Electronic Supplementary Material (ESI) for CrystEngComm.

Capturing the structural diversification upon thermal desolvation of a robust metal organic frameworks via a single-crystal-to-single-crystal transformation†

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Supplementary Information

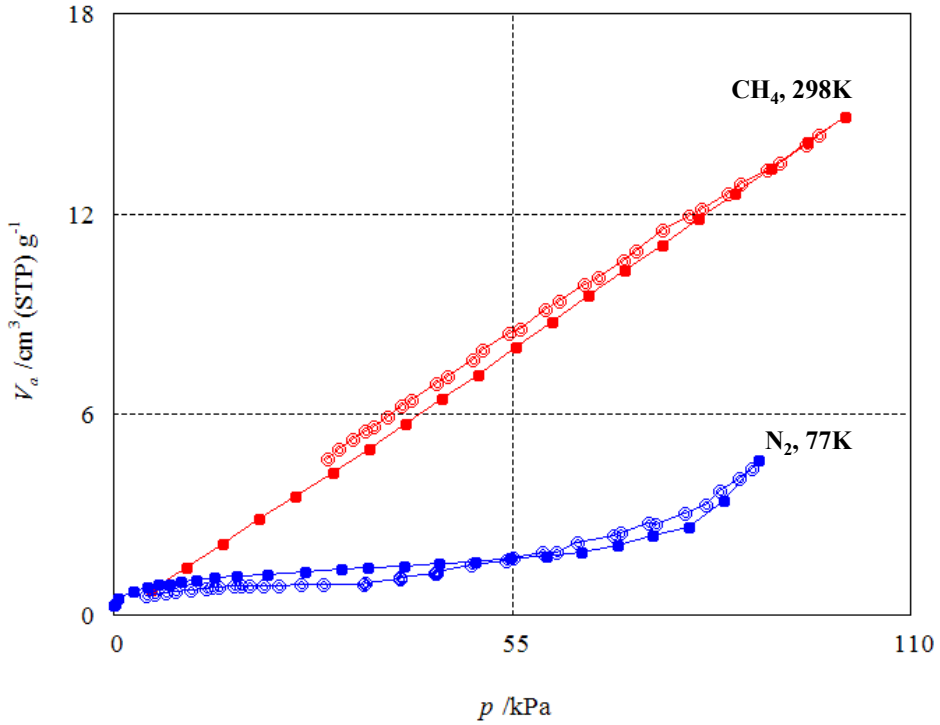


Fig S1. Gas adsorption isotherms for **2** (desolvated **1**). Filled squares, adsorption; circles, desorption.

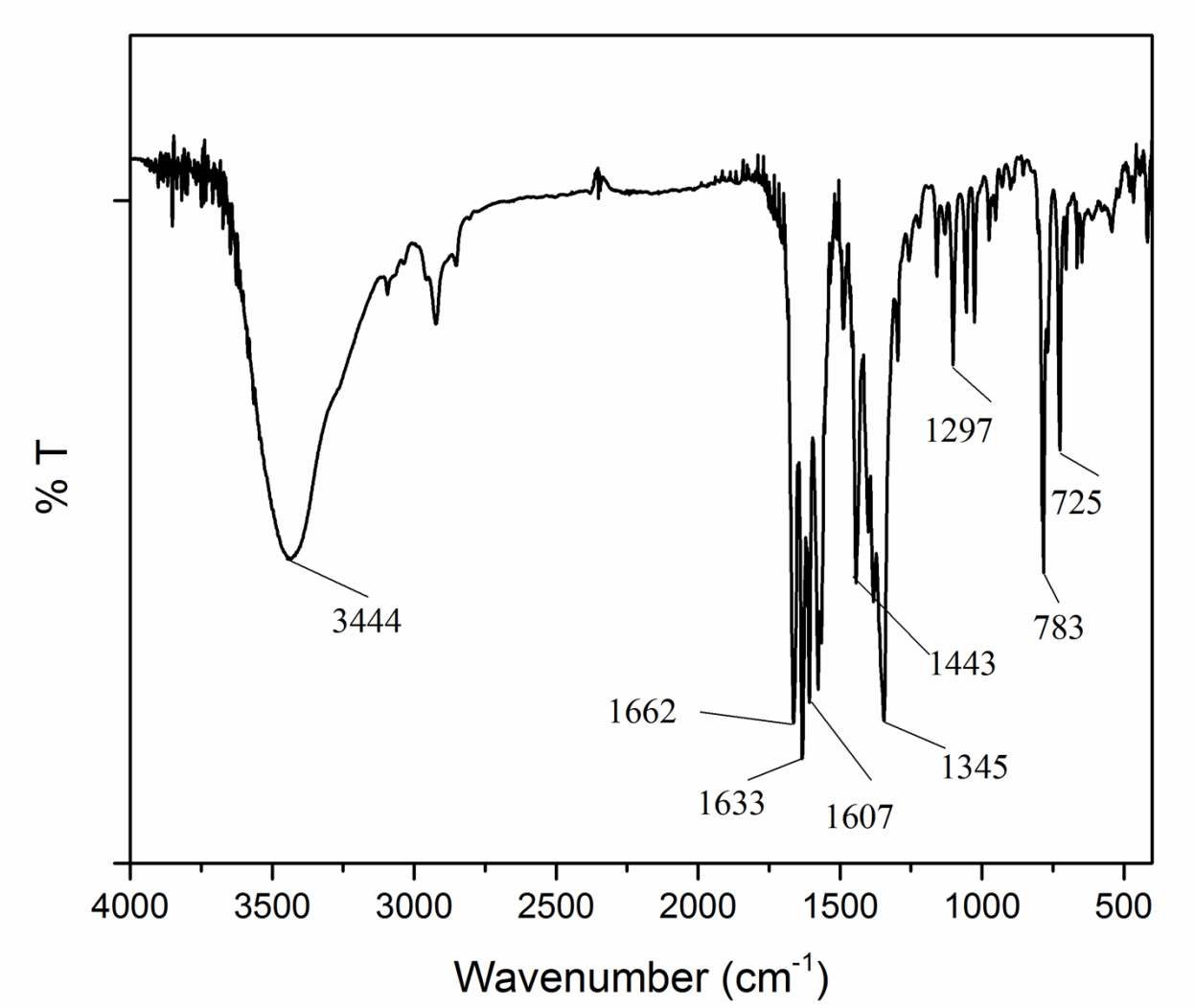


Fig S2. FTIR spectrum of **1**.

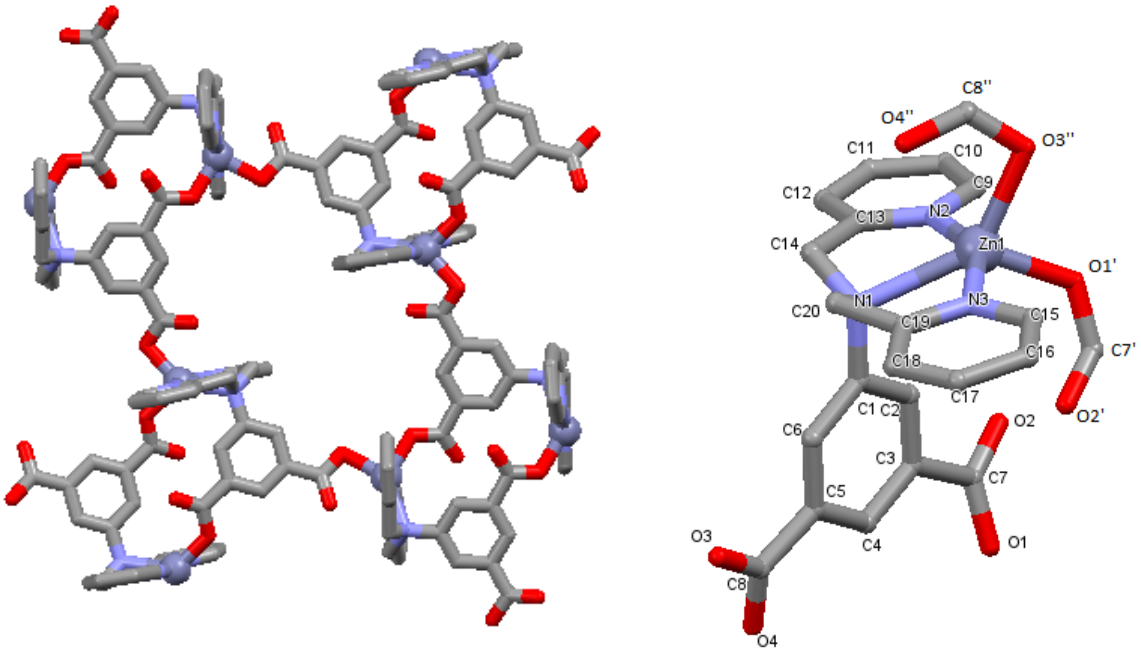


Fig S3. Crystal structure of **1** with the coordination environment around Zn shown on the right (symmetry codes for equivalent positions are: ' = -x, -y+1, -z+2; '' = x+1/2, -y+3/2, z+1/2. Hydrogen atoms are omitted for clarity.

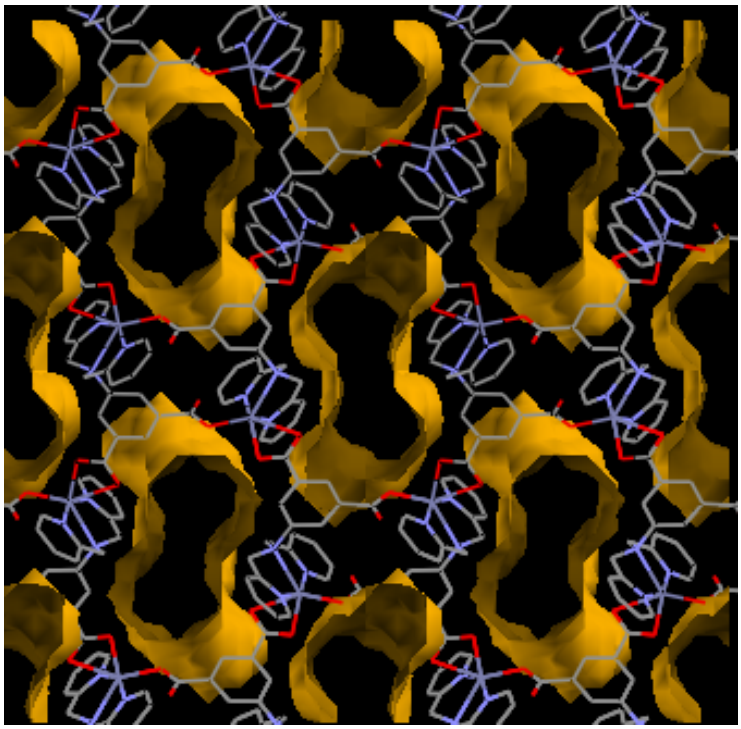


Fig S4. Schematic representaion of the pores in **1** without the solvent molecules.

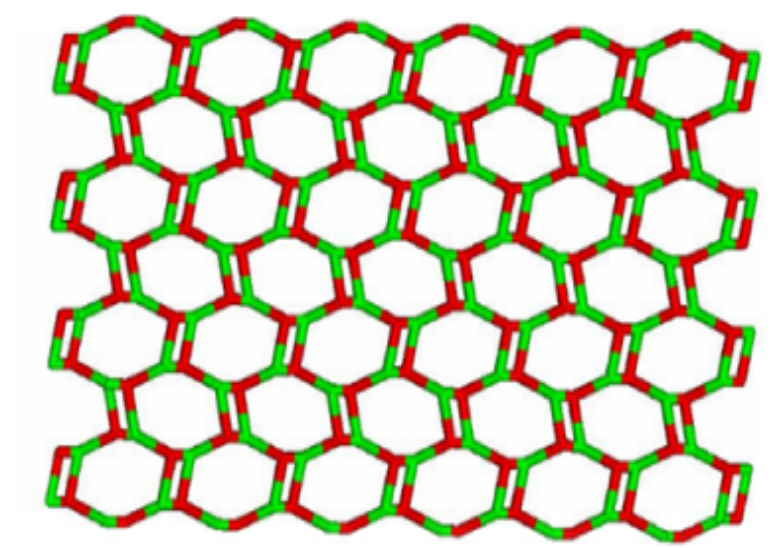


Fig S5. Topological view of **1**.

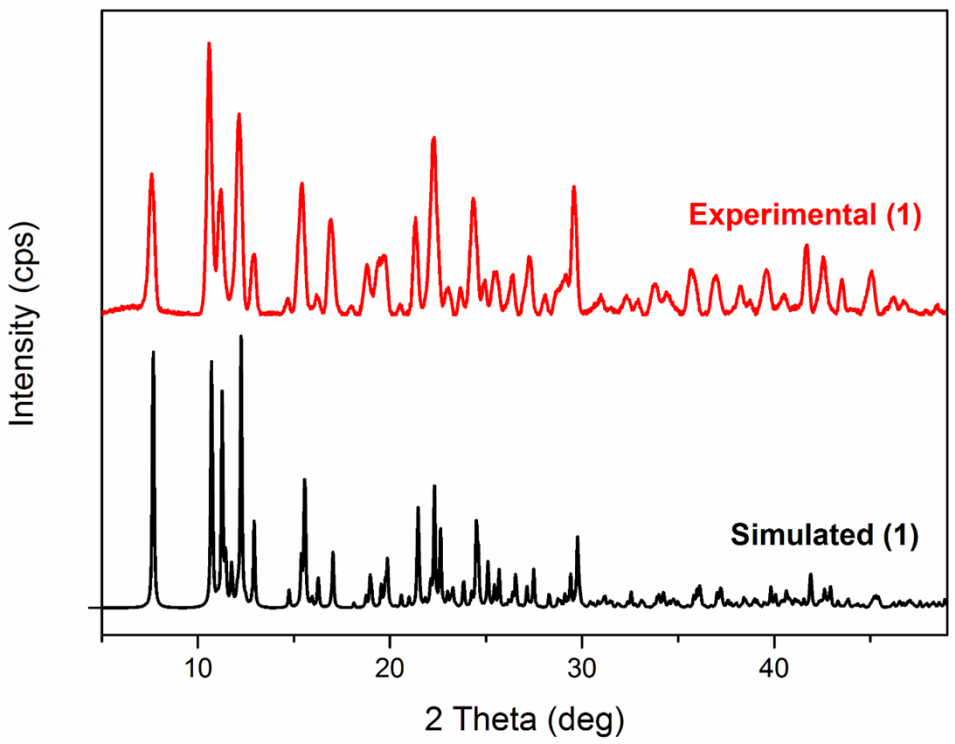


Fig S6. Simulated and experimental powder X-ray diffraction patterns of **1**.

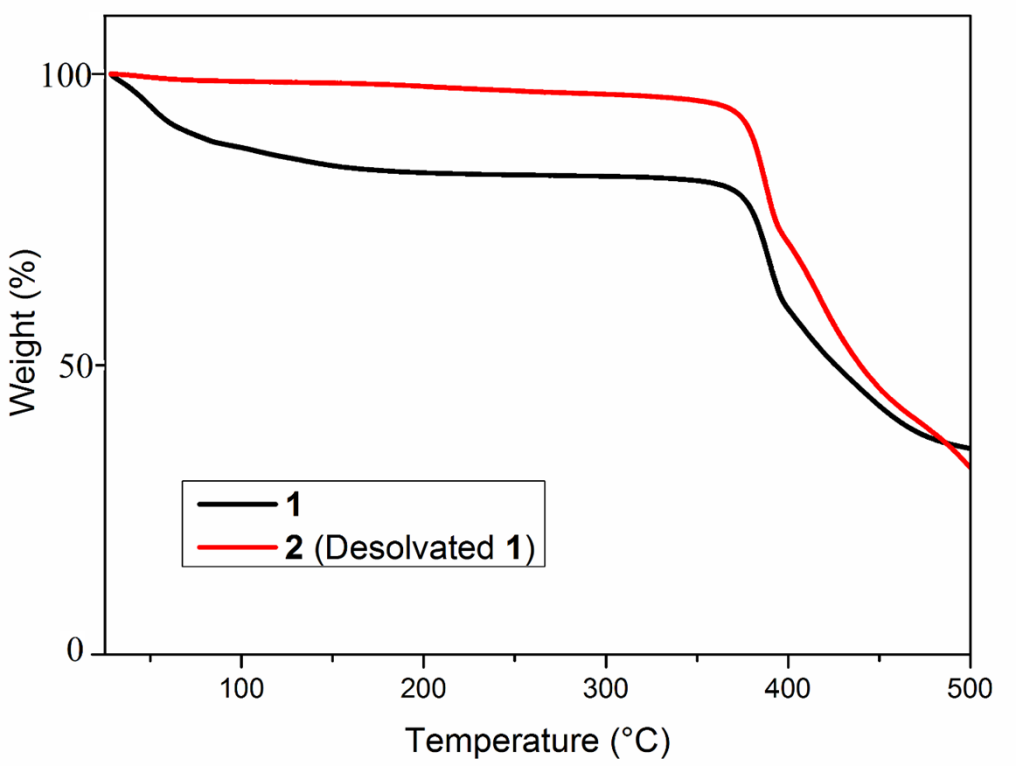


Fig S7. TGA scans of **1** and **2**.

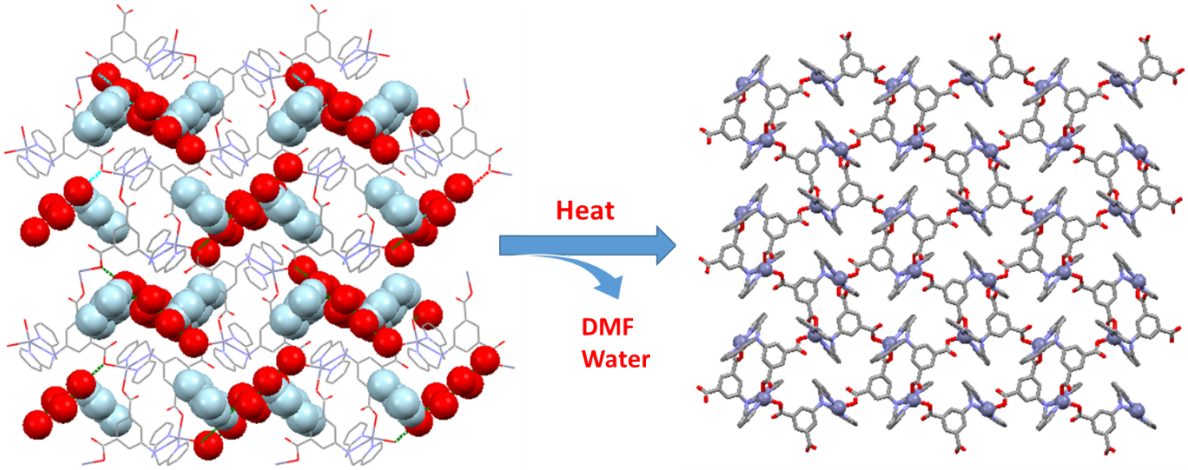


Fig S8. Schematic representation of the desolvation process (loss of DMF and water molecules in the pores) of **1** to **2**.

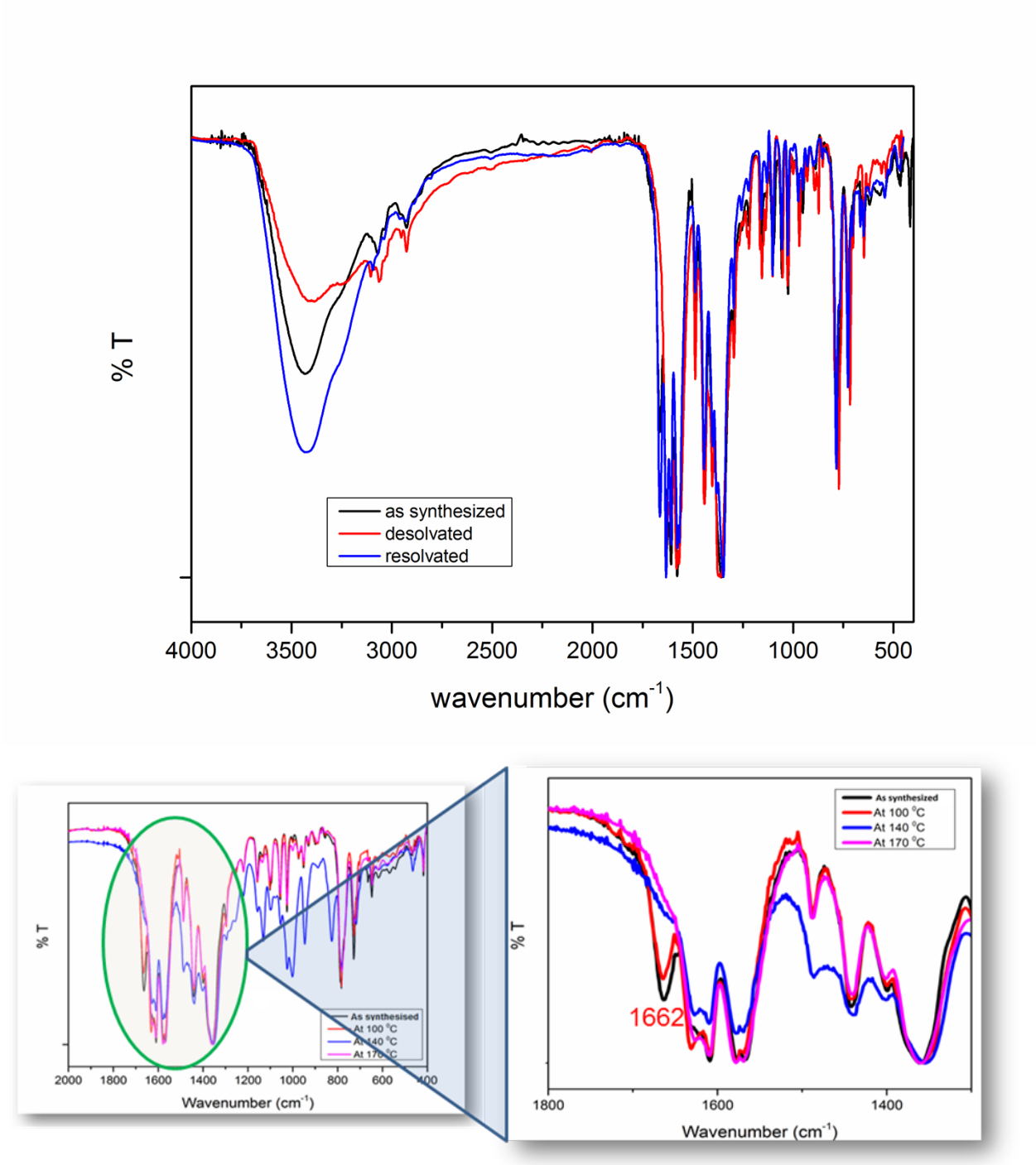


Fig S9. Monitoring of the desolvation (loss of DMF and water molecules in the pores) of **1** to **2** by FTIR spectroscopy. Note that only partial decrease in the intensity of the peak at 3433 cm^{-1} due to water is observed because of the re-absorption of moisture during the recording of the spectrum under ambient condition with the ground sample having a lot more surface area. On the other hand, re-absorption of DMF by **2** to form **1** was found to indicate the reversibility of the process.

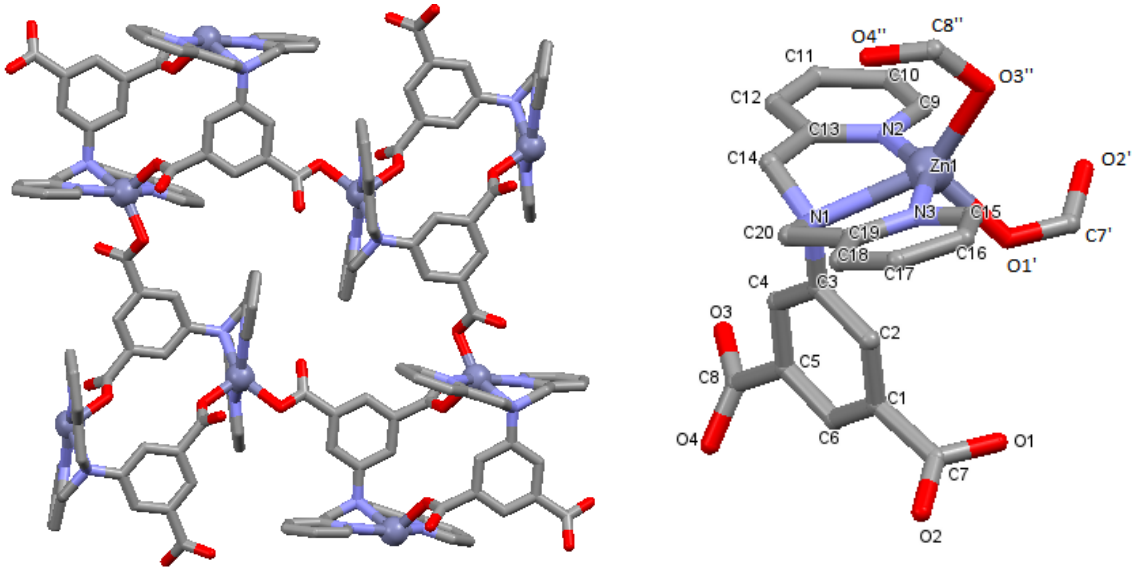


Fig S10. Crystal structure of **2** with the coordination environment around Zn shown on the right (symmetry codes for equivalent positions are: ' = -x, -y, -z+1; '' = x+1/2, -y+1/2, z-1/2). Hydrogen atoms are omitted for clarity.

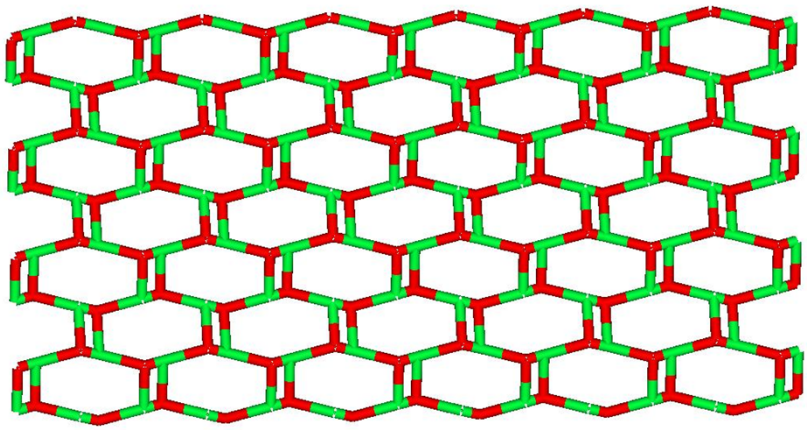


Fig S11. Topological view of **2**.

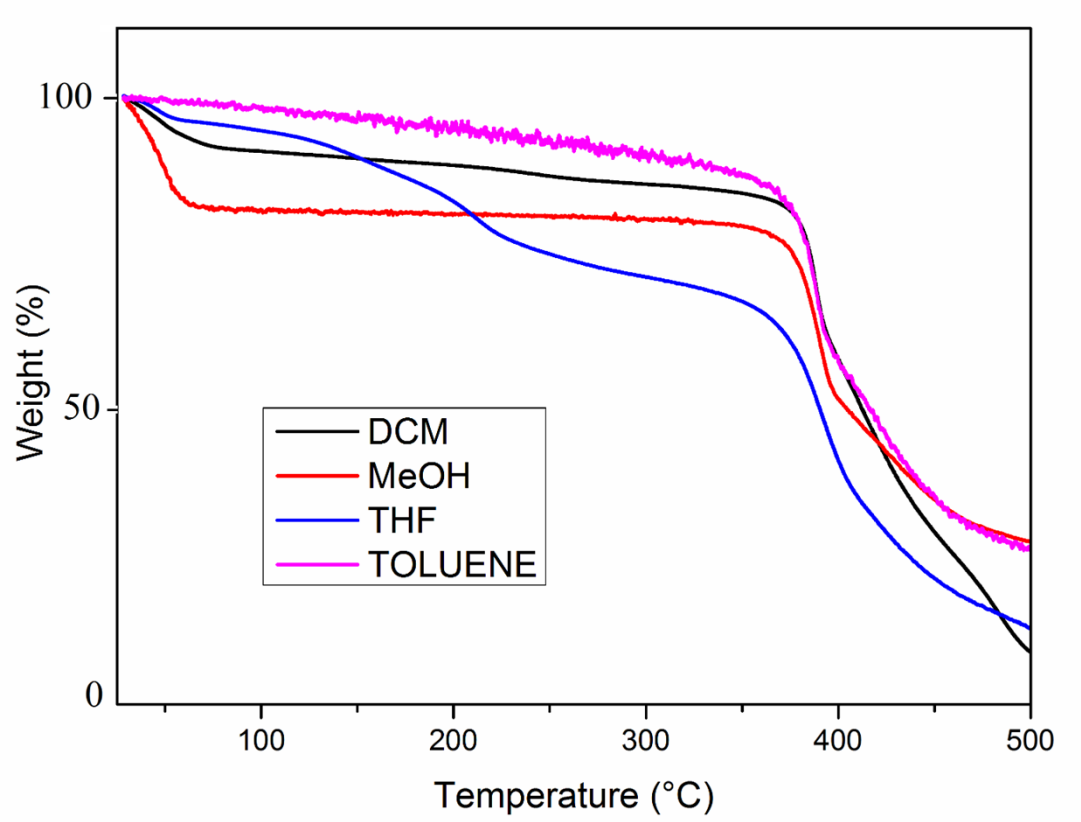
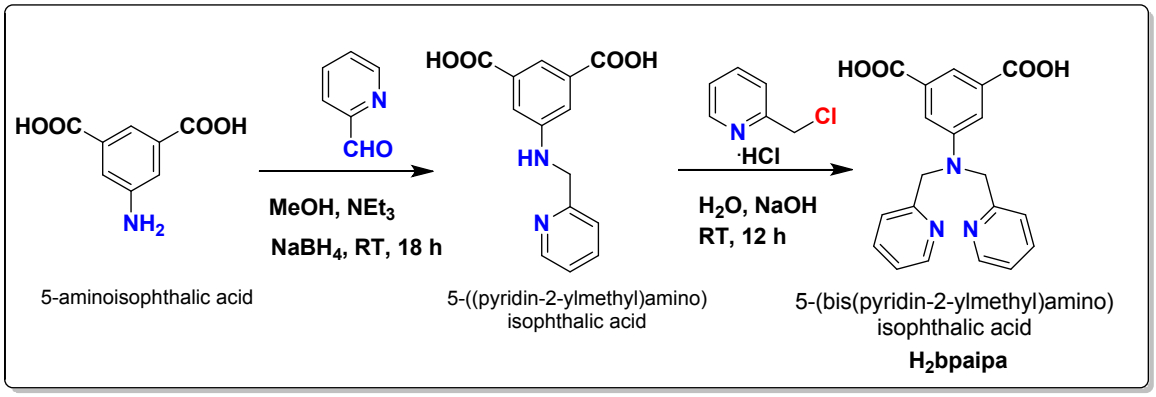


Fig S12. TGA scans of various solvates of **1**.



Scheme S1. Synthesis of H_2bpaipa.

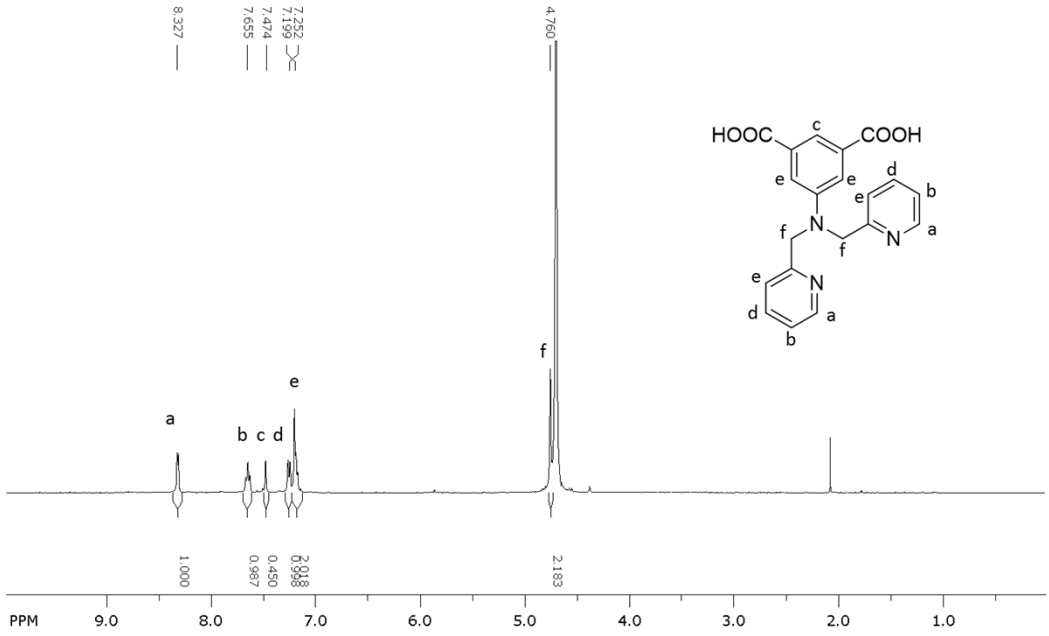


Fig S13. ^{1}H NMR spectrum of H_2bpaipa in D_2O.

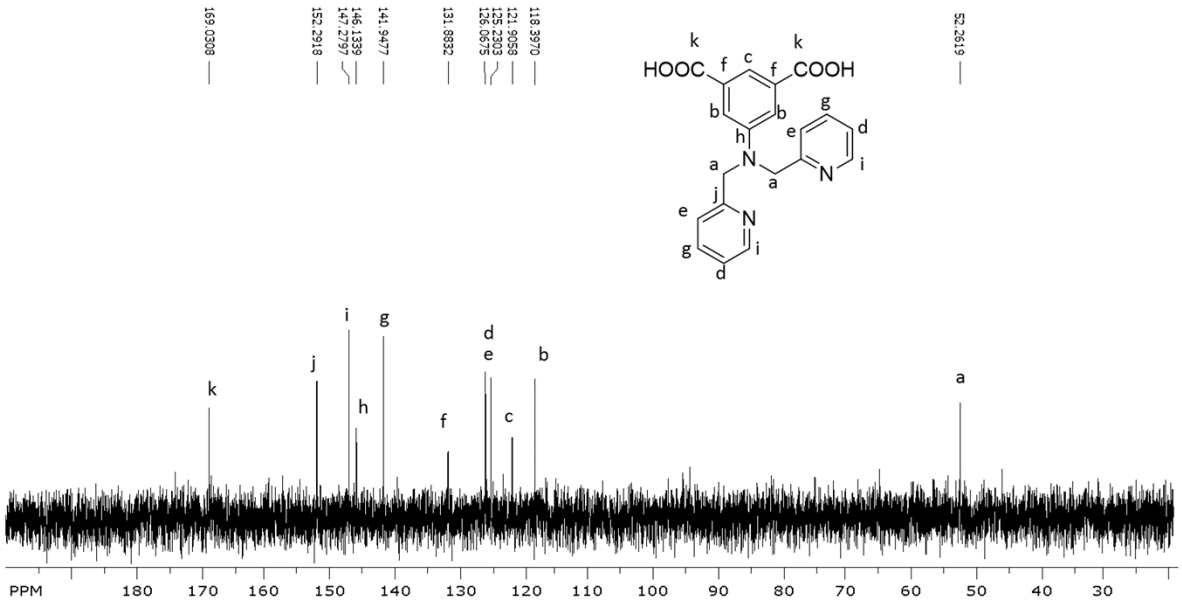


Fig S14. ^{13}C NMR spectrum of H_2bpaipa in D_2O.

Table S1. Crystallographic data and refinement parameters for **1** and **2**.

Compound	**1**	**2**
Chemical Formula	$C_{23}H_{26}N_4O_7Zn$	$C_{20}H_{15}N_3O_4Zn$
Formula Weight	535.85	426.72
Temperature (K)	100	100
Wavelength (Å)	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$
a (Å)	8.7542(8)	8.485(5)
b (Å)	16.4242(15)	14.529(9)
c (Å)	15.9879(15)	14.073(8)
a (°)	90	90
β (°)	91.709(2)	94.11(3)
g (°)	90	90
Z	4	4
V (Å^3)	2297.7(4)	1730.4(17)
Density (mg/cm^3)	1.549	1.638
μ(mm^{-1})	1.122	1.454
F(000)	1112	872
Theta (°) Range for Data Coll.	1.78 to 25.00	2.02 to 25.40
Reflections Collected	12340	8187
Independent Reflections	4026	3130
Reflections with I >2σ(I))	3076	1399
R_{int}	0.0467	0.138
No. of Parameters refined	318	253
GOF on F^2	1.091	0.980
Final R_1[a]/wR_2[b] (I >2σ(I))	0.0443/0.1123	0.0817/0.1894
Weighted R_1/wR_2(all data)	0.0606/0.1215	0.1826/0.2307
Largest diff. peak and hole(eÅ^{-3})	0.704 and -0.722	0.768 and -0.473

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Selected bond distances (Å) and angles (degree) for **1** and **2**.

1

Bond Lengths (Å)

Zn1-O1'	1.989(2)	Zn1-N3	2.059(3)
Zn1-O3"	2.059(2)	Zn1-N2	2.088(3)
Zn1-N1	2.399(3)		

Bond Angles (°)

O1'-Zn1-N3	107.49(11)	O1'-Zn1-O3"	91.11(9)
N3-Zn1-O3"	102.97(11)	O1'-Zn1-N2	93.18(11)
N3-Zn1-N2	150.47(11)	O3"-Zn1-N2	97.32(10)
O1'-Zn1-N1	130.53(10)	N3-Zn1-N1	75.50(10)
O3"-Zn1-N1	137.45(9)	N2-Zn1-N1	75.04(10)

Symmetry codes for equivalent positions are:
' = -x, -y+1, -z+2; " = x+1/2, -y+3/2, z+1/2

2

Bond Lengths (Å)

Zn1-O1'	1.938(7)	Zn1-N3	2.116(8)
Zn1-O3"	2.007(7)	Zn1-N2	2.065(9)
Zn1-N1	2.340(8)		

Bond Angles (°)

O1'-Zn1-N3	92.5(3)	O1'-Zn1-O3"	103.0(3)
N3-Zn1-O3"	89.3(3)	O1'-Zn1-N2	107.4(3)
N3-Zn1-N2	149.2(3)	O3"-Zn1-N2	108.1(3)
O1'-Zn1-N1	113.8(3)	N3-Zn1-N1	74.9(3)
O3"-Zn1-N1	140.1(3)	N2-Zn1-N1	75.7(3)

Symmetry codes for equivalent positions are:
' = -x, -y, -z+1; " = x+1/2, -y+1/2, z-1/2