Electronic Supplementary Material (ESI) for Dalton Transactions

Zn(II) coordination polymer of an in-situ generated 4-pyridyl (^{4}Py) attached bis(amido)phosphate ligand, $[PO_2(NH^4Py)_2]^-$ showing preferential water uptake over aliphatic alcohols

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Supporting Information

Table S1: Crystallographic Data

Compound	**1**	**2**	**3**	**4**	**3a (data squeezed)**
Chemical formula	$C_{20}H_{20}N_8PCl$	$C_{16}H_{21}N_6O_3P$	$C_{14}H_{20}N_5O_6PZn$	$C_{14}H_{20}N_5O_6PZn$	$C_{12}H_{17}N_4O_6PZn$
Formula weight	438.86	376.36	450.69	450.69	409.64
Temperature	150(2)K	296(2)K	100(2)K	100(2)K	100(2)K
Crystal system	cubic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
Space group	I -43d	Pc	Pbca	P2(1)/n	Pbca
a (Å); α (°)	18.926(5); 90	10.922(6); 90	14.073(2); 90	11.522(15); 90	14.135(2); 90
b (Å); β(°)	18.926(5); 90	9.348(5); 110.05(3)	15.623(3); 90	13.900(19); 103.70(3)	15.420(3); 90
c (Å); γ (°)	18.926(5); 90	9.763(5); 90	18.459(3); 90	11.714(16); 90	18.524(3); 90
V (Å^3); Z	6779(3); 12	936.42(9); 2	4058.3(12); 8	1822.7(4); 4	4037.5(12); 8
ρ (calc.) mg m^{-3}	1.290	1.335	1.475	1.642	1.348
μ(Mo K_α) mm^{-1}	0.263	0.176	1.328	1.478	1.326
$2\theta_{max}$ (°)	56	56	50	56	56
R(int)	0.0417	0.0742	0.186	0.0544	0.0779
Completeness to θ	99.5 %	98.1 %	99.8%	99.2%	99.5%
Data / param.	1398 / 75	4083 / 243	3576 / 253	4492 / 244	4988/190
GOF	1.190	1.070	1.001	1.031	1.036
R1 [F>4σ(F)]	0.0707	0.0476	0.0499	0.0470	0.0455
wR2 (all data)	0.2389	0.1389	0.1302	0.1194	0.1169
max. peak/hole (e.Å^{-3})	1.064/ -0.329	0.438/ -0.448	0.973 / -0.445	1.471 / -1.089	1.026/-0.467

Compound	**3a**
Chemical formula	$C_{12}H_{17}N_4O_6PZn$
Formula weight	409.64
Temperature	100(2)K
Crystal system	Orthorhombic
Space group	Pbca
a (Å); α (°)	14.135(2); 90
b (Å); β(°)	15.420(3); 90
c (Å); γ (°)	18.524(3); 90
V (Å^3); Z	4037.5(12); 8
ρ (calc.) mg m^{-3}	1.348
μ(Mo K_α) mm^{-1}	1.326
$2\theta_{max}$ (°)	56
R(int)	0.0831
Completeness to θ	99.5%
Data / param.	4988 / 215
GOF	1.102
R1 [F>4σ(F)]	0.0598
wR2 (all data)	0.1700
max. peak/hole (e.Å^{-3})	1.335 / -0.511

Table S2: Selected bond-lengths and angles for **1**, **2**, **3, 4** and **3a**

Compound	Bond lengths	Bond Angles
1	P(1)-N(1)#1: 1.631(3) P(1)-N(1)#2: 1.631(3) P(1)-N(1)#3: 1.631(3) P(1)-N(1): 1.631(3)	N(1)#1-P(1)-N(1)#2: 107.02(8) N(1)#1-P(1)-N(1)#3: 107.02(8) N(1)#2-P(1)-N(1)#3: 114.49(16) N(1)#1-P(1)-N(1): 114.49(16) N(1)#2-P(1)-N(1): 107.02(8) N(1)#3-P(1)-N(1): 107.02(8)
2	P(1)-O(1): 1.4781(17) P(1)-N(3): 1.638(2) P(1)-N(2): 1.649(2) P(1)-N(1): 1.660(2)	O(1)-P(1)-N(3): 115.66(11) O(1)-P(1)-N(2): 114.60(11) N(3)-P(1)-N(2): 102.51(10) O(1)-P(1)-N(1): 112.73(10) N(3)-P(1)-N(1): 105.17(11) N(2)-P(1)-N(1): 104.95(11)
3	Zn(1)-O(2): 1.927(3) Zn(1)-O(3): 1.945(4) Zn(1)-N(14)#1: 1.993(4) Zn(1)-N(24)#2: 2.007(4) P(1)-O(1): 1.481(4) P(1)-O(2): 1.503(3) P(1)-N(1): 1.665(4) P(1)-N(2): 1.670(4)	O(2)-Zn(1)-O(3): 121.88(16) O(2)-Zn(1)-N(14)#1: 109.80(16) O(3)-Zn(1)-N(14)#1: 108.15(18) O(2)-Zn(1)-N(24)#2: 101.00(15) O(3)-Zn(1)-N(24)#2: 102.52(17) N(14)#1-Zn(1)-N(24)#2: 113.17(17) O(1)-P(1)-O(2): 119.2(2) O(1)-P(1)-N(1): 105.7(2) O(2)-P(1)-N(1): 108.1(2) O(1)-P(1)-N(2): 111.5(2) O(2)-P(1)-N(2): 104.6(2) N(1)-P(1)-N(2): 107.1(2) P(1)-O(2)-Zn(1): 139.0(2)
4	Zn(1)-O(4): 2.044(2) Zn(1)-N(14)#1: 2.045(3) Zn(1)-N(24)#2: 2.067(3) Zn(1)-O(2): 2.095(2) Zn(1)-O(3): 2.167(3) P(1)-O(1): 1.488(2) P(1)-O(2): 1.498(2) P(1)-N(1): 1.680(3) P(1)-N(2): 1.682(3)	O(4)-Zn(1)-N(14)#1: 138.19(11) O(4)-Zn(1)-N(24)#2: 112.00(11) N(14)#1-Zn(1)-N(24)#2: 109.55(11) O(4)-Zn(1)-O(2): 90.33(10) N(14)#1-Zn(1)-O(2): 93.50(11) N(24)#2-Zn(1)-O(2): 90.93(10) O(4)-Zn(1)-O(3): 80.96(10) N(14)#1-Zn(1)-O(3): 90.29(11) N(24)#2-Zn(1)-O(3): 96.18(10) O(2)-Zn(1)-O(3): 170.34(9) O(1)-P(1)-O(2): 119.75(14) O(1)-P(1)-N(1): 105.16(15) O(2)-P(1)-N(1): 109.83(14) O(1)-P(1)-N(2): 110.13(14) O(2)-P(1)-N(2): 104.43(14) N(1)-P(1)-N(2): 106.99(15) P(1)-O(2)-Zn(1): 145.31(14)
3a	Zn(1)-O(1): 1.934(2) Zn(1)-O(3): 1.954(2) Zn(1)-N(14)#1: 1.994(2) Zn(1)-N(24)#2: 2.013(2) P(1)-O(2): 1.484(2) P(1)-O(1): 1.505(2) P(1)-N(1): 1.668(2) P(1)-N(2): 1.676(2)	O(1)-Zn(1)-O(3): 122.74(10) O(1)-Zn(1)-N(14)#1: 108.16(10) O(3)-Zn(1)-N(14)#1: 107.40(10) O(1)-Zn(1)-N(24)#2: 100.51(9) O(3)-Zn(1)-N(24)#2: 102.95(10) N(14)#1-Zn(1)-N(24)#2: 115.30(10) O(2)-P(1)-O(1): 119.61(12) O(2)-P(1)-N(1): 105.66(12) O(1)-P(1)-N(1): 108.14(12) O(2)-P(1)-N(2): 111.49(12) O(1)-P(1)-N(2): 104.07(12) N(1)-P(1)-N(2): 107.33(13) P(1)-O(1)-Zn(1): 140.05(13)

Table S3: Table of hydrogen bonding parameters for **1**, **2**, **3**, **4** and **3a**

Compound	D-H...A	d(H...A)Å	d(D...A)Å	<(DHA)°
1	N(1)-H(1)...Cl(1)#4	1.96	2.801(4)	160.8
	Symmetry transformations used to generate equivalent atoms:			
	#1 -x+2,-y+3/2,z #2 -y+7/4,x-1/4,-z+1/4 #3 y+1/4,-x+7/4,-z+1/4			
	#4 -y+5/4,-x+7/4,z-1/4			
2	N(1)-H(1)...O(1)#1	2.11	2.872(3)	146.9
	N(2)-H(2)...O(1S)#2	2.02	2.852(3)	163.7
	N(3)-H(3)...N(21)#3	2.12	2.897(3)	150.9
	O(1S)-H(1S)...O(2M)#4	2.32(6)	2.902(6)	130(5)
	O(1S)-H(2S)...N(31)#5	2.36(5)	2.877(4)	123(5)
	O(2M)-H(2M)...N(11)	1.91	2.700(5)	161.5
	Symmetry transformations used to generate equivalent atoms:			
	#1 x,-y+1,z-1/2 #2 x,-y+1,z+1/2 #3 x,-y+2,z-1/2			
	#4 x,-y,z-1/2 #5 x+1,y,z			
3	N(1)-H(1)...O(1)#5	1.93	2.806(5)	170.3
	N(2)-H(2)...O(4)	1.96	2.797(6)	158.9
	O(1W)-H(1W)...O(1)#5	2.11(3)	2.943(6)	161(7)
	O(1W)-H(2W)...O(1S)	1.92(4)	2.773(9)	162(9)
	Symmetry transformations used to generate equivalent atoms:			
	#1 -x+1/2,y+1/2,z #2 -x+1/2,-y+2,z-1/2 #3 -x+1/2,y-1/2,z			
	#4 -x+1/2,-y+2,z+1/2 #5 -x+1,-y+2,-z+1			
4	O(3)-H(1W)...O(4)#5	2.01(3)	2.775(3)	170(4)
	O(3)-H(2W)...O(1)#6	1.89(3)	2.666(3)	170(4)
	N(1)-H(1)...O(6')#7	2.00	2.862(17)	166.5
	N(1)-H(1)...O(6)#7	2.13	2.955(5)	155.6
	N(2)-H(2)...O(5)	1.97	2.842(4)	169.7
	Symmetry transformations used to generate equivalent atoms:			
	#1 x+1/2,-y+3/2,z+1/2 #2 x-1/2,-y+3/2,z+1/2			
	#3 x-1/2,-y+3/2,z-1/2 #4 x+1/2,-y+3/2,z-1/2			
	#5 -x,-y+1,-z+2 #6 -x+1/2,y-1/2,-z+5/2 #7 x,y+1,z			
3a	N(1)-H(1)...O(2)#5	1.95	2.828(3)	171.9
	N(2)-H(2)...O(4)	1.97	2.805(3)	158.9
	Symmetry transformations used to generate equivalent atoms:			
	#1 -x+3/2,y+1/2,z #2 -x+3/2,-y+2,z-1/2 #3 -x+3/2,y-1/2,z			
	#4 -x+3/2,-y+2,z+1/2 #5 -x+2,-y+2,-z+1			

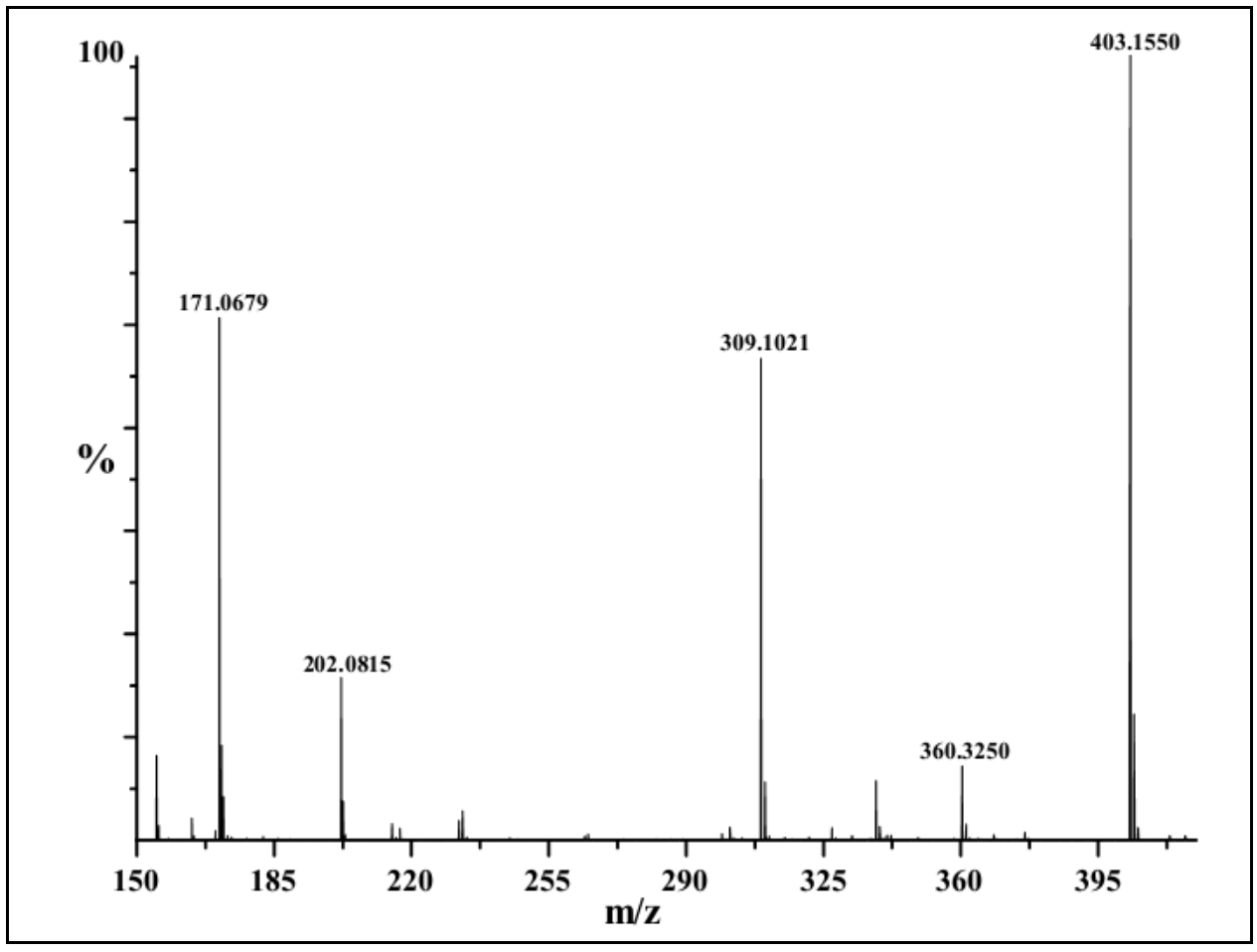

Figure S1: ESI(+) Mass spectra of **1**.

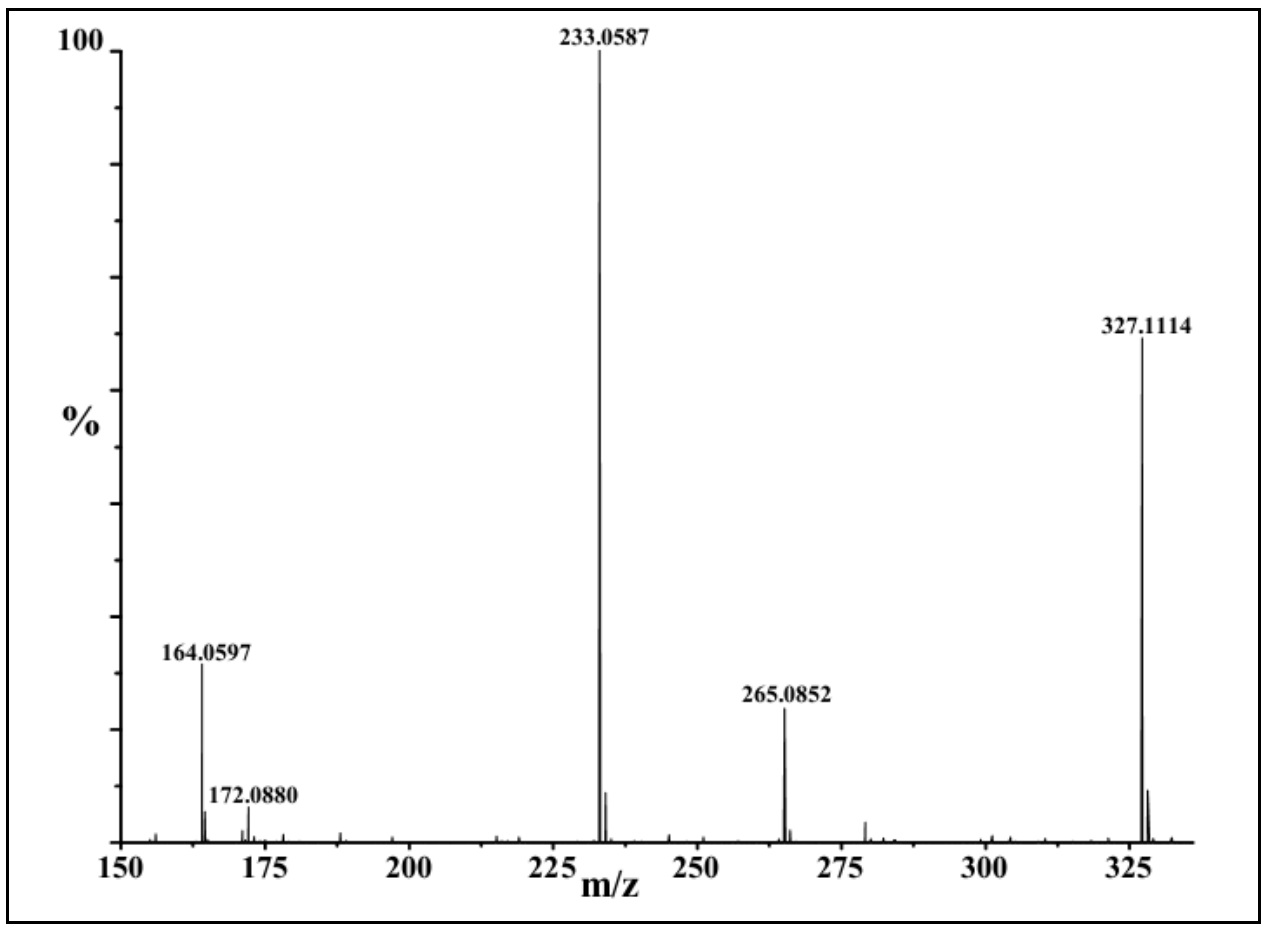

Figure S2: ESI(+) Mass spectra of **2**.

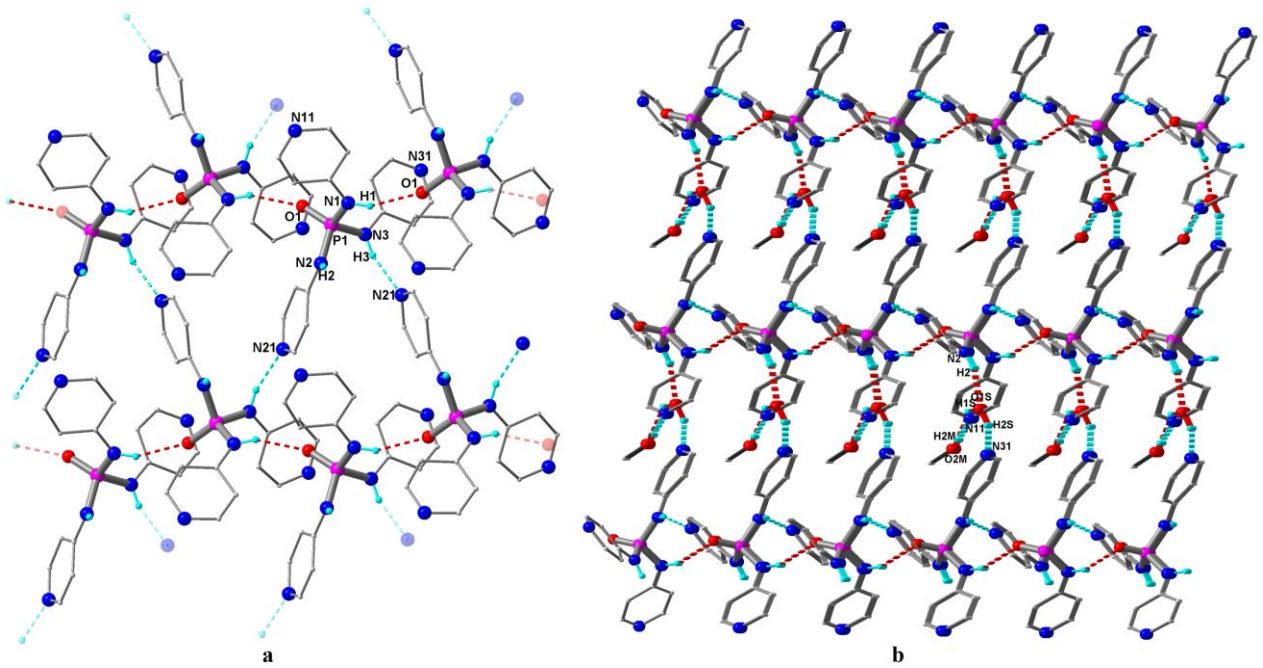

Figure S3: (a) View of the H-bonded 2D-sheet in **2** formed by the interaction of amino protons with P=O and pyridyl groups; (b) formation the 3D-network mediated by the solvated water molecules. The layers are slightly offset to show the 3D-nature of the network.

Interaction of one of the amino protons (N1−H1) with the nearby P═O group (O1) initially forms a 1D-chain structure along the c-axis. Interaction of the second amino-proton (N3−H3) with the pyridyl groups (N21) that belongs to N2 connects the adjacent chains resulting in a 2D-sheet structure running along the bc-plane (Figure S3a). Finally, the solvated water molecules act as a linker between the individual 2D-sheets and connects the remaining amino protons (N2-H2…O1S) and one of the pyridyl nitrogens (O1S-H2S…N31) forming the 3D-network. The solvated molecules of methanol are located along the 1D-channel inside the network and involved in H-bonding with water (O1S-H1S…O2M) and the remaining pyridyl moiety (O2M-H2M…N11) (Figure S3b).

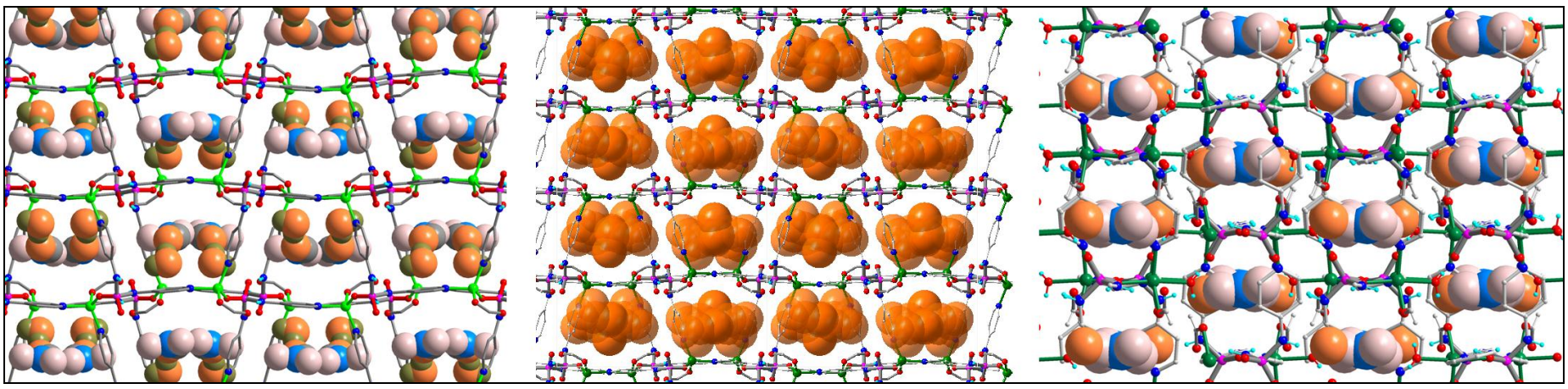

Figure S4: Packing diagram of **3** (left), **3a** (middle) and **4** (right) with solvated molecules shown in space fill representation. **3** contains solvated DMF and water, **3a** contains disordered methanol and water and **4** contains disordered DMF. The solvent disorder in **3a** could not be resolved and hence they are refined as partially occupied oxygen atoms. In **4** the whole DMF molecule was disordered over two positions of which only one of them is shown in the packing. *Color code for solvent atoms:* **oxygen:** ***orange***; **hydrogen:** ***dusty green***; **nitrogen:** ***light blue***; **carbon:** ***light pink***.

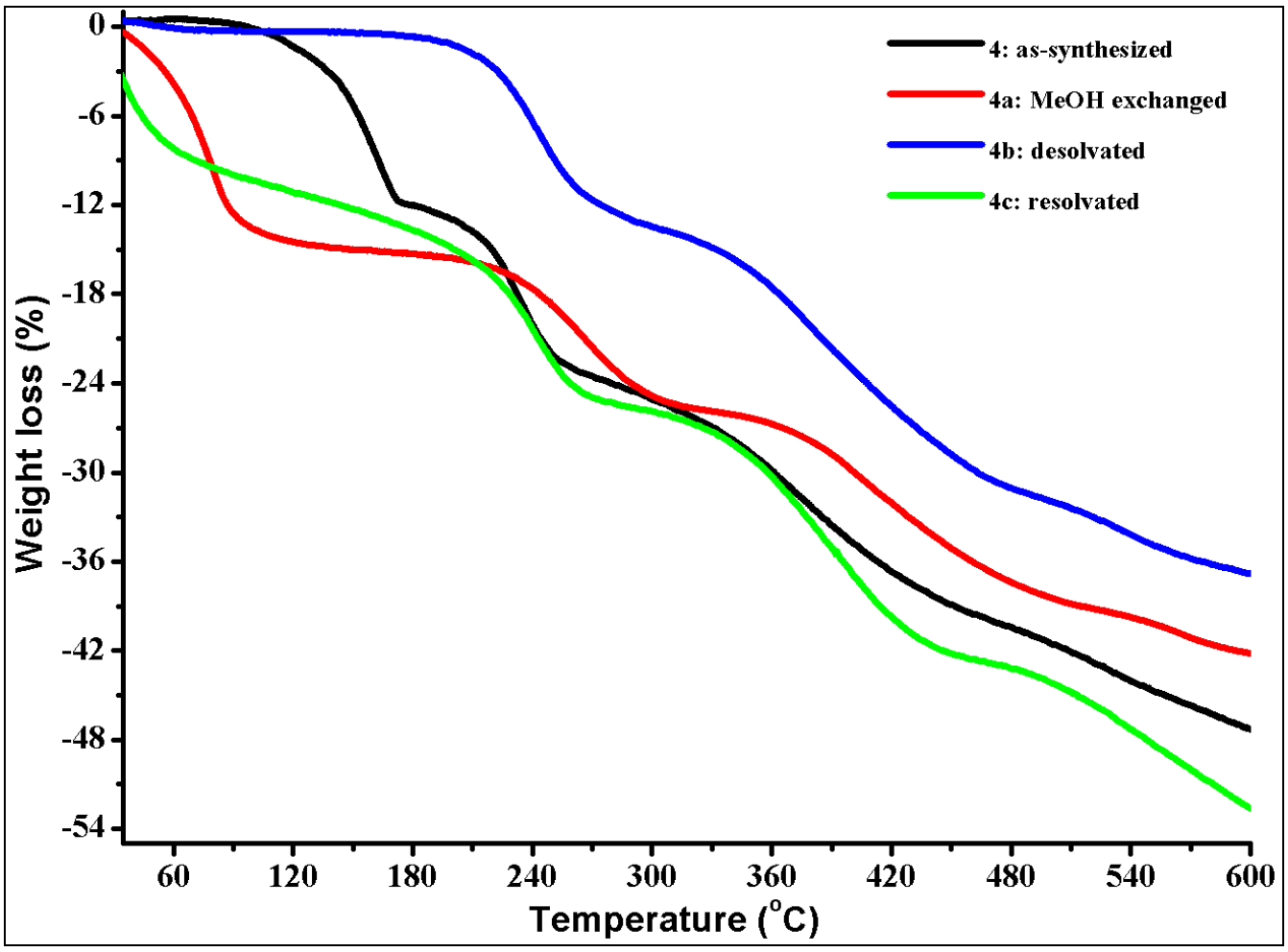

Figure S5: TGA graphs for various samples of **4**

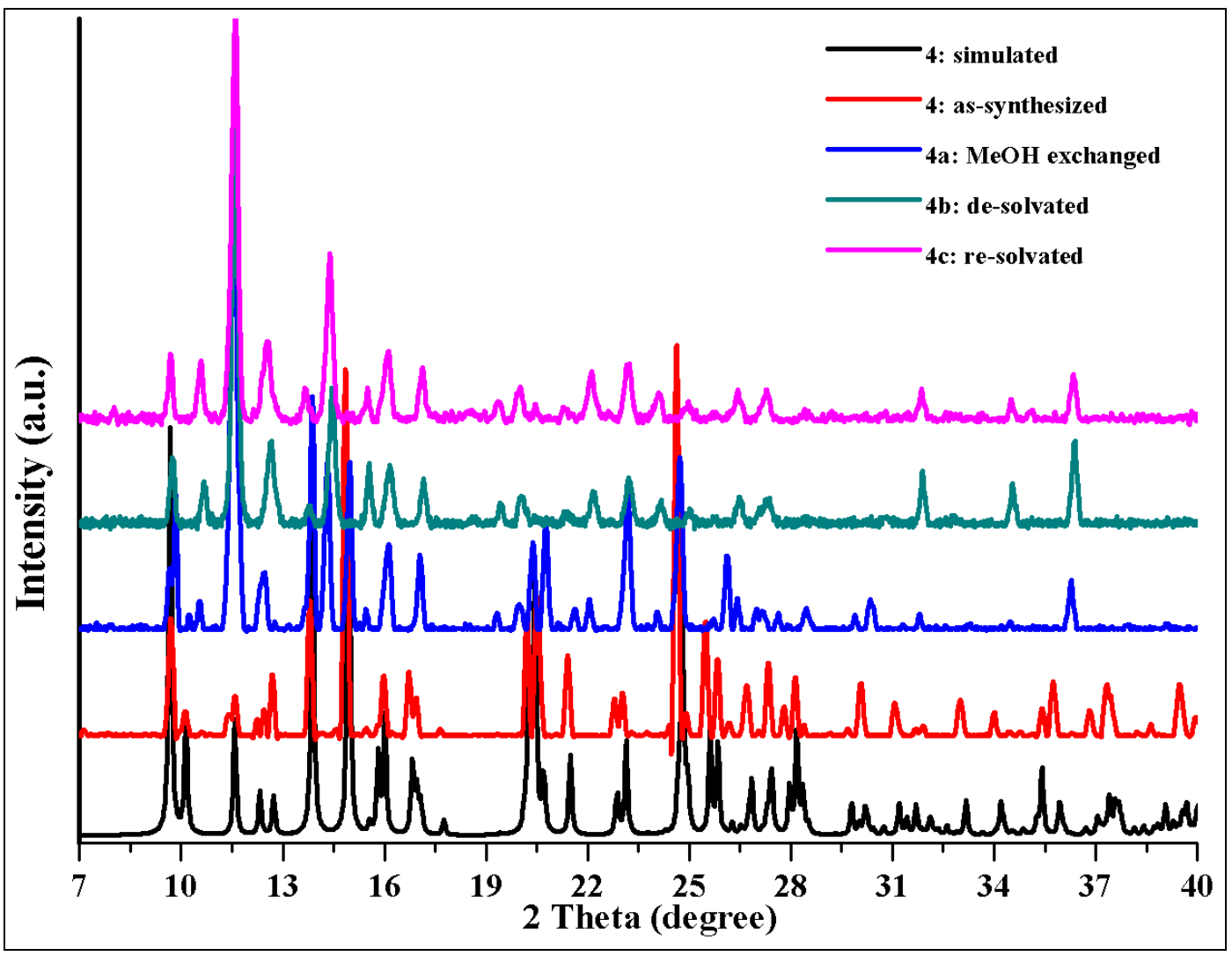

Figure S6: PXRD patterns for various samples of **4**

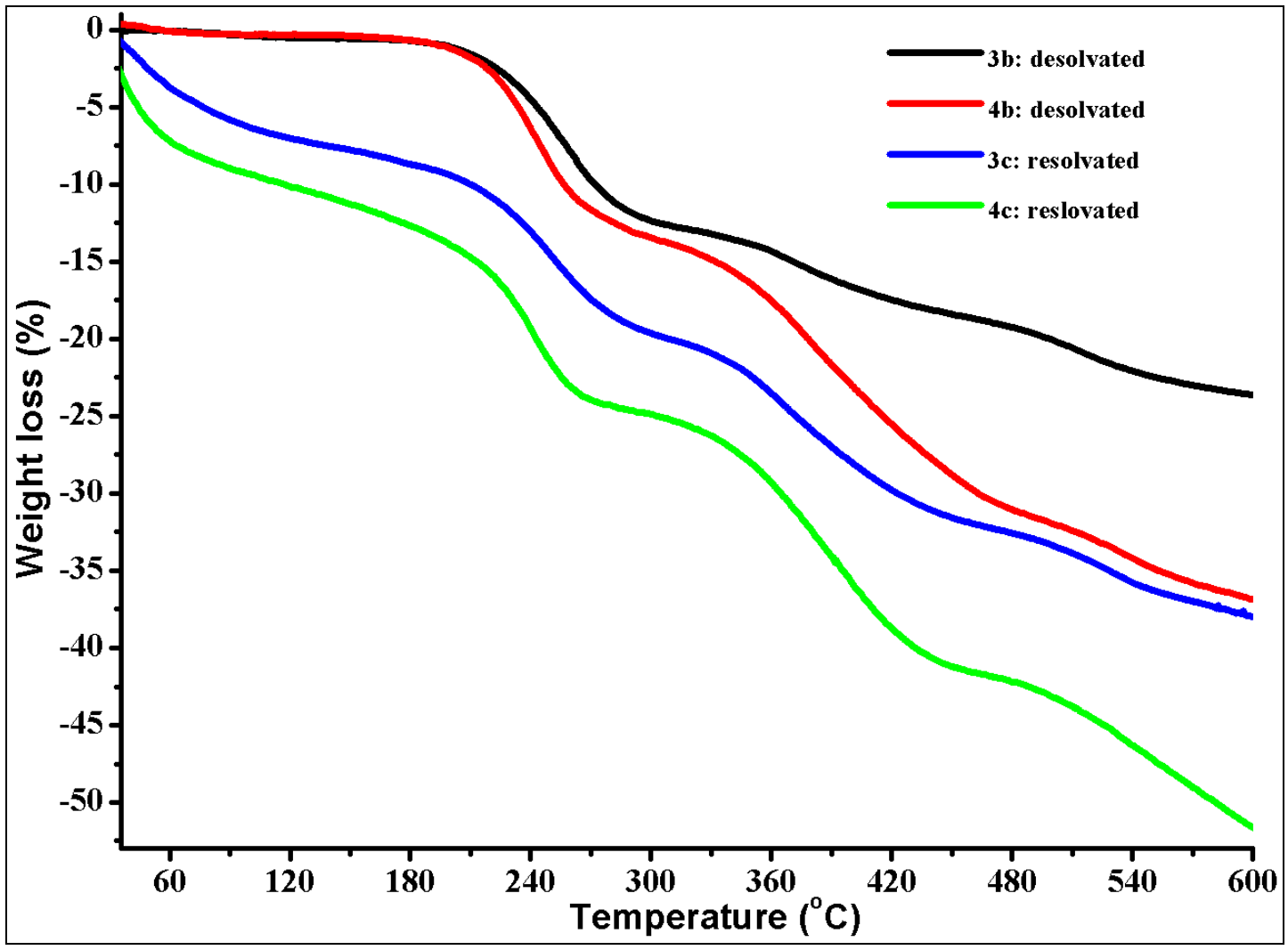

Figure S7: TGA comparison plots for de-solvated and re-solvated samples of **3** and **4**

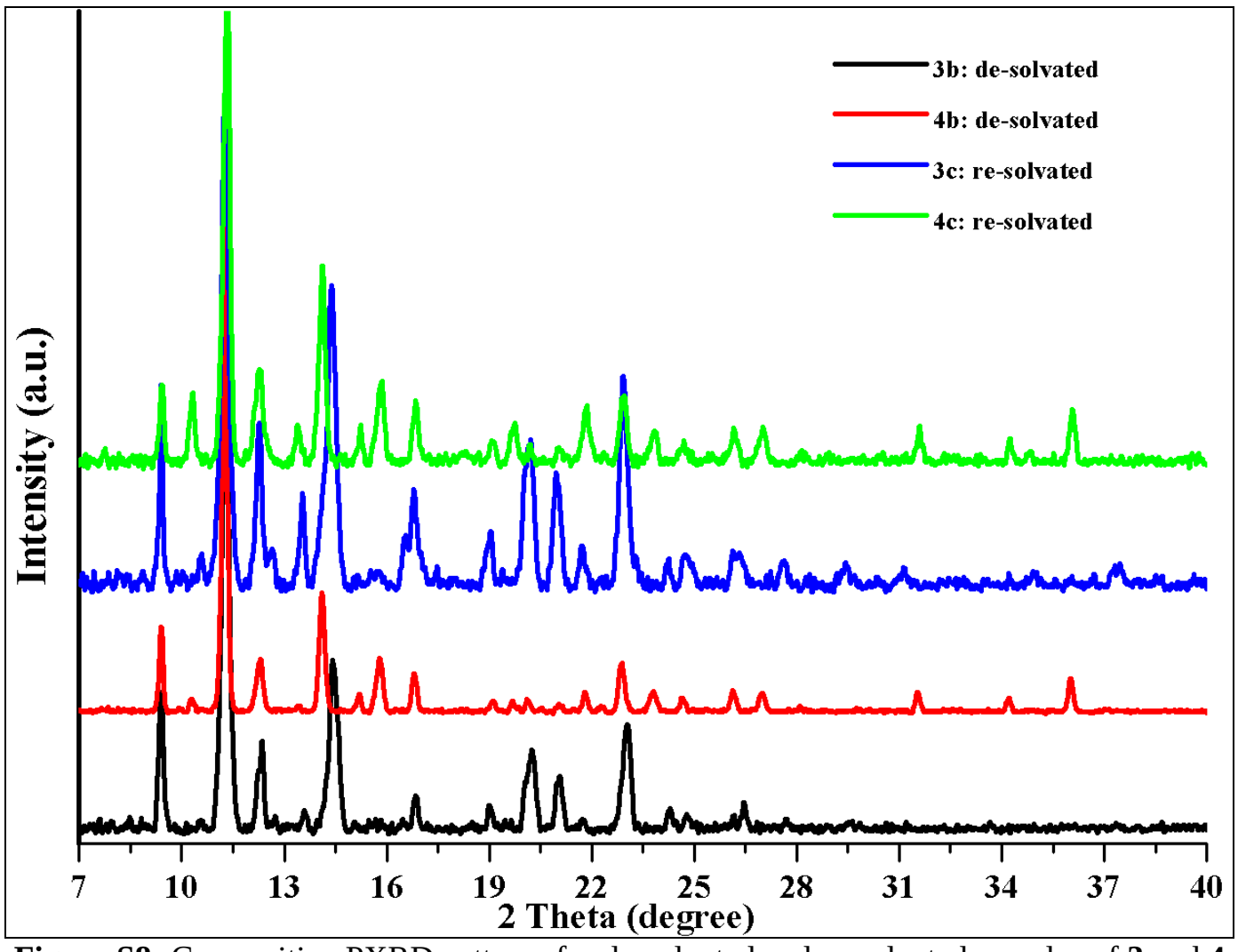

Figure S8: Comparitive PXRD patterns for de-solvated and re-solvated samples of **3** and **4**

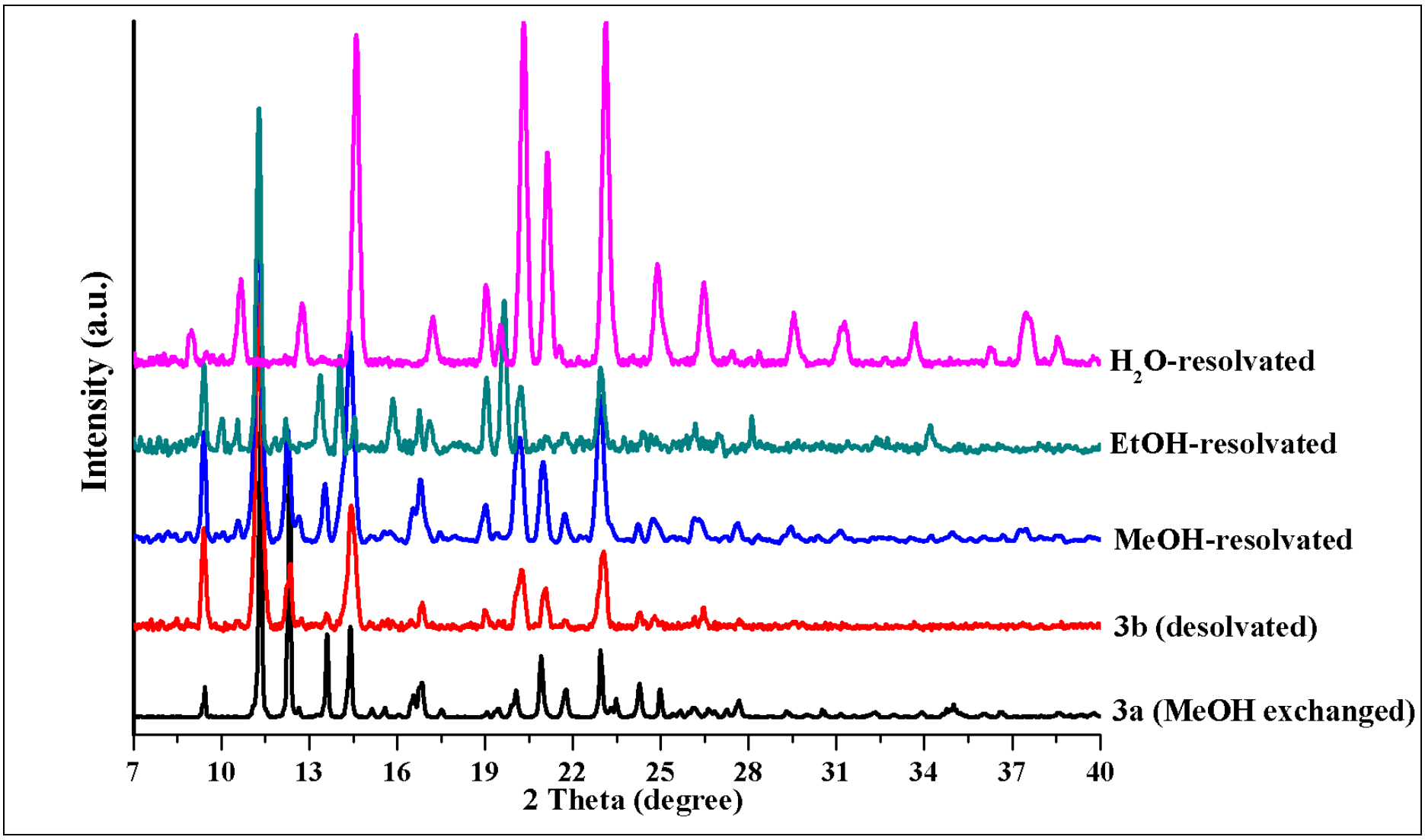

Figure S9: Comparitive PXRD patterns for methanol exchanged (3a), de-solvated (3b) and various re-solvated samples

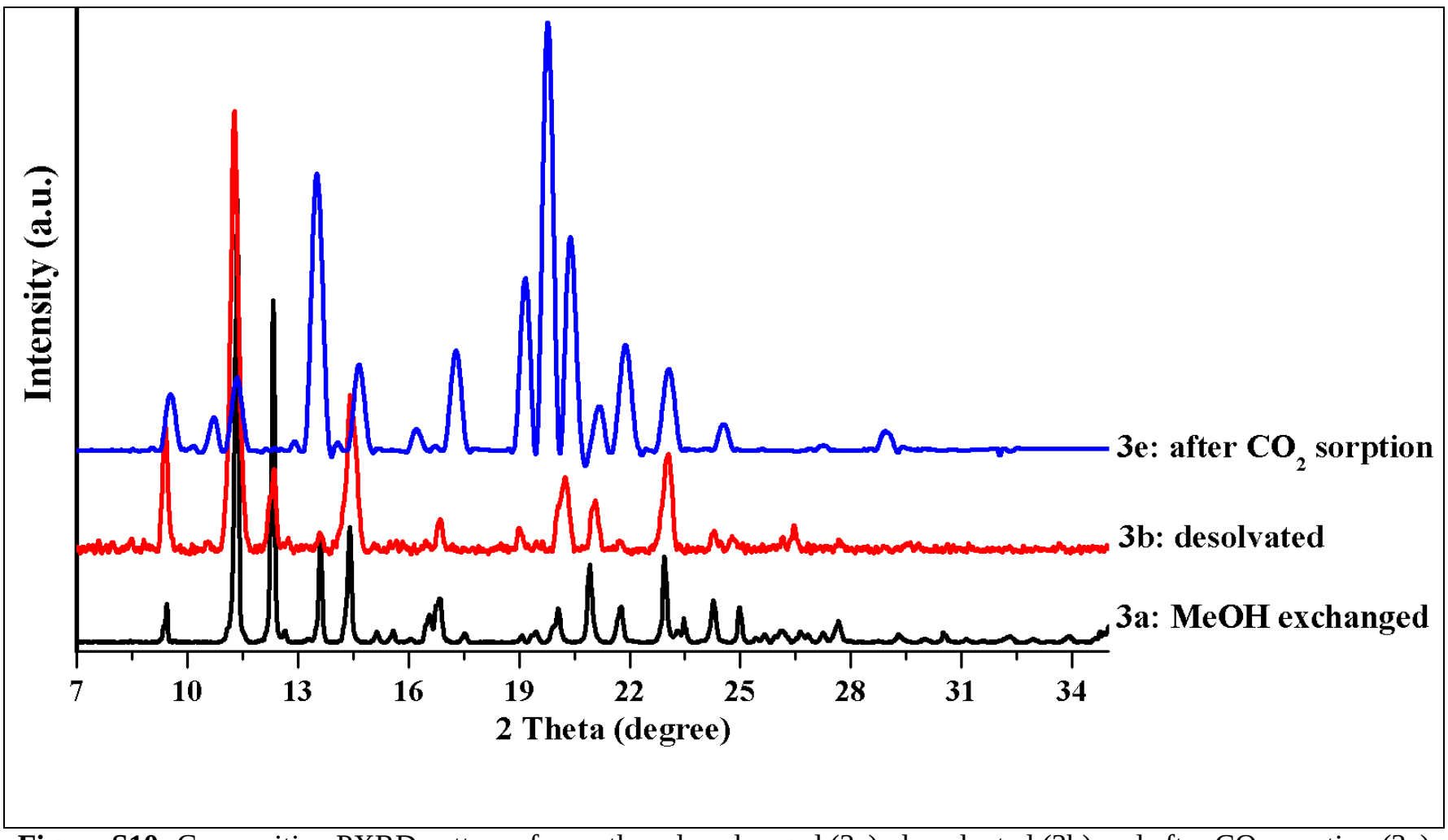

Figure S10: Comparitive PXRD patterns for methanol exchanged (3a), de-solvated (3b) and after CO_2 sorption (3e)

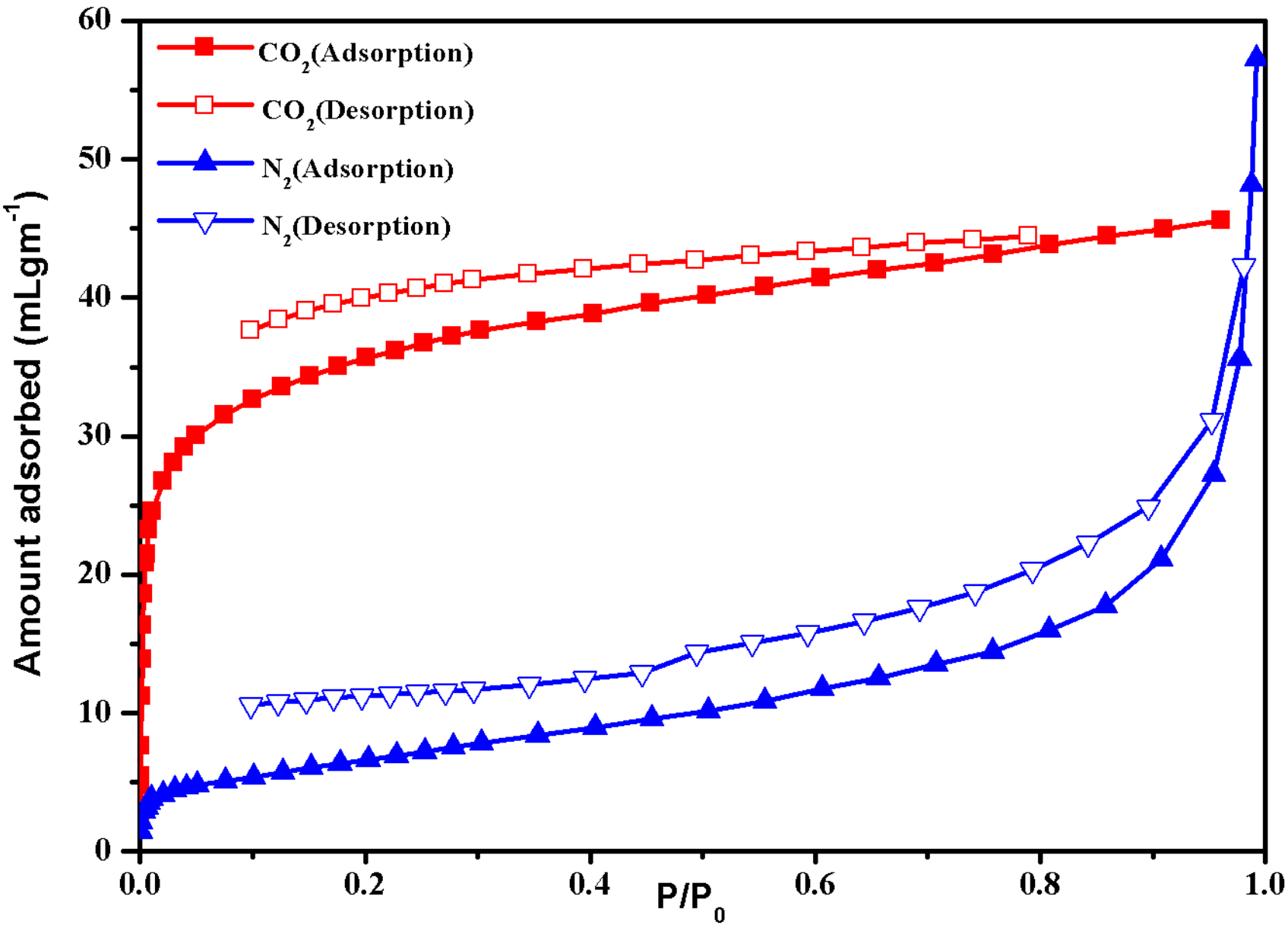

Figure S11: CO_2 and N_2 adsorption and desorption isotherms of **3b** at 195K and 77K, respectively. The BET surface area is calculated to be 133.4 m^2g^{-1}

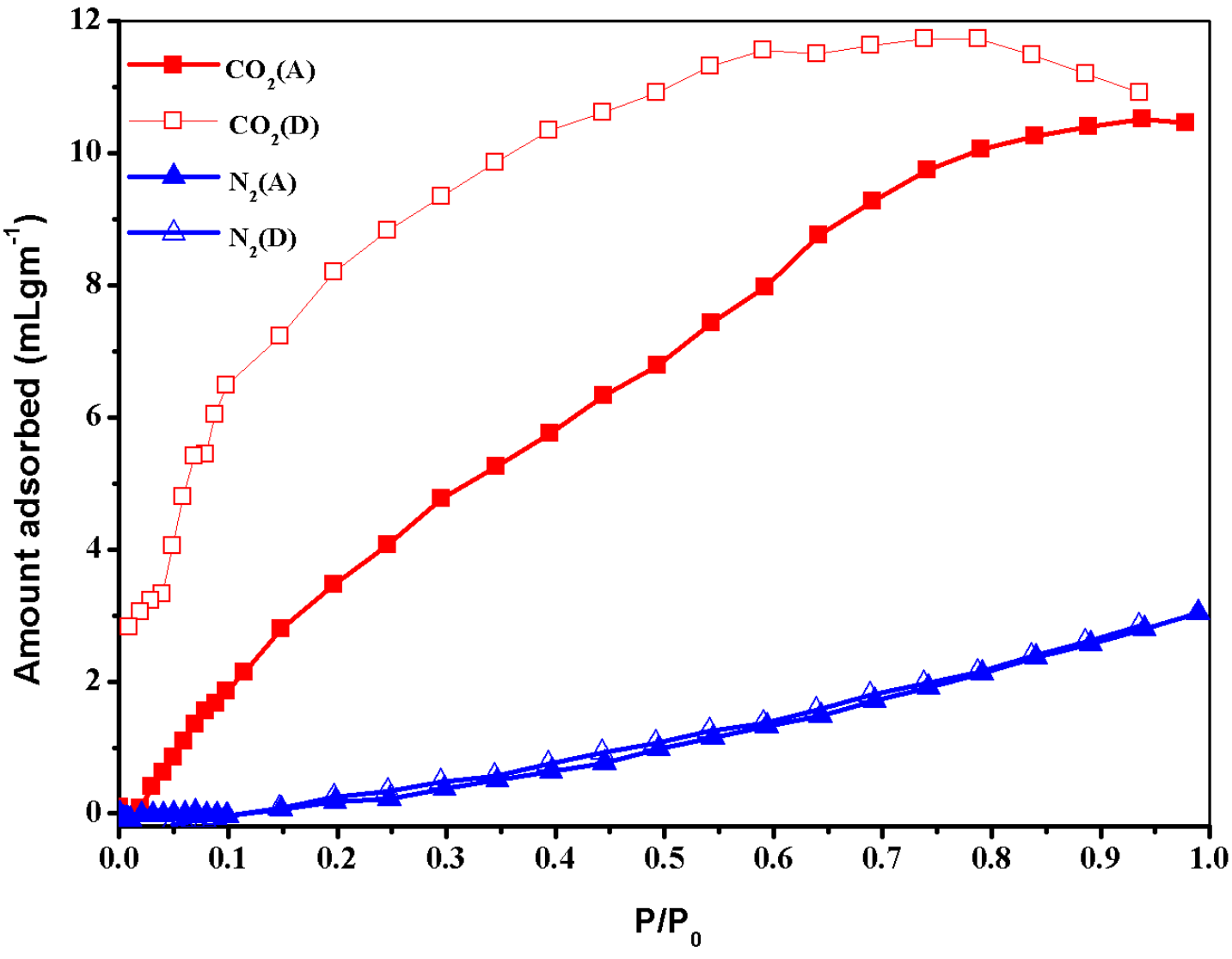

Figure S12: CO_2 and N_2 adsorption and desorption isotherms of **3b** at room temperature.

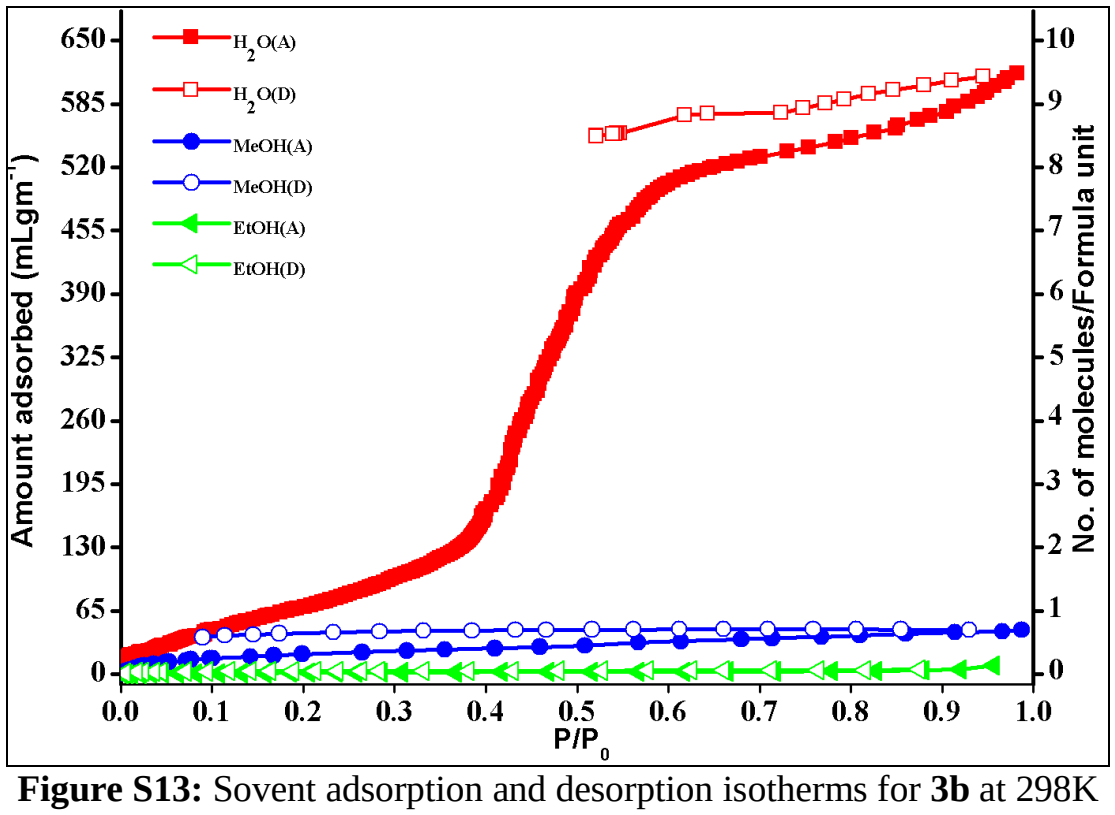

Figure S13: Sovent adsorption and desorption isotherms for **3b** at 298K

Number of solvent molecules per formula (N) unit has been calculated by

$$N = \frac{\text{Volume adsorbed (V) } \mathbf{X} \text{ Formula weight of the de-solvated sample (F)}}{\text{Molar volume of 1 mol. of a gas at STP (M)}}$$

M = 22.4 litre or 22400 mL for the gases at STP
F = 360.59 g/mol
From the graph, V = 615.91 ml/g for water, V = 45.63 for methanol and V= 8.79 for ethanol
For water adsorption N(w) = 9.91
For methanol adsorption N(m) = 0.734
For ethanol adsorption N(e) = 0.141

The ratio of N(w) / N(m) = 13.5
The ratio of N(w) / N(e) = 70.3

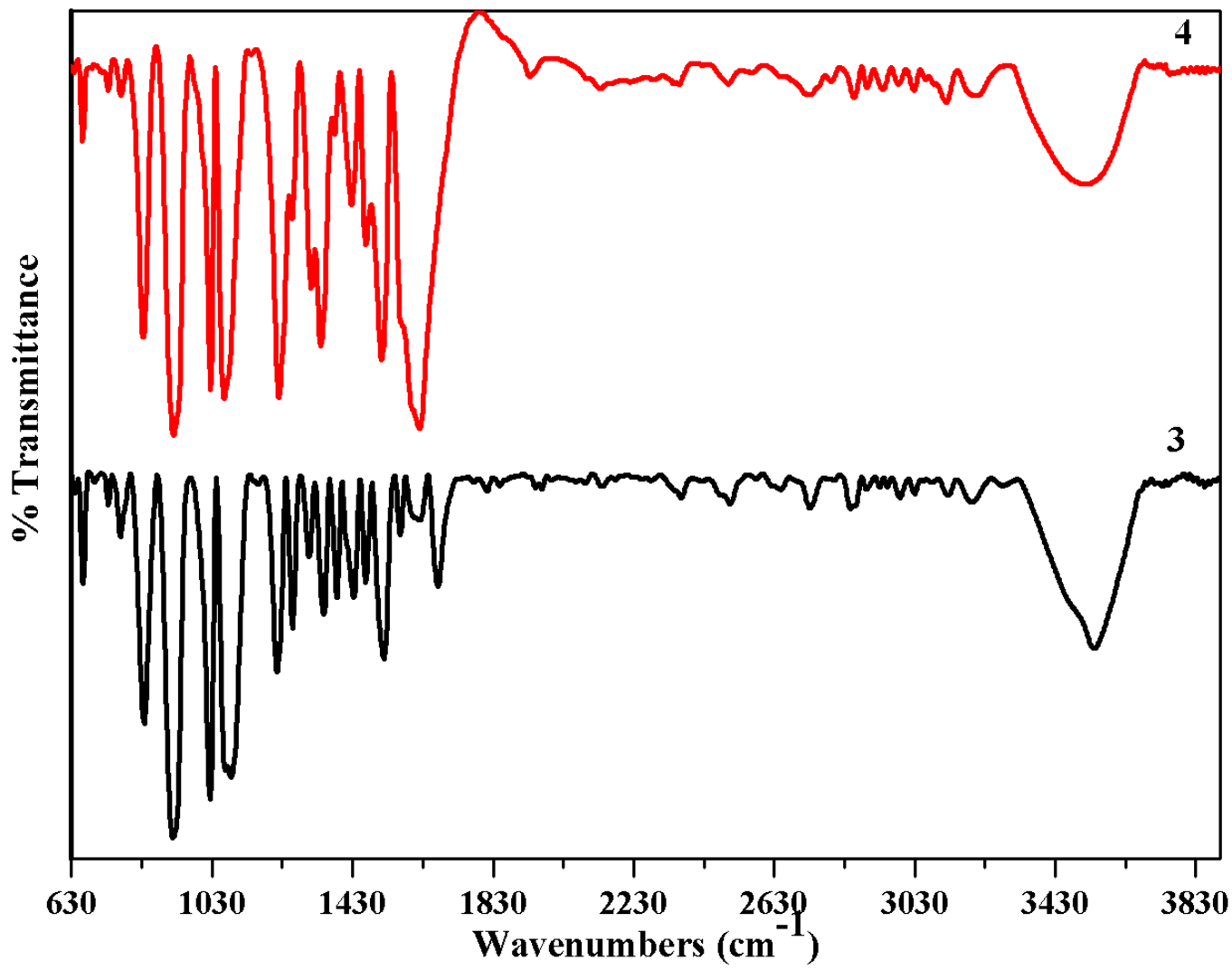

Figure S14: Infra Red spectra for **3** and **4**