have been integrated using the SAINT² program and by utilizing SADABS,³ the absorption corrections were performed. The structures have been solved by SHELXL-2016/6,⁴ and full-matrix least-squares refinements on F^2 for all non-hydrogen atoms were performed by SHELXL-2016/6,⁴ with anisotropic displacement parameters. For complex **1**, Due to thermal disorder hydrogen atom in C22 carbon atom cannot be fixed. Also, hydrogen atoms in solvents molecules (methanol and water) cannot be fixed in complex **1** due to thermal disorder. For complex **1a**, hydrogen atom in solvent water molecules have not fixed as well as for complex **1'** hydrogen

atoms of solvent methanol molecules, water molecules, C23, and C6 atom cannot be fixed. In case of complex **2**, hydrogen atoms of solvent methanol molecules, for complex **2a** hydrogen atoms of coordinated water molecules as well as solvent water molecules and similarly for compound **2'** hydrogen atoms of solvent molecules have not fixed by HFIX for thermal disorder atom and solvents molecules. All the calculations and molecular graphics were done by SHELXL-2016/6,⁴ PLATON v1.15,⁵ WinGX system Ver-1.80,⁶ Diamond v3.2, Mercury,⁷ and TOPOS.^{8,9} All the crystallographic data and structural refinement parameters for the compounds **1**, **1a**, **1'**, **2**, **2a**, and **2'** have been mentioned in Table 1. CCDC 2208735–2208740 contain the supplementary crystallographic data for this paper.

UV-visible spectroscopy study

UV-visible spectroscopy of complexes **1**, **1a**, **1'**, **2**, **2a**, **2'** and di(1H-imidazol-1-yl)methane have been study in PerkinElmer Lambda 35 instrument with integrating sphere attachment instrument. The solid sample of crystal puts in a holder with specific quartz attached, transfers Uv-vis radiation within ranges of 200nm to 500nm through the sample. The absorption maxima have been observed at 330nm wavelength for compound **1**, **1a**, and **1'**. The absorption maxima of compound **2**, **2a**, **2'** and di(1H-imidazol-1-yl)methane have been observed at 300nm, 340nm, 300nm and 320nm wavelength respectively.

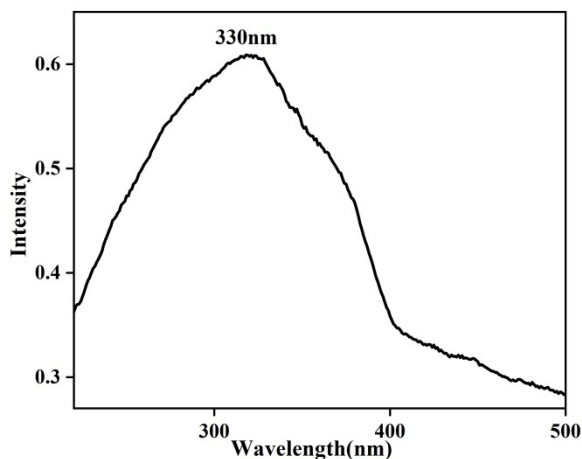


Fig. S1 UV-vis spectra of complex **1**

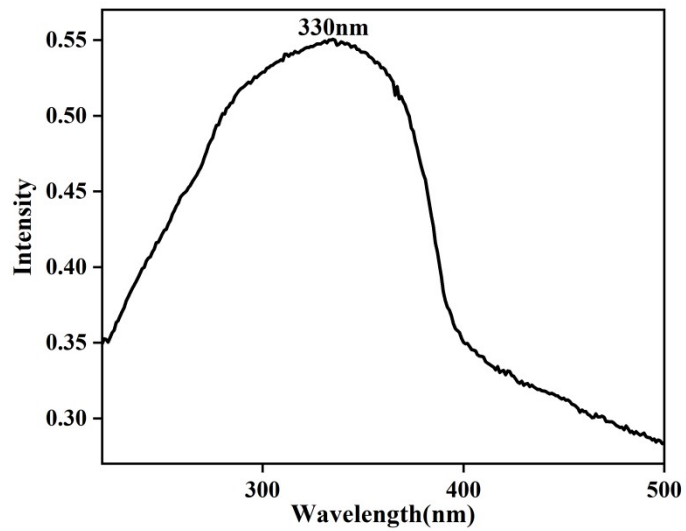


Fig. S2 UV-vis spectra of complex **1a**

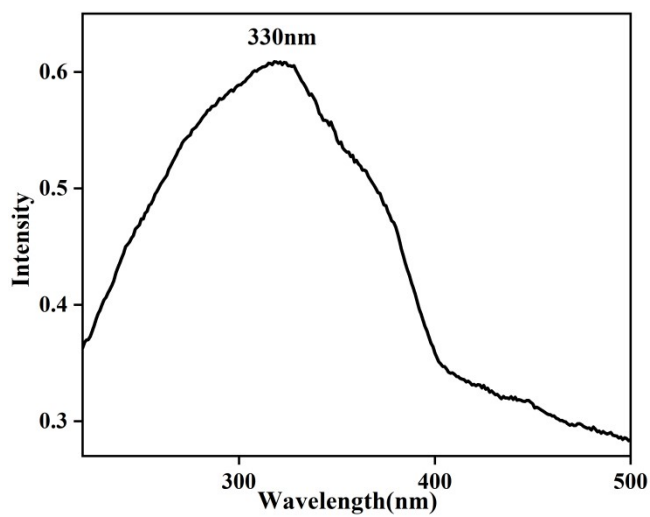


Fig. S3 UV-vis spectra of complex **1'**

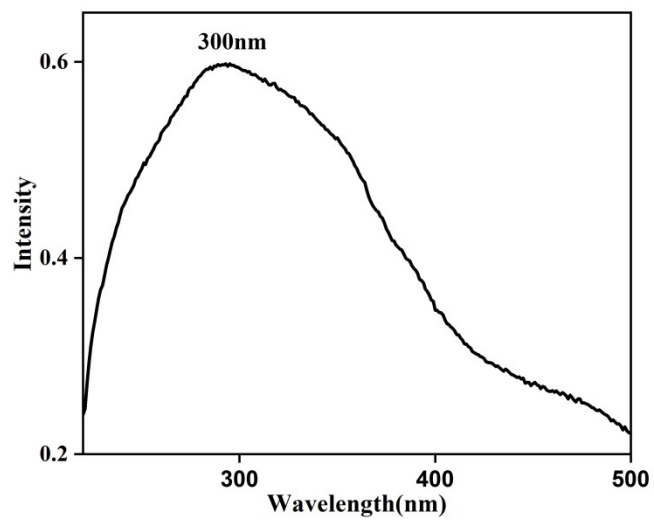


Fig. S4 UV-vis spectra of complex **2**

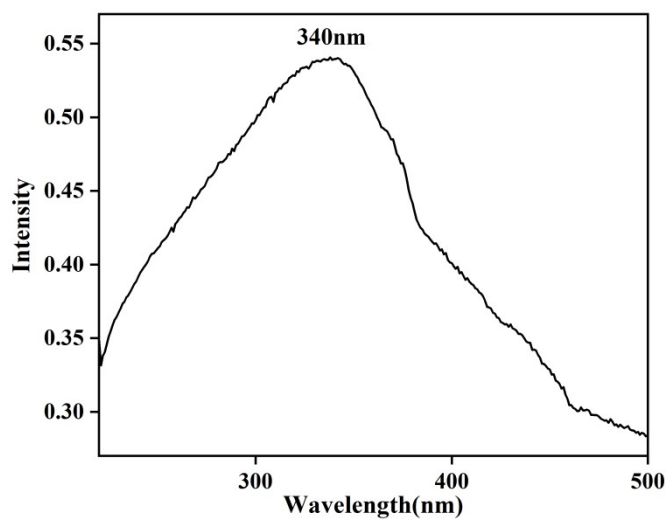


Fig. S5 UV-vis spectra of complex **2a**

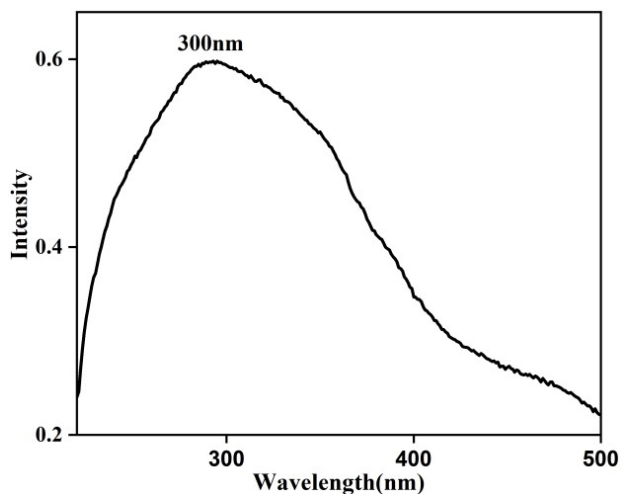


Fig. S6 UV-vis spectra of complex 2'

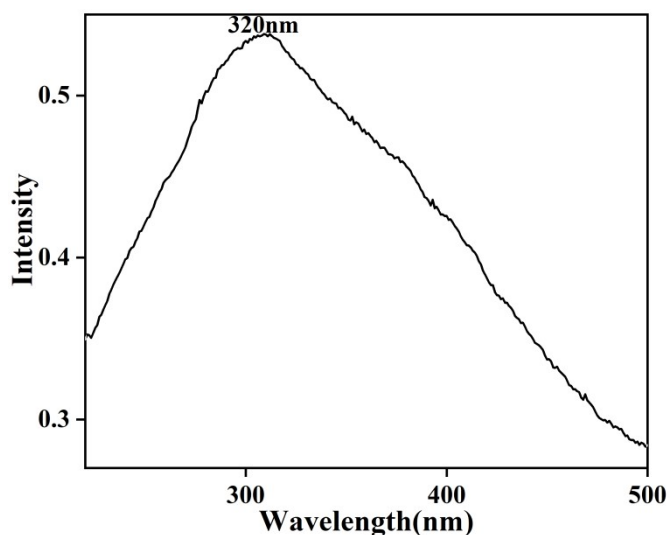


Fig. S7 UV-vis spectra of di(1H-imidazol-1-yl)methane ligand

FT-IR spectroscopy study

FT-IR spectra of complexes **1**, **1a**, **1'**, **2**, **2a**, and **2'** have been study in PerkinElmer spectrometer (Spectrum II) instrument. The pinch of solid sample of crystal puts in a mortar pastel with the pinch of dry KBr, paste the mixture to powder, forms a transparent KBr plate, through which the radiate passes with in the ranges of 4000cm^{-1} to 400cm^{-1} . The specific characterisation peaks of all the complexes have been mentioned in their respective figure.

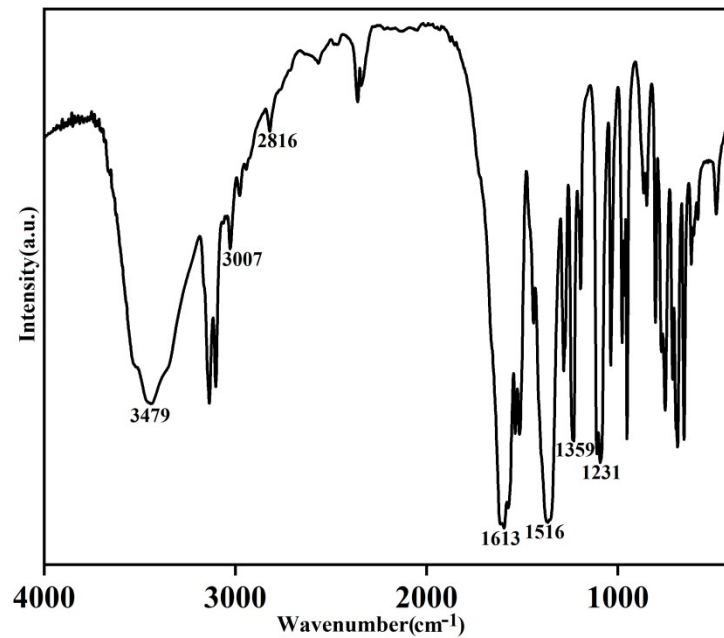


Fig. S8 FT-IR spectra of **1**

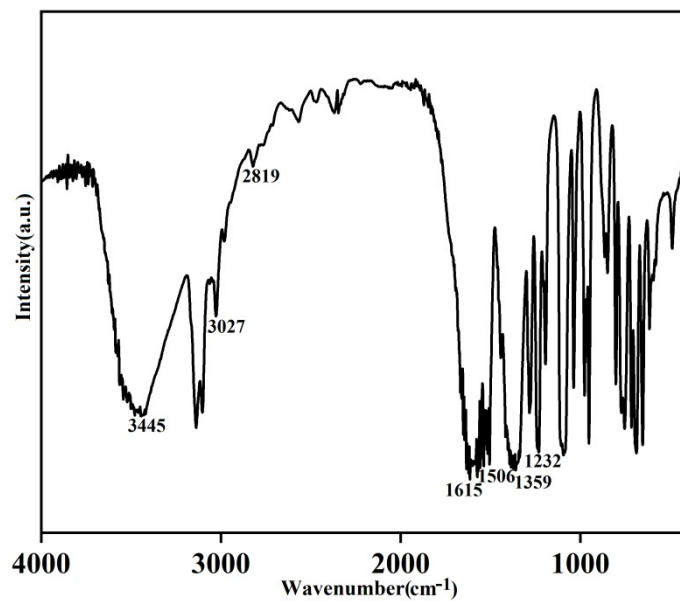


Fig. S9 FT-IR spectra of **1a**

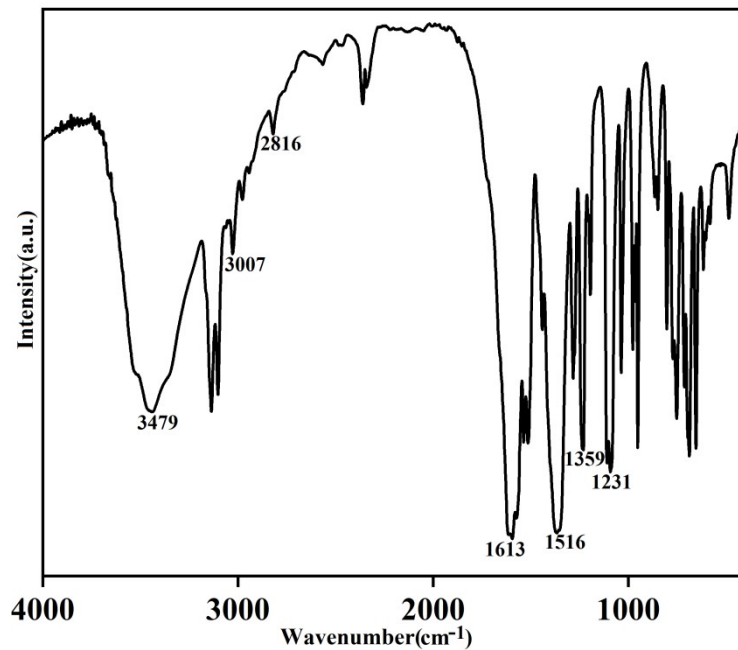


Fig. S10 FT-IR spectra of 1'

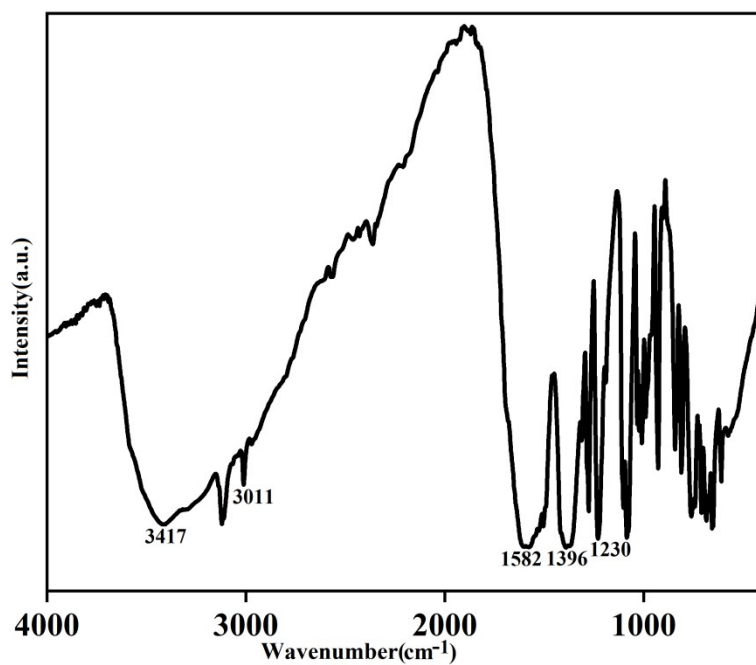


Fig. S11 FT-IR spectra of 2

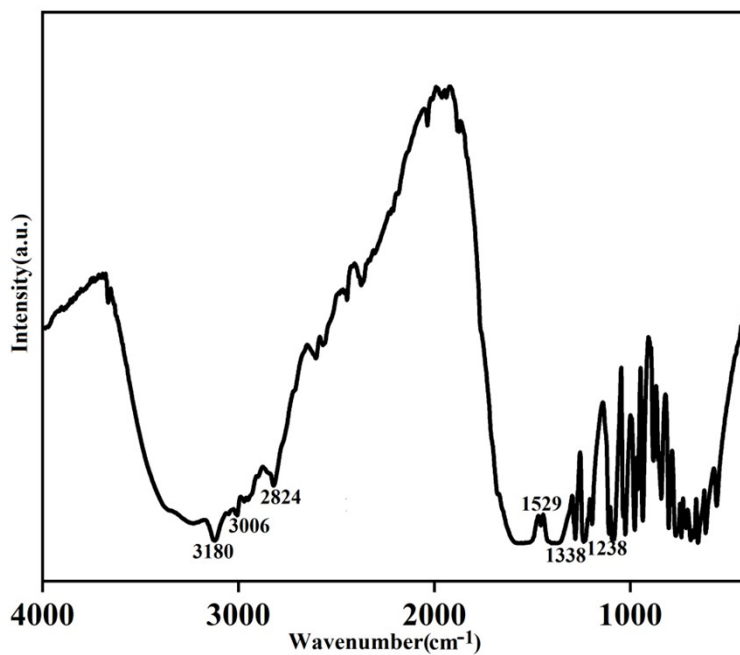


Fig. S12 FT-IR spectra of 2a

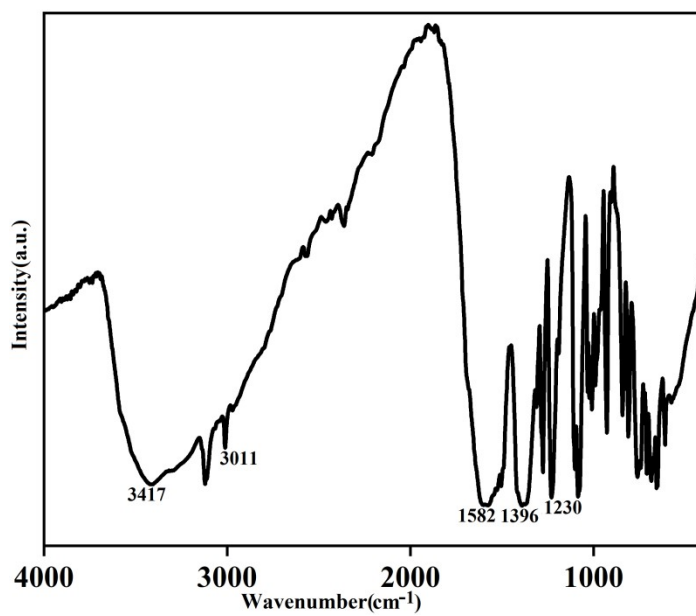


Fig. S13 FT-IR spectra of complex 2'

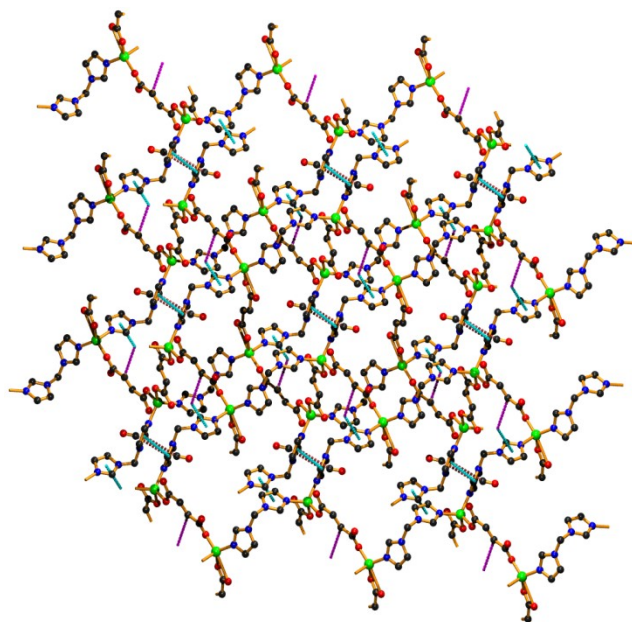


Fig. S14 Intermolecular π - π & C-H... π interactions in complex **1**.

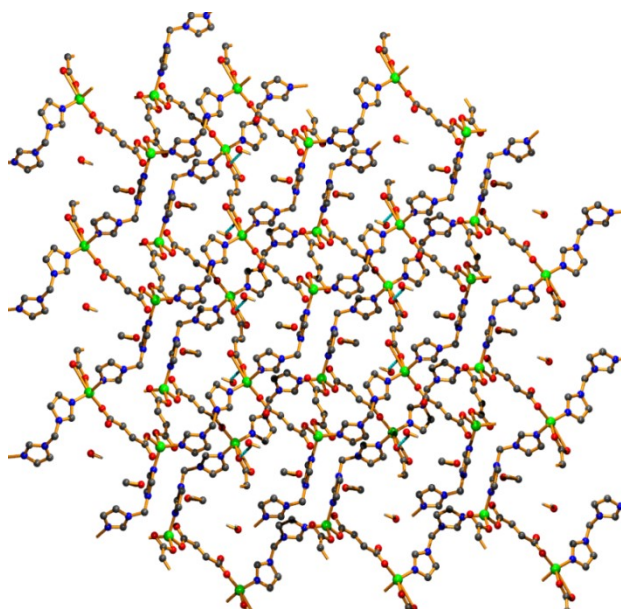


Fig. S15 Intermolecular H-bonding interactions in **1**

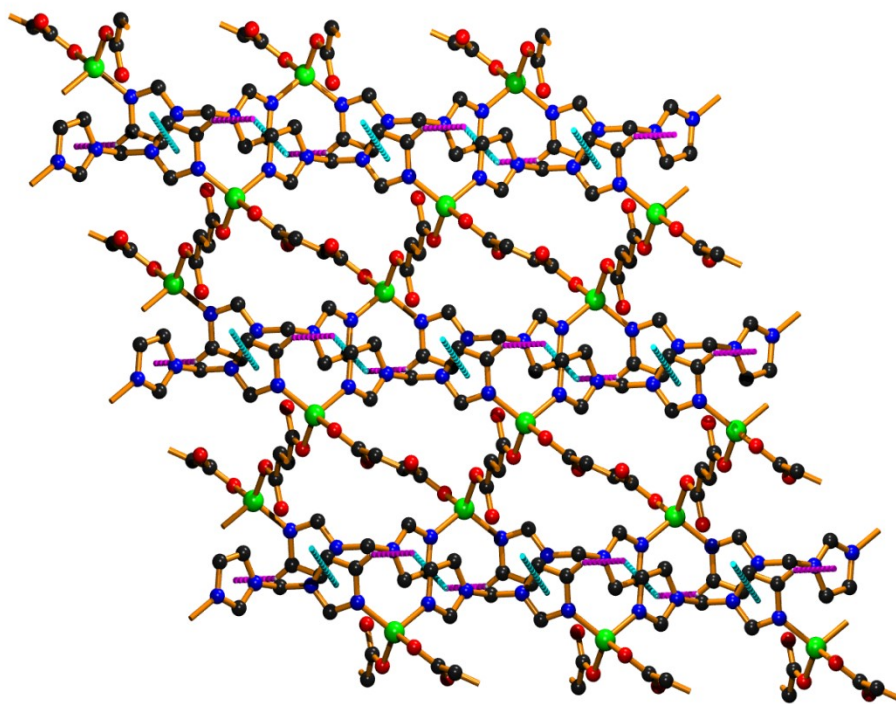


Fig. S16 Intermolecular π - π & C-H... π interactions in complex **1a**

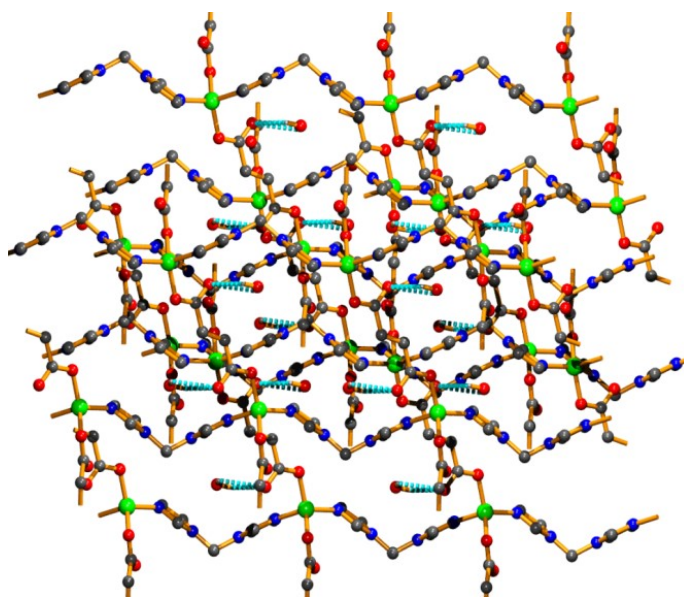


Fig. S17 Intermolecular H-bonding interactions in complex **1a**

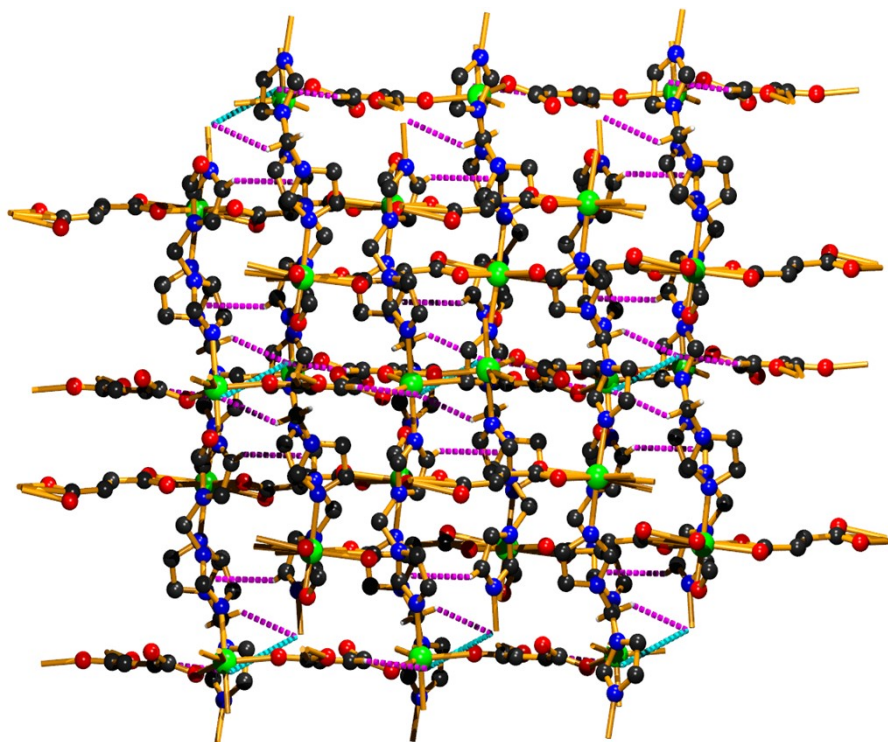


Fig. S18 Intermolecular π - π & C-H... π interactions in **2**

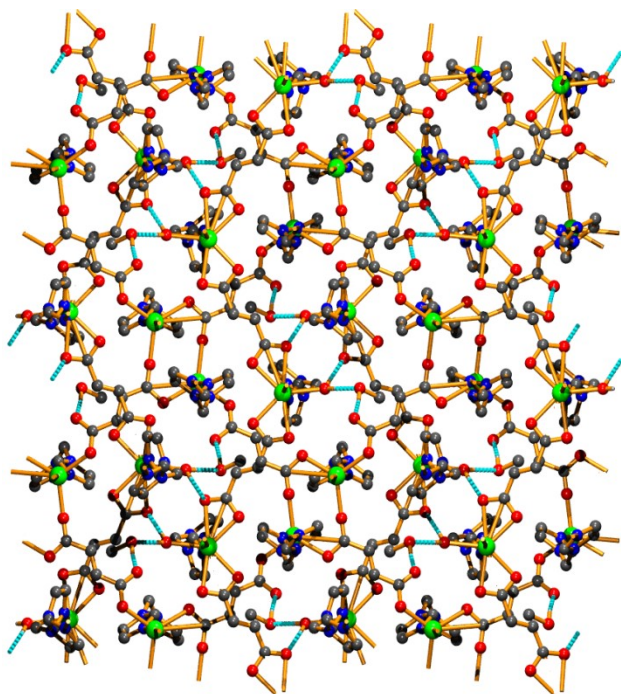


Fig. S19 Intermolecular H-bonding interactions in complex **2**

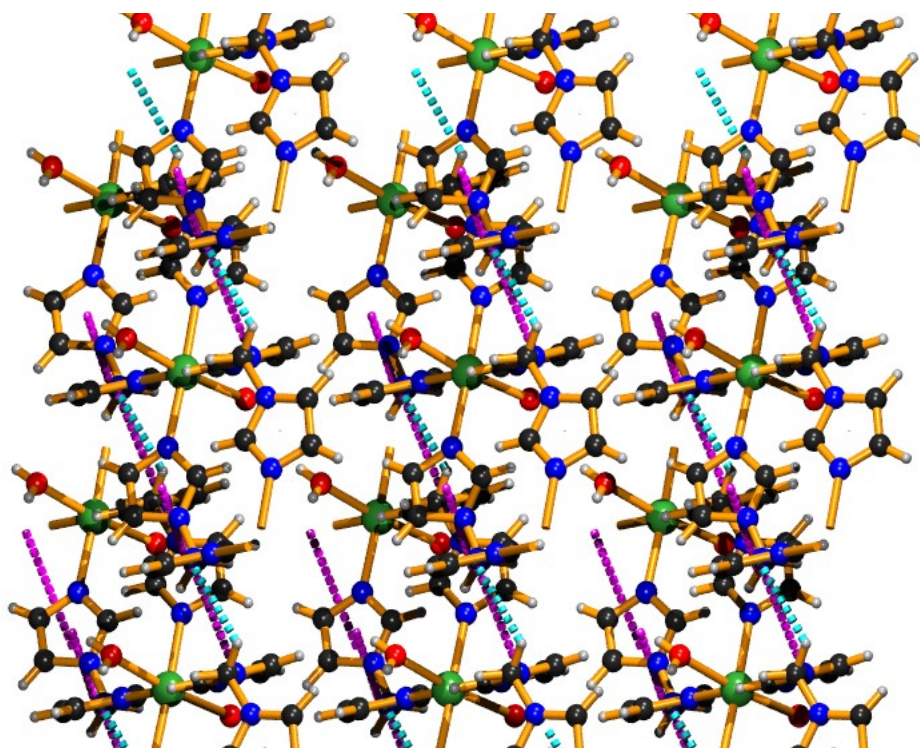


Fig. S20 Intermolecular π - π & C-H... π interactions in 2a

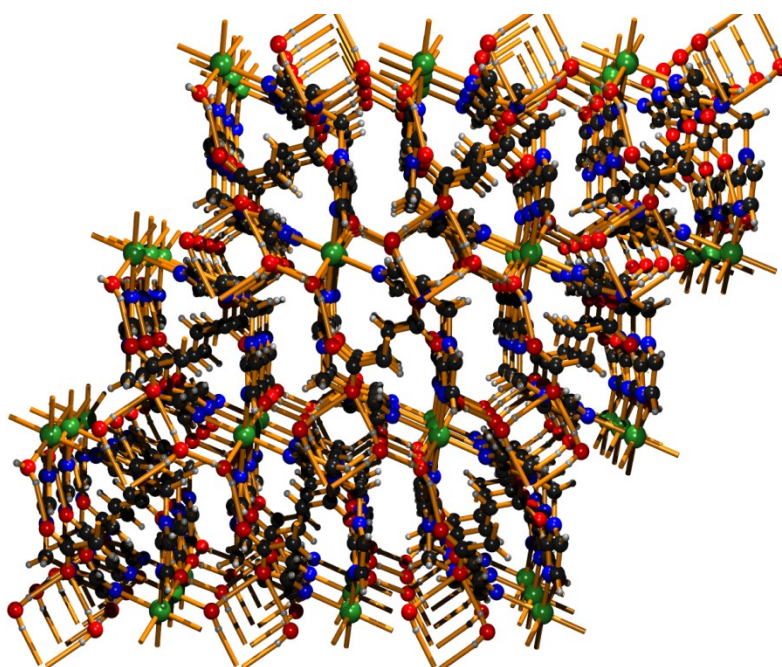


Fig. S21 Intermolecular H-bonding interactions in complex 2a

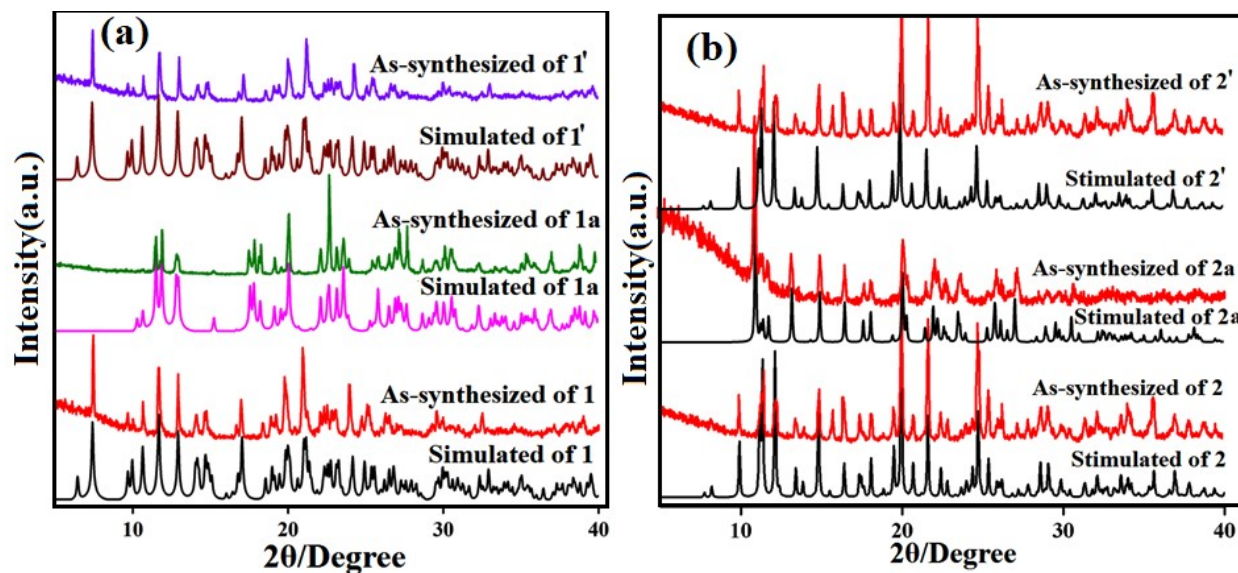


Fig. S22 (a) PXRD pattern of complexes 1, 1a and 1' in different phase. (b) PXRD pattern of complexes 2, 2a and 2' in different phase

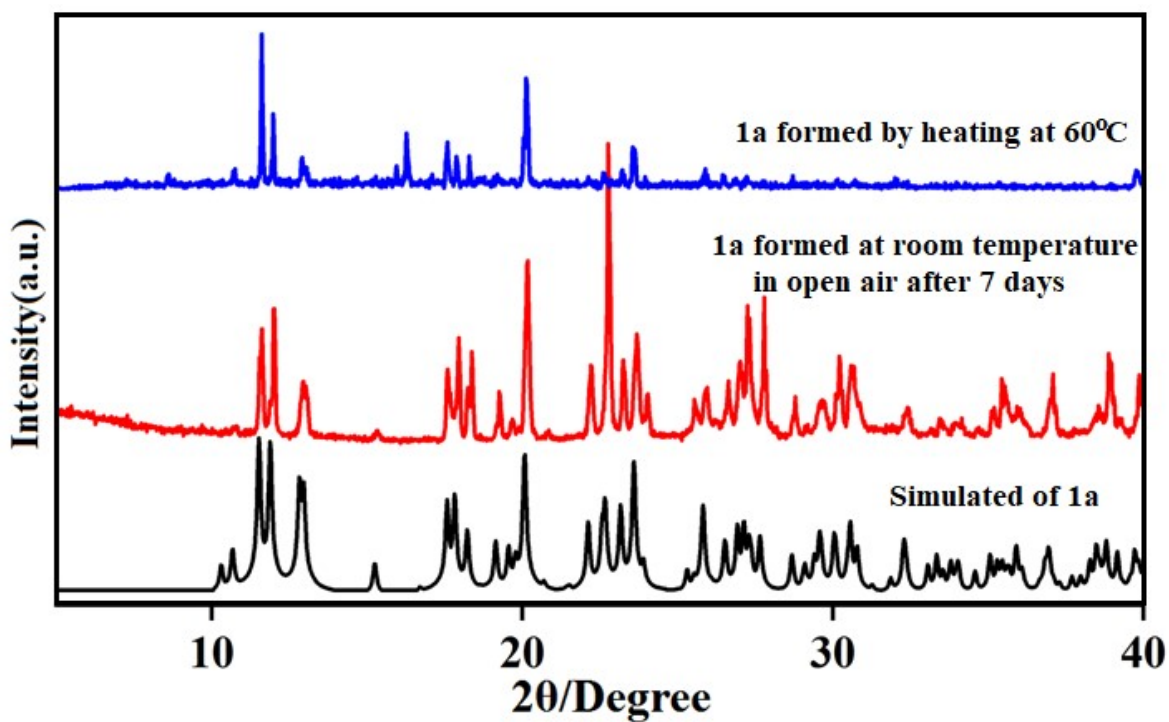


Fig. S23 Comparison of PXRD pattern of simulated form, formed in open air at room temperature and formed by heating at 60°C of complex 1a

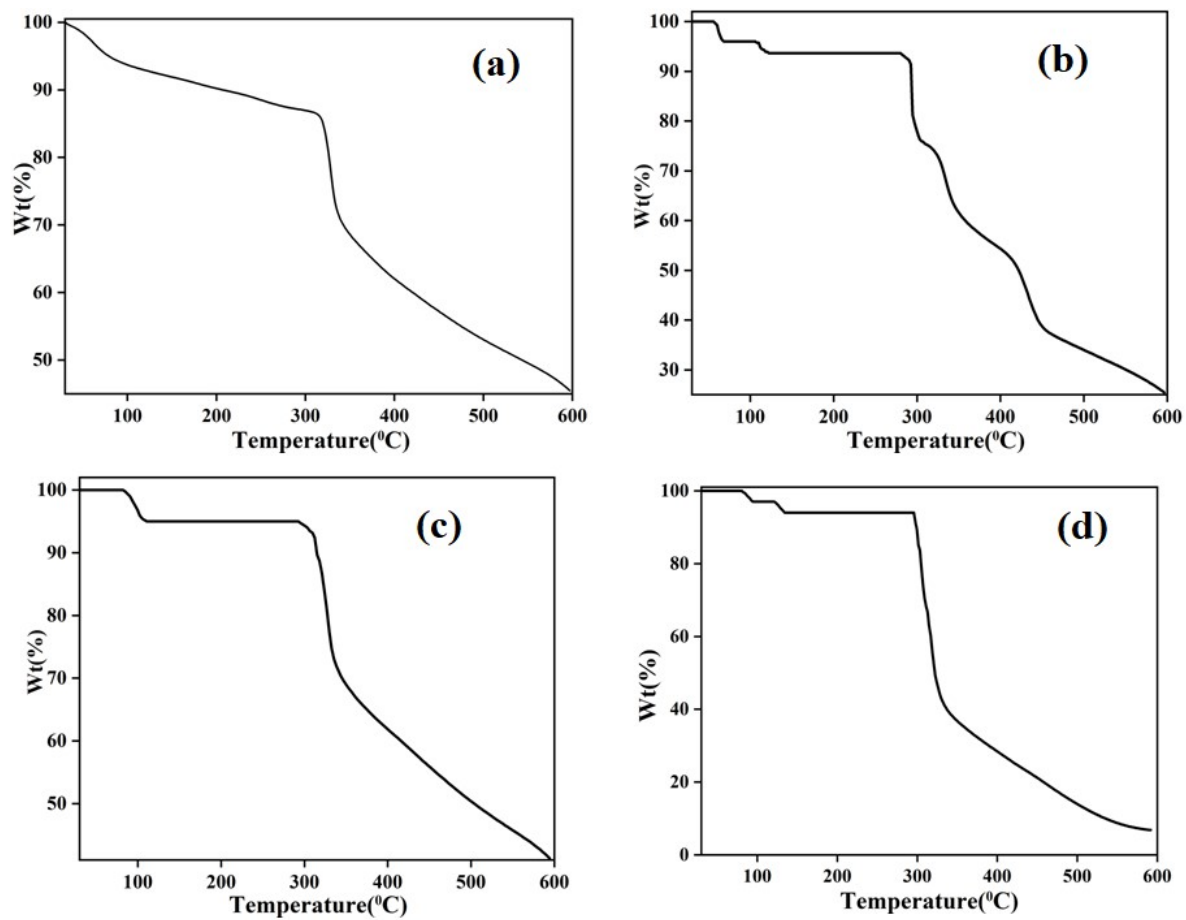


Fig. S24 (a). TGA of complex **1** (b). TGA of complex **2** (c). TGA of complex **1a** (d). TGA of complex **2a**

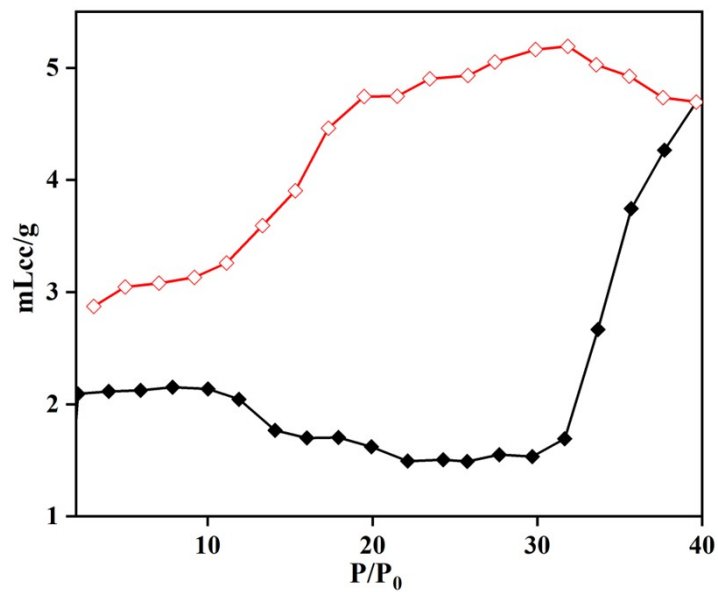


Fig. S25 high pressure gas adsorption of complex **1a**

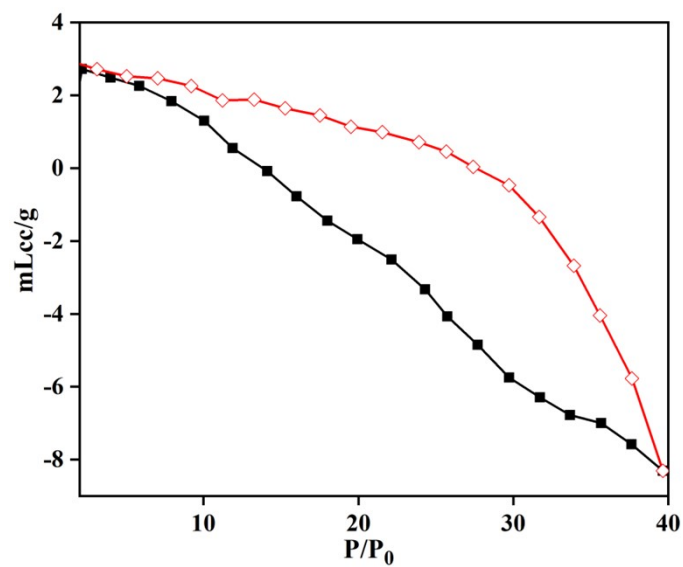


Fig. S26 High pressure H₂ gas adsorption of complex **2**

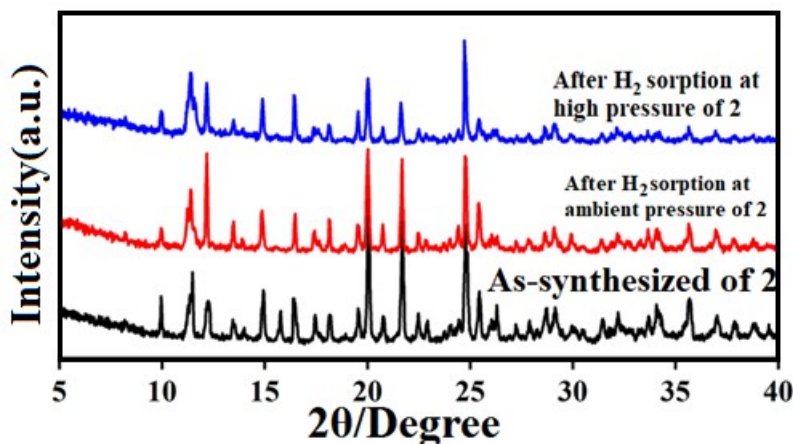


Fig. S27 PXRD pattern of complexes **2** after H₂ sorption

Table S1 Intermolecular π - π & C-H... π interactions in complex **1**

ring(i) \rightarrow ring(j)	distance of centroid(i) from ring(j), (Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids, (Å)
R(1) \rightarrow R(1) ⁱ	4.499(4)	0	3.259
R(2) \rightarrow R(3) ⁱⁱ	4.032(3)	4.2	1.985
R(3) \rightarrow R(2) ⁱⁱ	4.032(3)	4.2	2.169
C-H ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
C(17)-H(17) \rightarrow R(3) ⁱⁱⁱ	2.91	148	3.704(5)

Symmetry code: i = -X,1-Y,1-Z; ii = 2-X,1-Y,-Z; iii = 2-X,-Y,-Z;

R(i)/R(j) denotes the ith/jth rings in the corresponding structures: R(1) = N(1)/C(8)/C(9)/N(2)/C(10); R(2) = N(3)/C(12)/N(4)/C(23)/C(13); R(3) = N(7)/C(5)/C(24)/N(8)/C(6).

Table S2 Selected bond Lengths (Å) and bond angles (°) for complex **1**

Zn1-O3	1.953(3)	Zn2-O2	1.940(3)
Zn1-O7	1.984(4)	Zn2-O5	1.982(3)
Zn1-N1	2.003(4)	Zn2-N5	1.987(3)
Zn1-N8 ^a	1.993(3)	Zn2-N4 ^c	2.025(3)
O3-Zn1-O7	100.60(12)	O2-Zn2-N5	114.99(11)
O3-Zn1-N1	111.83(12)	O2-Zn2-O5	97.38(11)
O3-Zn1-N8 ^a	108.74(13)	O2-Zn2-N4 ^c	106.16(11)
O7-Zn1-N1	108.34(13)	O5-Zn2-N5	121.18(12)
O7-Zn1-N8 ^a	112.14(12)	O5-Zn2-N4 ^c	106.47(11)
N1-Zn1-N8 ^a	114.37(11)	N4 ^c -Zn2-N5	109.23(14)

$a = -1+x, y, 1+z$, $c = 1+x, -1+y, z$.

Table S3 Intermolecular H-bonding interactions in **1**

D-H...A	D-H	H...A	D...A	∠D-H...A
O1W-H1WB...O5	0.96	2.11	2.897(7)	138

Table S4 Intermolecular π - π & C-H... π interactions in complex **1a**

ring(i) → ring(j)	distance of centroid(i) from ring(j), (Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids, (Å)
R(1)→R(1) ⁱ	4.192(3)	0	1.903
R(2)→R(2) ⁱⁱ	3.983(3)	0	1.816
C-H ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
C(2)-H(2)→R(2) ⁱ	2.92	137	3.660(5)

Symmetry code: i = 2-X,1-Y,1-Z; ii = 1-X,-Y,1-Z;

R(i)/R(j) denotes the ith/jth rings in the corresponding structures: R(1) = N(1)/C(1)/N(2)/C(3)/C(2); R(2) = N(3)/C(5)/C(6)/N(4)/C(11).

Table S5 Selected bond Lengths (Å) and bond angles (°) for complex **1a**

Zn1-O1	1.945(4)	Zn1-N1	2.026(4)
Zn1-O3	1.965(3)	Zn1-N4 ^b	2.049(4)
O1-Zn1-O3	117.94(14)	O1-Zn1-N1	110.24(17)
O1-Zn1-N4 ^b	103.83(16)	O3-Zn1-N1	109.97(16)
O3-Zn1-N4 ^b	105.84(16)	N1-Zn1-N4 ^b	108.40(15)

$b = x, 1+y, z$

Table S6 Intermolecular H-bonding interactions in complex **1a**

D-H...A	D-H	H...A	D...A	∠D-H...A
O1W-H1WA...O2	0.85	2.52	2.87(3)	106
O1W-H1WB...O2	0.85	2.43	2.87(3)	112

Table S7 Intermolecular π - π & C-H... π interactions in **2**

ring(i) → ring(j)	distance of centroid(i) from ring(j), (Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids, (Å)
R(1)→R(1) ⁱ	4.2485(19)	0	2.484
C-H ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
C(20)-H(20)→R(1) ⁱⁱ	2.86	159	3.726(3)
C(19)-H(19)→R(1) ⁱ	2.72	140	3.526(4)
C(8)-H(8)→R(2) ⁱⁱⁱ	2.85	148	3.593(3)

Symmetry code: i = 3-X,-Y,-Z; ii = 2-X,1/2+Y,1/2-Z; iii = 2-X,-Y,1-Z;

R(i)/R(j) denotes the ith/jth rings in the corresponding structures: R(1) = N(7)/C(100)/C(131)/N(11)/C(102); R(2) = N(1)/C(1)/N(2)/C(2)/C(3).

Table S8 Selected bond Lengths (Å) and bond angles (°) for complex **2**

Cd1-O10	2.252(2)	Cd2-O2	2.464(2)
Cd1-N1	2.256(2)	Cd2-N5	2.302(2)
Cd1-N10 ^e	2.252(2)	Cd2-O3 ^c	2.351(2)
Cd1-O5 ^g	2.268(2)	Cd2-N11 ^a	2.295(2)
Cd1-O6 ^k	2.287(3)	Cd2-O4 ^c	2.561(2)
O10-Cd1-N1	86.76(8)	Cd2-O1W	2.421(2)
O10-Cd1-N10 ^e	86.13(8)	Cd2-O1	2.360(2)
O5 ^g -Cd1-O10	118.62(9)	O1W-Cd2-O4 ^c	79.80(7)
O6 ^k -Cd1-O10	116.89(10)	O2-Cd2-N5	89.02(8)
N1-Cd1-N10 ^e	171.75(9)	O2-Cd2-N11 ^a	91.45(8)
O5 ^g -Cd1-N1	91.91(8)	O2-Cd2-O3 ^c	139.72(7)
O6 ^k -Cd1-N1	87.46(10)	O2-Cd2-O4 ^c	166.75(7)
O5 ^g -Cd1-N10 ^e	95.16(8)	N5-Cd2-N11 ^a	166.73g(9)
O6 ^k -Cd1-N10 ^e	92.03(10)	O3 ^c -Cd2-N5	101.49(8)
O5 ^g -Cd1-O6 ^k	124.35(10)	O4 ^c -Cd2-N5	83.89(8)
O3 ^c -Cd2-N11 ^a	86.65(8)	O4 ^c -Cd2-N11 ^a	92.92(8)
O3 ^c -Cd2-O4 ^c	53.13(7)	O1W-Cd2-O3 ^c	131.89(7)
O1-Cd2-N11 ^a	102.03(8)	O1W-Cd2-O2	88.00(7)
O1W-Cd2-N5	80.41(8)	O1W-Cd2-N11 ^a	86.35(8)

$$a = -1+x, y, 1+z, c = 1+x, -1+y, z.$$

Table S9 Intermolecular H-bonding interactions in complex **2**

D-H...A	D-H	H...A	D...A	∠D-H...A
O1W-H1WA...O1S	0.82	1.94	2.758(3)	177
O1S-H1S...O20	0.88	1.85	2.686(4)	157
O1W-H2WB...O4	0.78	2.05	2.834(3)	176

Table S10 Intermolecular π - π & C-H... π interactions in **2a**

ring(i) → ring(j)	distance of centroid(i) from ring(j), (Å)	dihedral angle (i,j) (deg)	distance between the (i,j) ring centroids, (Å)
R(1)→R(4) ⁱ	3.560(5)	1.6	1.443
R(2)→R(3) ⁱⁱ	4.151(5)	2.2	2.366
C-H ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
C(11)-H(11B)→R(2) ⁱⁱⁱ	2.85	118	3.414(9)

Symmetry code: I= X,Y,-1+Z, ii= X,-1+Y,Z, iii= X,1+Y,Z.

R(i)/R(j) denotes the ith/jth rings in the corresponding structures: R(1) = N1/ C1/N2/C3/C2 ;
 R(2) = N3/C5/ N4/ C7/ C6; R(3) = N5/ C8/C10/N6/C9; R(4) = N7/C12/C14/ N8/C13.

Table S11 Selected bond Lengths (Å) and bond angles (°) for complex **2a**

Cd1-O1W	2.358(8)	Cd1-O2W	2.380(8)
Cd1-N1	2.327(6)	Cd1-N5	2.332(6)
Cd1-N4 ^b	2.303(6)	Cd1-N8 ^b	2.303(9)
O1W-Cd1-O2W	173.9(3)	O1W-Cd1-N1	94.3(3)
O1W-Cd1-N5	87.4(2)	O1W-Cd1-N4 ^b	91.3(2)
O1W-Cd1-N8 ^b	87.9(3)	O2W-Cd1-N1	89.6(3)
O2W-Cd1-N5	88.1(2)	O2W-Cd1-N4 ^b	93.2(2)
O2W-Cd1-N8 ^b	88.4(3)	N1-Cd1-N5	86.0(2)
N1-Cd1-N4 ^b	93.9(2)	N1-Cd1-N8 ^b	177.7(2)
N4 ^b -Cd1-N5	178.7(2)	N5-Cd1-N8 ^b	94.9(3)
N4 ^b -Cd1-N8 ^b	85.3(3)		

$$b = x, 1+y, -1+z.$$

Table S12 Intermolecular H-bonding interactions in complex **2a**

D-H...A	D-H	H...A	D...A	∠D-H...A
O2W --H2WA...O1	0.73(3)	2.03(3)	2.734(11)	160(4)
O2W --H2WB...O4W	0.77(3)	1.98(3)	2.745(12)	169(4)
O4W --H4WA...O2	0.83(3)	1.93(3)	2.750(10)	178(3)
O4W --H4WB...O4	0.87(4)	2.04(4)	2.888(11)	167(3)

References

1. E. Diez-barra, A. De la hoz, A. Sanchez-migallon and J. Tejada, *Heterocycles(sendai)*., 1992, **34**, 1365-1373.
2. SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc.: Madison, WI, 2004.
3. G. M. Sheldrick, SADABS, Version 2.03; University of Göttingen: Germany, 2002.
4. G. M. Sheldrick, SHELX 2016/6: Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014.
5. A. L. Spek, *Acta Crystallogr. Sect. D.*, 2009, **65**, 148–155.
6. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837–838.
7. C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. V. D. Streek, *J. Appl. Cryst.*, 2006, **39**, 453–457.

8. V. A. Blatov, A. P. Shevchenko and V. N. Serezhkin, *J. Appl. Crystallogr.*, 2000, **33**, 1193.
9. V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm.* 2004, **6**, 377–395.