

Supplementary materials for Some aspects of MOF-74 (Zn₂DOBDC) metal-organic framework formation using THF as the solvent

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Table S1 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Zn₂DOBDC \times 1.5H₂O. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Zn1	4212.7(6)	4336.7(6)	6273(2)	25.5(4)
Zn2A	3402(11)	1099(7)	2960(7)	31.2(9)
Zn2B	3676(3)	1238.3(18)	3033(2)	31.2(9)
O1	3643(5)	1750(4)	7220(6)	35.2(15)
O2	3401(6)	1784(4)	3745(5)	35.2(15)
O3	3168(6)	475(4)	3792(6)	44.6(18)
O6	4261(5)	3548(4)	5867(6)	40.3(15)
O4	2575(5)	15(4)	4934(6)	40.3(15)
O5	3833(6)	3066(4)	7057(5)	44.6(18)
C1	3249.9(4)	1173.6(10)	5052(3)	25.0(16)
C2	3333.0(9)	1198(2)	5923(7)	45(2)
C7	2968.1(9)	488(3)	4592(6)	44(2)
C4	3744.4(9)	2363(2)	5917(6)	25.0(16)
C8	4029.4(10)	3065(3)	6349(6)	44(2)

Atom	x	y	z	U(eq)
C3	3574.5(10)	1770(2)	6383(6)	30.0(18)
C6	3429.3(3)	1805.5(7)	4537.5(16)	30.0(18)
C5	3675.1(3)	2369.5(8)	5080.3(19)	45(2)

Table S2. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for Zn2DOBDC \times 1.5H₂O. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Zn1	21.4(6)	25.4(6)	16.8(7)	1.5(5)	0.9(4)	2.1(5)
Zn2A	52(3)	34.9(13)	12.1(7)	0.7(8)	1.1(11)	26.0(16)
Zn2B	52(3)	34.9(13)	12.1(7)	0.7(8)	1.1(11)	26.0(16)
O1	75(5)	29(3)	13(3)	0(2)	-7(3)	35(3)
O2	75(5)	29(3)	13(3)	0(2)	-7(3)	35(3)
O3	99(6)	27(3)	14(3)	6(2)	15(3)	36(4)
O6	63(4)	14(3)	30(3)	-7(2)	-2(3)	9(3)
O4	63(4)	14(3)	30(3)	-7(2)	-2(3)	9(3)
O5	99(6)	27(3)	14(3)	6(2)	15(3)	36(4)
C1	34(4)	23(4)	22(4)	0(3)	-1(3)	17(3)
C2	68(7)	37(5)	41(6)	11(4)	4(5)	35(5)
C7	73(7)	34(5)	21(4)	-11(4)	-18(4)	24(5)
C4	34(4)	23(4)	22(4)	0(3)	-1(3)	17(3)
C8	73(7)	34(5)	21(4)	-11(4)	-18(4)	24(5)
C3	50(5)	24(4)	11(3)	8(3)	7(3)	15(4)
C6	50(5)	24(4)	11(3)	8(3)	7(3)	15(4)
C5	68(7)	37(5)	41(6)	11(4)	4(5)	35(5)

Alpha phase

The alpha phase exhibits a monoclinic structure with space group $C2/c$. The asymmetric unit comprises one Zn crystallographic position and half of the DOBDC molecule. Zn is situated in a distorted tetrahedral position ZnO_4 , with two oxygens originating from COO^- groups of two DOBDC molecules and two oxygens originating from water molecules (Figure 2). The Zn-O bonds have an almost equal length of approximately 2Å. The overall structure is built upon zig-zag chains forming the line $-(-DOBDC-Zn(H_2O)_2-)_n-$, where Zn ions occupy the corners of the zig-zag. The zig-zag angle is nearly 92.67(1) degrees, considering the Zn-Zn-Zn angle. Through hydrogen bonding, the hydrogen present in the hydroxyl group forms a bond with the oxygen molecule connected to the Zn.

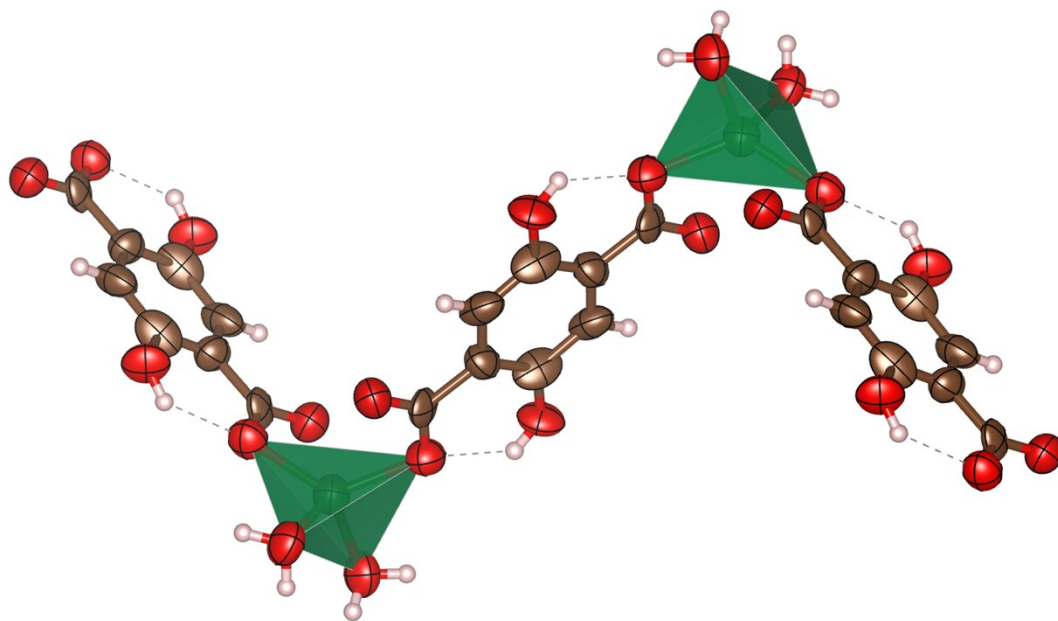


Figure S1. The chain unit of the ZnDOBDC(H₂O)₂ structure. The green tetrahedron represents the ZnO₄ unit, while the brown atoms signify carbon, red represents oxygen, and beige denotes hydrogen.

The Zn-DODBC chains are arranged in vertical stacks through the hydrogen bonds of water molecules. These stacks also connect to other stacks through hydrogen bonds. As a result, each water molecule binds chains in the stacks and links them, forming the crystal lattice. The structure does not demonstrate any evidence of disorder.

To ensure the stability of the DOBDC molecule after solvothermal synthesis, we assessed the organic skeleton's bonds and angles. The confirmation of aromaticity is supported by the typical C-C bond length of 1.4 Å for the benzene ring and the very narrow distribution of the ring angles equal to 120°. The carboxylic group's C-O bonds have similar lengths, measuring 1.241(6) and 1.289(6) Å, corresponding to the typical conjugated double and single bond system. The slightly longer bond is related to the oxygen linked to the Zn ion, while the shorter bond belongs to oxygen having a hydrogen bond with the nearest hydroxyl group. The observed structure matches the one reported by Ghermani *et al.*²⁶ as expected. The difference from their study is that the authors obtained this phase as a precipitate of interaction between the disodium salt of DOBDC and zinc sulfate in the aqueous media.

To confirm the correctness of the calculated structural model on the bulk powder material, the Rietveld refinement was performed on the powder XRD data (Figure 3). Upon analyzing the gathered data, it was confirmed that no impurity phases were present. The data for refinement was obtained at room temperature, resulting in a change in the unit cell parameters as the unit cell volume increased. The room temperature unit cell parameters

are noted in Table 1 and marked with an asterisk. The room temperature unit cell volume is $945.60(7) \text{ \AA}^3$, therefore being $\sim 3\%$ larger than at 100K. Although the temperature affects the bond expansion, the structure remains unchanged apart from minor variations, thus confirming the absence of the phase transitions between 100K and RT.

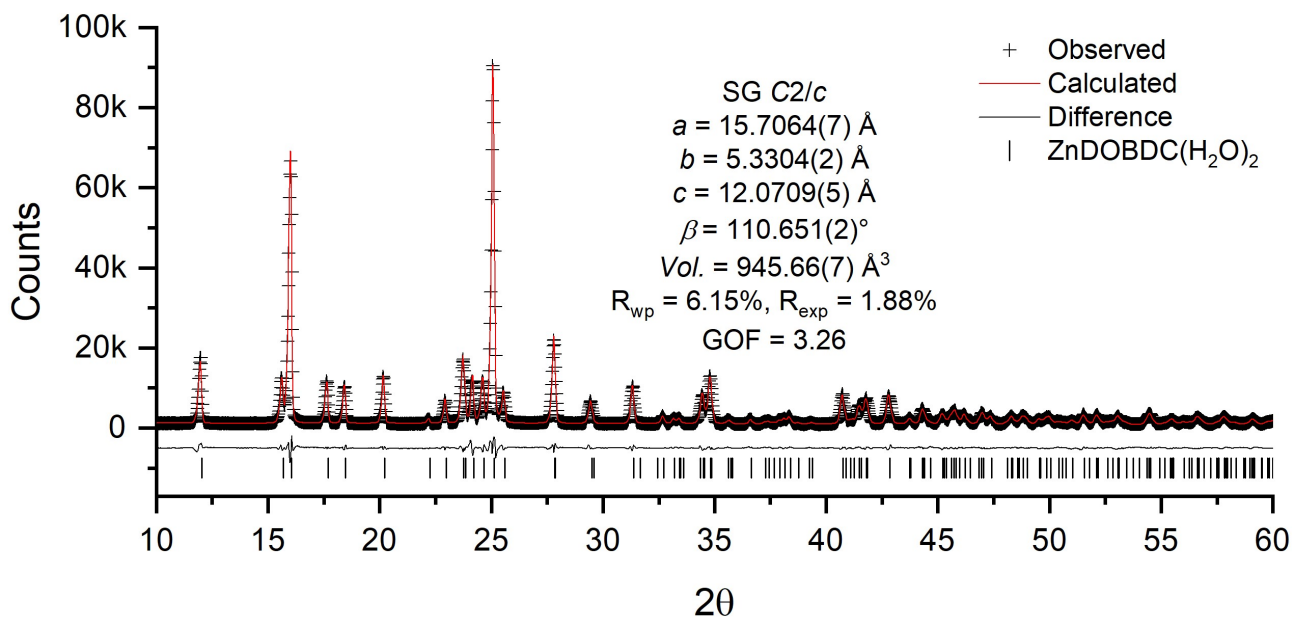


Figure S2. Observed, calculated, and difference plot of Rietveld refinement on the X-ray diffraction data of alpha phase ZnDOBDC(H₂O)₂ (SG - C2/c).

A TGA was carried out to determine the thermal stability of the phases acquired. The analysis was conducted in the air, allowing the organic linkers to be burned off as water and carbon dioxide.

The alpha phase ZnDOBDC(H₂O)₂ exhibits a mass loss curve with two distinct steps (Figure S1). These steps correspond to the loss of crystalline water at approximately 220 °C (13.22%) and the gradual decomposition of the organic linker, which begins at around 280 °C (59.19%). The observed mass losses closely match the theoretical values based on the sample's composition, with the first step at 12.1% and the second at 60.5%. Based on the indistinct character of the step's transition, it appears that the removal of water leads to a decrease in the stability of the structure, resulting in a lower decomposition temperature for the organic linker. Additionally, the residual mass of 27.59% aligns well with the ZnO weight fraction in the theoretical formula unit, which is 27.35%. Based on the research, it has been determined that the breakdown of the organic linker starts at approximately 350 °C, while the alpha phase decomposition is completed at around 450 °C. These results support the expected composition of ZnDOBDC(H₂O)₂.

To investigate in more details the local structure and potential defects within the ZnDOBDC(H₂O)₂ sample, we conducted an Infrared Spectroscopy (IR) analysis. Notably, the IR spectrum of the product did not exhibit the characteristic peak at 1641 cm^{-1} , typically

associated with the C=O carbonyl stretching vibration of the carboxylic acid group H₄DOBDC. Instead, it revealed a new peak around 1590 cm⁻¹, corresponding to the carboxylate group within the metal-organic framework. This suggests the absence of impurities with carboxylic groups, such as residual acids or other derivatives. The broad peak in the 3500-2600 cm⁻¹ range corresponds to the molecular water and OH groups within the structure closely bound to metal^{27,28}.

The observed absorption bands were attributed to the carbonyl stretching vibrations of the carboxylate groups in the MOF ligand within the spectral range of 1600-1500 cm⁻¹ (specifically, at 1574 cm⁻¹, Figure S3). Peaks around 1400 cm⁻¹ were assigned to the aromatic C=C groups, ranging from 1493 to 1334 cm⁻¹. Furthermore, the stretching vibrations associated with the C-O and C-C bonds in the ligand DOBDC manifested within the 1300-1000 cm⁻¹ region, ranging from 1230 to 1120 cm⁻¹. Bands with wavenumbers below 1000 cm⁻¹ were associated with C-H vibrations (ranging from 914 to 880 cm⁻¹) and Zn-O vibrations (ranging from 798 to 754 cm⁻¹). The IR spectrum confirms the structure obtained from single-crystal XRD as expected.

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for ZnDOBDC(H₂O)₂. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	x	Y	Z	$U_{\text{(eq)}}$
Zn1	5000	305.7(17)	2500	13.7(3)
O1	7251(3)	10712(7)	6655(3)	15.2(9)
O2	5387(3)	3556(7)	4206(3)	15.1(9)
O3	6225(3)	2096(7)	3214(3)	14.2(9)
O4	5559(3)	-2160(7)	1716(3)	16.6(9)
C1	7393(4)	9172(10)	5832(5)	14.2(13)
C2	6732(4)	7257(9)	5332(5)	14.1(13)
C3	6833(4)	5588(9)	4499(4)	12.2(12)
C4	6099(4)	3643(10)	3964(5)	11.4(11)
H1	7563.76 ^{2c}	12058.06 ^{2c}	6730.72 ^{2c}	23 ¹
H4A	5486.87 ^{2a}	-3728.11 ^{2a}	1923.98 ^{2a}	25 ¹
H4B	6165.28 ^{2a}	-1951.02 ^{2a}	1983.4 ^{2a}	25 ¹
H2	6210.29 ^{2b}	7096.48 ^{2b}	5562.39 ^{2b}	17 ¹

¹Fixed U_{iso} at 1.2 times of: All C(H) groups; at 1.5 times of: all O(H) groups, all O(H,H) groups; ^{2a}Rotating group: O4(H4A,H4B); ^{2b}Aromatic/amide H refined with riding coordinates: C2(H2); ^{2c}Idealised tetrahedral OH refined as rotating group: O1(H1).

Table S4. Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $\text{ZnDOBDC}(\text{H}_2\text{O})_2$. The Anisotropic displacement factor exponent is $-2\pi^2[h^2a^*2U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn1	11.2(5)	13.8(5)	15.3(5)	0	4.0(4)	0
O1	20(3)	12(2)	14.1(19)	-5.1(15)	7(2)	-0.9(17)
O2	12(2)	14(2)	19(2)	-0.6(15)	4(2)	-1.3(17)
O3	14(2)	13(2)	15(2)	-1.7(15)	4.7(19)	1.1(17)
O4	12(3)	18(2)	20(2)	-0.3(16)	7(2)	-2.0(18)
C1	20(4)	17(3)	5(3)	0(2)	5(3)	5(3)
C2	17(4)	10(3)	19(3)	3(2)	10(3)	4(2)
C3	12(3)	11(3)	12(3)	-1(2)	2(2)	-1(2)
C4	7(3)	14(3)	9(3)	0(2)	-2(2)	2(2)

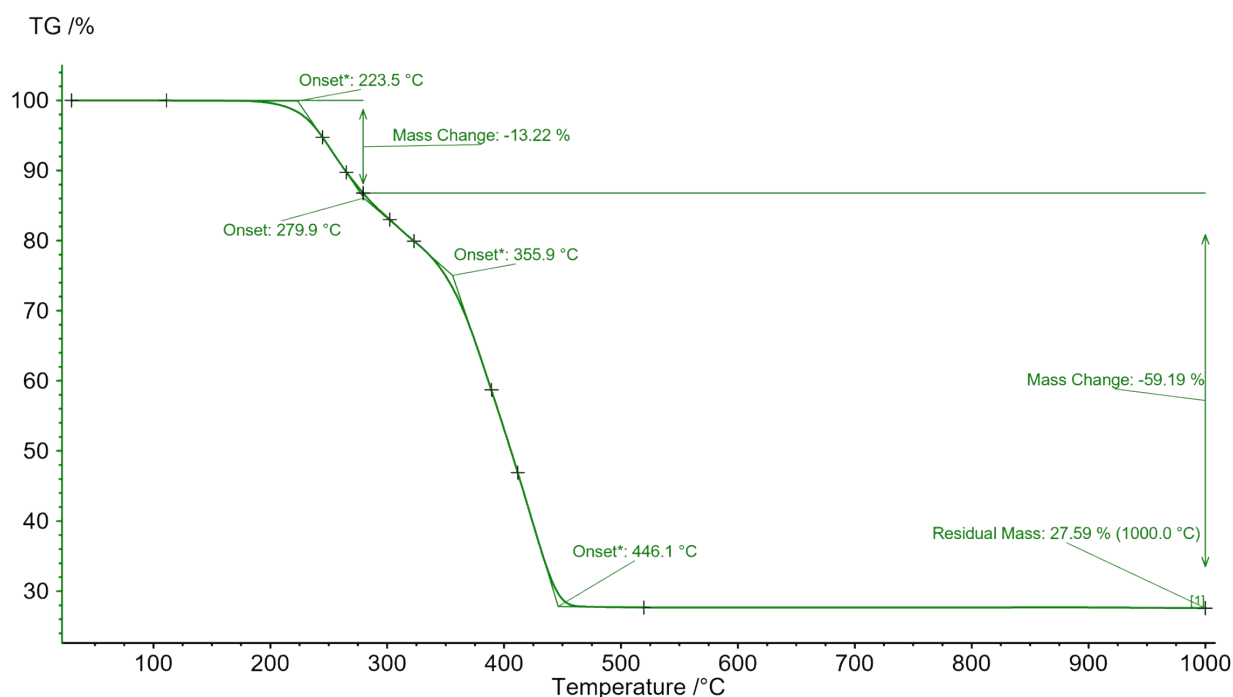


Figure S3. TG curve of the alpha phase $\text{ZnDOBDC}(\text{H}_2\text{O})_2$

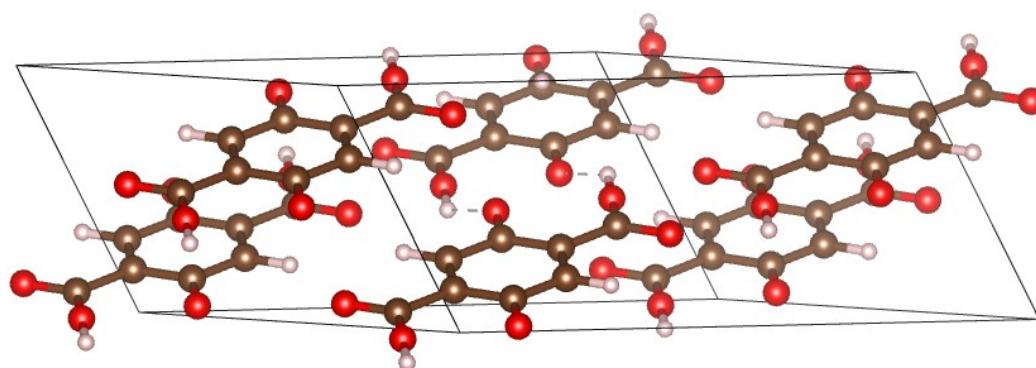


Figure S4. The crystal structure of H₂DOBDC.**Table S5. H₂DOBDC structural Rietveld refinement summary**

Space group	$P\bar{1}$
a/Å	6.6080(3)
b/Å	13.4068(8)
c/Å	7.4249(5)
α /°	136.601(5)
β /°	104.980(5)
γ /°	58.794(6)
Volume/Å ³	378.68(7)

Table S6. Fractional Atomic Coordinates ($\times 10^4$) for H₂DOBDC

Atom	x	Y	z
C1	0.6504(8)	0.1520(9)	0.8274(9)
C2	0.6312(9)	0.1676(9)	1.0326(13)
C3	0.8140(9)	-0.1478(9)	0.4975(13)
C4	0.7948(8)	-0.1321(9)	0.7027(9)
C5	0.7029(10)	0.0266(12)	0.9707(16)
C6	0.7423(10)	-0.0068(12)	0.5593(16)
C7	0.5743(12)	0.3014(12)	0.8930(13)
C8	0.8708(12)	-0.2816(12)	0.6370(13)
O1	0.5485(14)	0.3103(15)	1.275(2)
O2	0.8967(14)	-0.2905(15)	0.255(2)
O3	0.4923(15)	0.4430(14)	1.1320(18)
O4	0.5914(14)	0.2875(13)	0.710(2)
O5	0.9528(15)	-0.4232(14)	0.3980(18)
O6	0.8537(14)	-0.2677(13)	0.820(2)
H1	0.7573(15)	-0.0195(19)	0.403(2)
H2	0.6879(15)	0.0394(19)	1.127(2)
H3	0.421(4)	0.567(7)	1.341(8)
H4	1.025(4)	-0.547(7)	0.189(8)

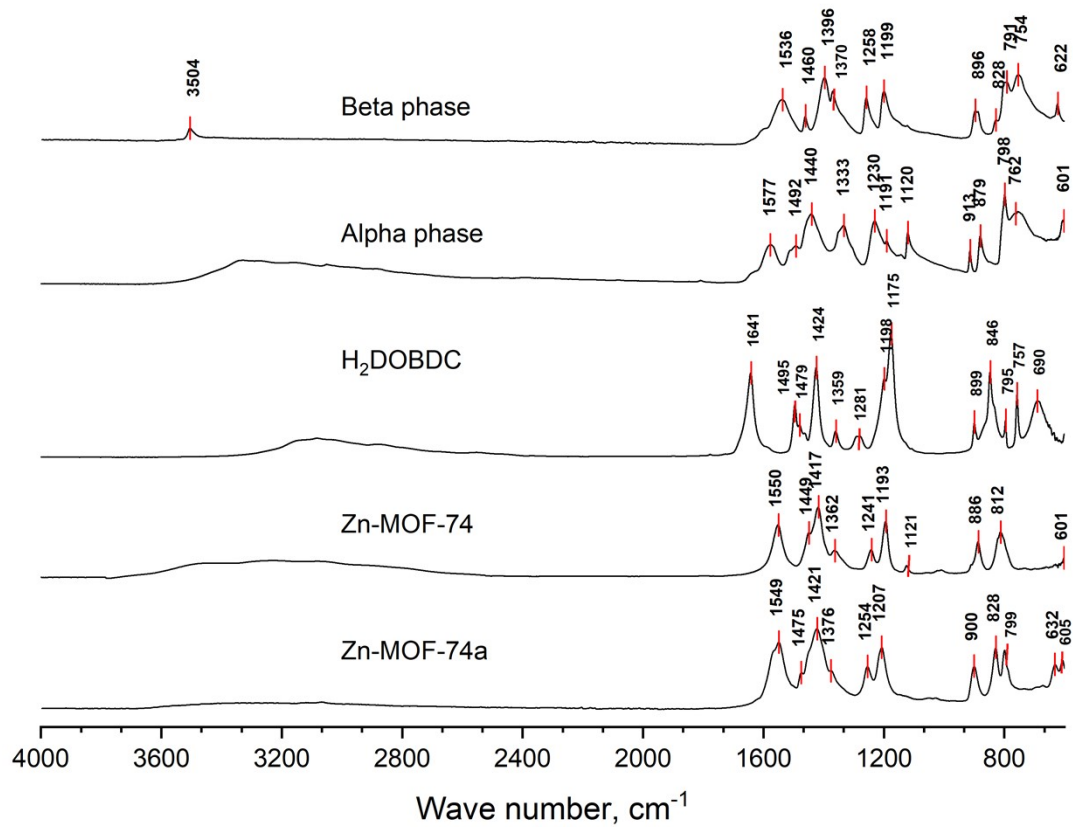


Figure S5. IR spectra of the following compounds: alpha phase $\text{ZnDOBDC}(\text{H}_2\text{O})_2$, beta phase $\text{Zn}_{2.5}\text{DOBDC}$, H_2DOBDC , Zn-MOF-74 , Zn_2DOBDC and Zn-MOF-74a , Zn_2DOBDC .