Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supporting Information

Dynamic metal-organic frameworks: syntheses, characterization, sorption study and their hydrolytic inter-conversion

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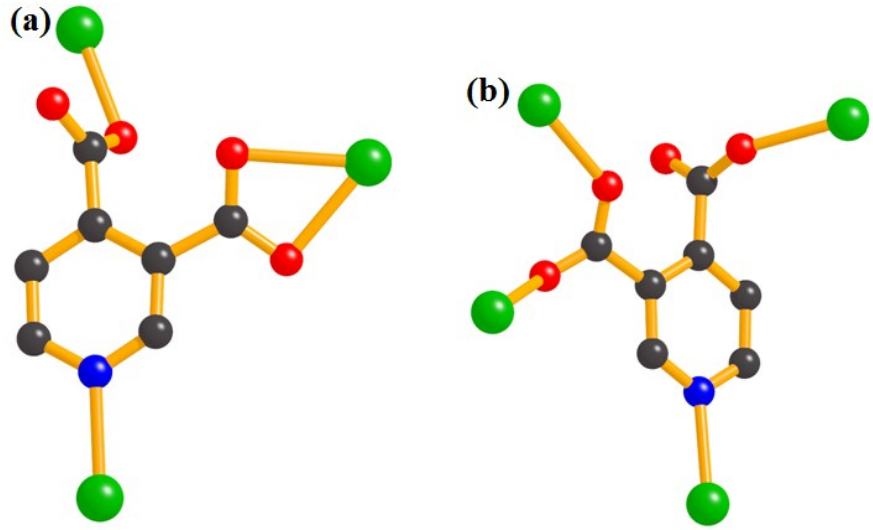

Fig. S1 (a, b) Binding mode of 3,4-pyrdc with Cd(II) in **1** and **2**, respectively.

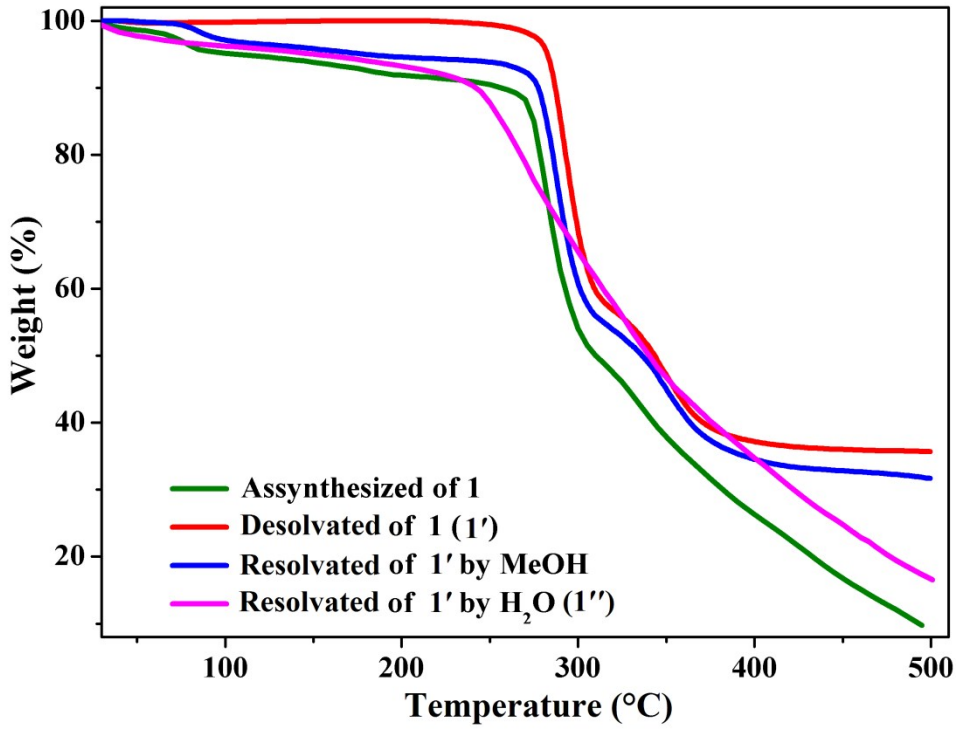

Fig. S2 Thermogravimetric analysis of compound **1** in different state.

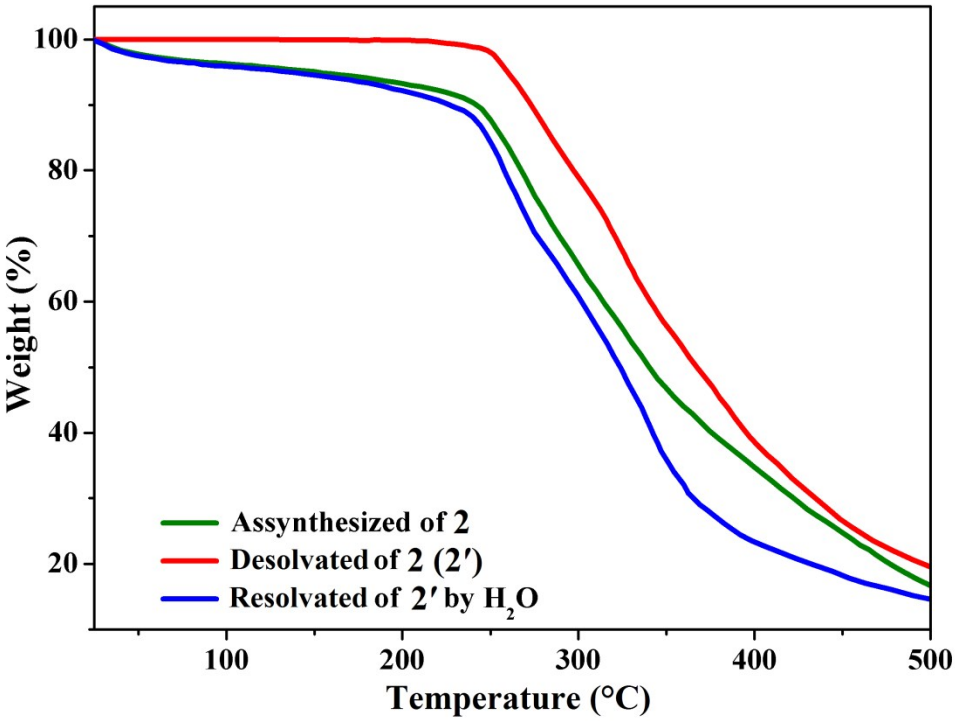

Fig. S3 Thermogravimetric analysis of compound **2** in different state.

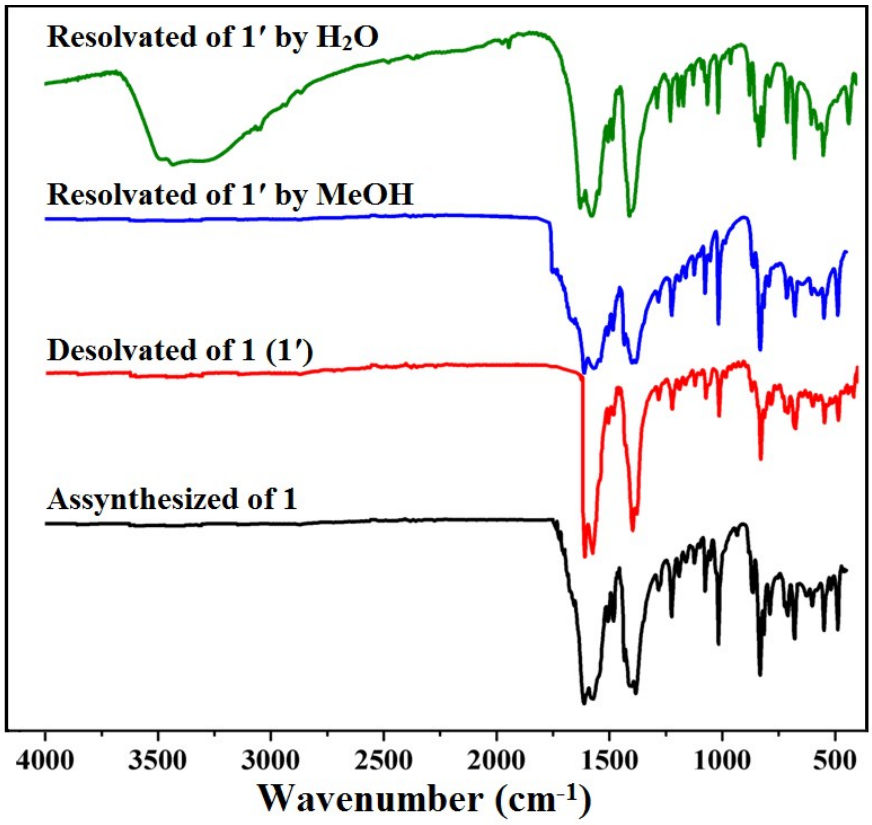

Fig. S4 IR spectrum of compound **1** in different state.

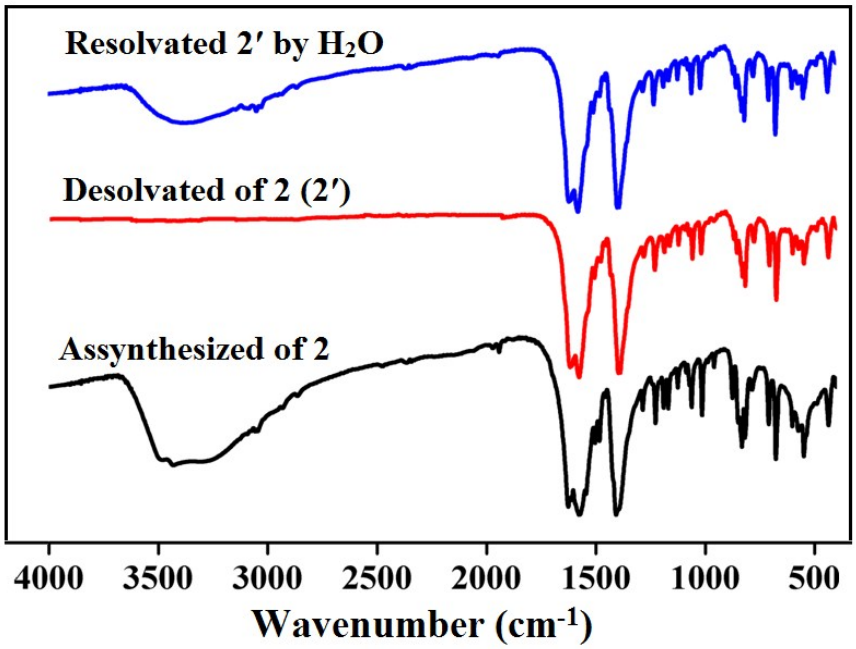

Fig. S5 IR spectrum of compound **2** in different state.

Table S1 Selected bond lengths (Å) and bond angles (°) for **1**.

Cd1-N1	2.3490(17)	Cd1-N2	2.3071(17)
Cd1-O1S	2.365(2)	Cd1-O2^a	2.2577(17)
Cd1-O3^b	2.5132(16)	Cd1-O4^b	2.3346(17)
O1S-Cd1-N1	79.23(6)	O1S-Cd1-N2	82.59(7)
O1S-Cd1-O2^a	125.05(7)	O1S-Cd1-O3^b	88.69(6)
O1S-Cd1-O4^b	140.04(6)	N1-Cd1-N2	161.68(6)
O2^a-Cd1-N1	92.80(6)	O3^b-Cd1-N1	91.62(6)
O4^b-Cd1-N1	87.87(6)	O2^a-Cd1-N2	99.45(6)
O3^b-Cd1-N2	85.76(6)	O4^b-Cd1-N2	104.92(6)
O2^a-Cd1-O3^b	146.19(6)	O2^a-Cd1-O4^b	92.94(6)
O3^b-Cd1-O4^b	53.75(6)		

Symmetry code: *a* = 1-x, 1/2+y, 1/2-z; *b* = -1/2+x, y, 1/2-z.

Table S2 π-π and C-H···π interactions in **1**.

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(3)^i	4.2818(15)	36.78(12)	2.5383(8)
R(3)→ R(1)^i	4.2818(15)	36.78(12)	4.0961(12)
C-H→ ring(j)	H...R distance (Å)	C-H...R angle (deg)	C...R distance (Å)
C17-H17→ R(2)^{ii}	2.73	159	3.619(3)

Symmetry code: i = 1-x, -y, -z; ii = 1/2+x, 1/2-y, -z.

R(i)/R(j) denotes the ith/jth rings: R(1) = N(1)/C(1)/C(2)/C(3)/C(4)/C(5); R(2) = N(2)/C(8)/C(9)/ C(10)/C(11)/C(12); R(3) = N(3)/C(17)/C(16)/C(15)/C(19)/C(18).

Table S3 Hydrogen bonding interactions (Å, °) of **1**.

D-H…A	D-H	H…A	D…A	<D-H...A
O1S- H1S… N3^i	0.84(2)	1.95(2)	2.764(3)	165(2)

Symmetry code: i = 1-x, -y, -z.

Table S4 Selected bond lengths (Å) and bond angles (°) for **2**.

Cd1-O1	2.268(2)	Cd1-O1W	2.348(3)
Cd1-N2	2.330(2)	Cd1-N1^a	2.339(2)
Cd1-O3^c	2.3143(18)	Cd1-O2^b	2.244(2)
O1-Cd1-O1W	174.49(7)	O1-Cd1-N2	88.97(8)
O1-Cd1-N1^a	81.08(8)	O1-Cd1-O3^c	89.81(7)
O1-Cd1-O2^b	107.57(8)	O1W-Cd1-N2	93.14(8)
O1W-Cd1-N1^a	96.01(8)	O1W-Cd1-O3^c	85.18(8)
O1W-Cd1-O2^b	76.77(8)	N1^a-Cd1-N2	166.63(8)
O3^c-Cd1-N2	87.94(7)	O2^b-Cd1-N2	105.53(7)
O3^c-Cd1-N1^a	83.14(7)	O2^b-Cd1-N1^a	86.09(7)
O2^b-Cd1-O3^c	157.87(8)		

Symmetry code: *a* = x, -y, -1/2+z; *b* = 1/2-x, 1/2-y, 1-z; *c* = 1/2-x, -1/2+y, 3/2-z.

Table S5: Indexing result from the powder data of desolvated frameworks of compounds 1 (1′) by TREOR 90 programme.

Conventional cell		Reduced-Cell	
a/ Å = 13.3916	α/° = 90.000000	*a* = 13.541243	α/° = 90.000000
b/ Å = 12.6857	β/° = 90.000000	*b* = 12.964687	β/° = 90.000000
c/ Å = 23.5448	γ/° = 90.000000	*c* = 20.947752	γ/° = 90.000000
Volume of the conventional cell = 3999.83 Å^3		Volume of the reduced cell = 3677.55 Å^3	
Orthorhombic system *Pbca* space group		Orthorhombic system *Pna*2$_1$ space group	

H	K	L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS	FREE PARAM.
1	1	0	0.004597	0.004588	0.008	7.776	7.768	11.3604	10
0	2	0	0.005427	0.005409	0.014	8.449	8.435	10.4560	100
1	1	1	0.008133	0.008118	0.010	10.348	10.339	8.5413	1
1	2	0	0.008653	0.008644	0.005	10.675	10.670	8.2806	52
0	0	2	0.014138	0.014120	0.009	13.657	13.649	6.4783	17
1	3	0	0.015420	0.015405	0.007	14.266	14.260	6.2031	17
0	1	2		0.015472			14.291		
2	0	1	0.016496	0.016473	0.010	14.759	14.748	5.9973	6
2	1	1	0.017835	0.017825	0.004	15.349	15.345	5.7678	7
1	3	1	0.018934	0.018935	-0.000	15.818	15.819	5.5979	3
0	4	0	0.021699	0.021634	0.026	16.942	16.916	5.2291	11
1	2	2	0.022747	0.022764	-0.007	17.349	17.356	5.1073	30
1	4	0	0.024867	0.024870	-0.001	18.146	18.147	4.8847	78
2	0	2	0.026964	0.027063	-0.035	18.903	18.937	4.6909	2
1	4	1	0.028361	0.028400	-0.013	19.391	19.404	4.5739	28
2	1	2		0.028415			19.409		
1	3	2	0.029550	0.029525	0.009	19.797	19.788	4.4809	5

3	2	0		0.034531			21.418		
2	4	0	0.034574	0.034577	-0.001	21.432	21.433	4.1426	4
0	4	2	0.035756	0.035754	0.001	21.800	21.799	4.0735	4
1	1	3	0.036284	0.036358	-0.023	21.962	21.985	4.0438	2
0	2	3	0.037229	0.037178	0.015	22.250	22.234	3.9922	4
0	5	1		0.037334			22.281		
1	4	2	0.039071	0.038990	0.024	22.801	22.777	3.8969	3
1	2	3		0.040414			23.195		
1	5	1	0.040527	0.040569	-0.012	23.227	23.240	3.8263	6
3	1	2		0.044594			24.382		
2	0	3	0.044699	0.044713	-0.004	24.411	24.415	3.6433	10
3	3	1		0.044821			24.445		
2	5	0	0.046715	0.046747	-0.009	24.964	24.973	3.5639	8
3	2	2		0.048651			25.485		
0	6	0	0.048684	0.048677	0.002	25.494	25.492	3.4911	6
2	4	2		0.048697			25.497		
2	2	3	0.050153	0.050122	0.008	25.882	25.874	3.4395	5
2	5	1		0.050277			25.915		
1	5	2	0.051089	0.051159	-0.018	26.127	26.145	3.4079	5
4	0	0		0.051773			26.304		
1	6	0	0.051881	0.051913	-0.008	26.332	26.340	3.3818	6
3	3	2		0.055411		27.230			
1	6	1	0.055484	0.055443	0.010	27.248	27.238	3.2701	7
1	4	3	0.056642	0.056640	0.001	27.537	27.536	3.2365	5
4	1	1		0.056655		27.540			
4	2	1	0.060740	0.060711	0.007	28.536	28.529	3.1254	8
2	5	2		0.060867		28.566			
3	0	3		0.060892		28.572			
2	6	0	0.061595	0.061620	-0.006	28.740	28.746	3.1037	7
0	6	2	0.062707	0.062797	-0.021	29.004	29.025	3.0760	10
3	4	2	0.064981	0.064876	0.024	29.537	29.513	3.0217	6
1	2	4		0.065124		29.570			
2	6	1		0.065150		29.576			
2	1	4	0.070888	0.070775	0.025	30.882	30.857	2.8931	5
1	7	1		0.073021		31.355			
3	3	3	0.073109	0.073061	0.010	31.375	31.364	2.8488	8
4	3	2		0.078062		32.448			
0	4	4	0.078199	0.078114	0.018	32.477	32.459	2.7545	7
2	7	1	0.082753	0.082728	0.005	33.437	33.432	2.6777	6
0	1	5		0.089602		34.835			
1	8	0	0.089736	0.089773	-0.007	34.862	34.870	2.5714	12
5	2	1		0.089833		34.882			
1	3	5	0.103736	0.103655	0.015	37.578	37.562	2.3916	11
1	8	2		0.103893		37.607			

Number of obs. lines = 39

Number of calc. lines = 61

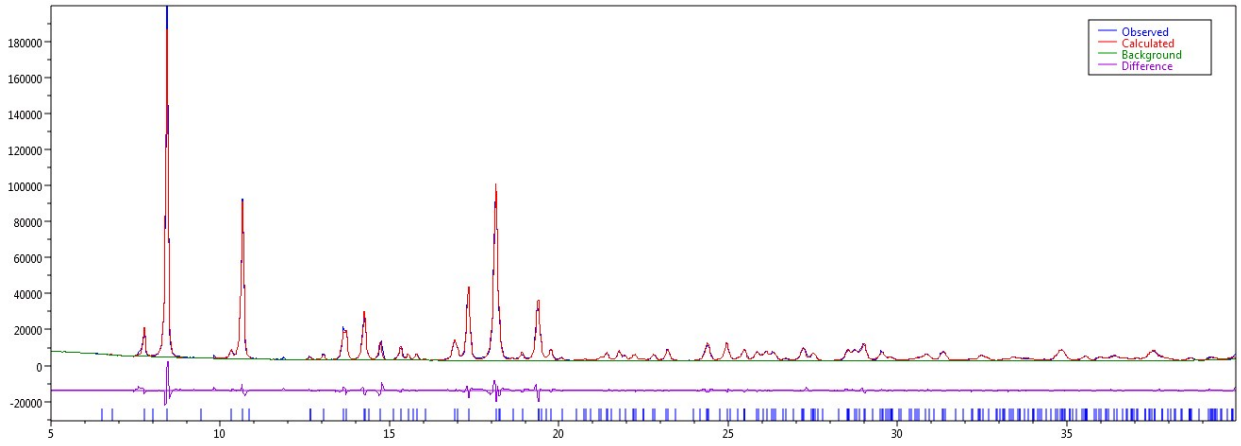

Fig. S6 LeBail fitting of powder pattern of **1′**.

Table S6: Indexing result from the powder data of desolvated frameworks of compounds 2 (2′) by TREOR 90 program.

Conventional cell		Reduced-Cell	
a/ Å = 22.4577	α/° = 90.000000	*a* = 12.91903	α/° = 95.355
b/ Å = 11.3406	β/° = 113.556	*b* = 11.80643	β/° = 107.787
c/ Å = 12.0773	γ/° = 90.000000	*c* = 10.27471	γ/° = 111.558
Volume of the conventional cell = 2819.6 Å^3		Volume of the reduced cell = 1350 Å^3	
Monoclinic system *C*2/*c* space group		Triclinic system *P*$\bar{1}$ space group	

H	K	L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS	FREE PARAM.
0	0	1	0.006553	0.006552	0.001	9.287	9.286	9.5153	0.03
-1	0	1	0.007201	0.007207	-0.004	9.736	9.740	9.0770	1.00
0	-1	1	0.009054	0.009043	0.007	10.920	10.913	8.0952	0.10
1	-1	1	0.013755	0.013734	0.010	13.470	13.460	6.5679	0.04
-1	2	0	0.017268	0.017251	0.008	15.102	15.094	5.8617	0.10
0	2	0	0.020777	0.020805	-0.011	16.575	16.586	5.3440	0.32
0	0	2	0.026209	0.026207	0.001	18.633	18.633	4.7580	0.06
-1	1	2	0.029255	0.029239	0.005	19.697	19.691	4.5035	0.13
				0.030592			20.146	4.4040	
2	1	0		0.032502			20.772		
2	-2	1	0.032590	0.032515	0.024	20.801	20.777	4.2669	0.05
-3	1	0	0.035493	0.035490	0.001	21.719	21.718	4.0886	0.21
-3	2	1	0.038309	0.038330	-0.006	22.574	22.581	3.9355	0.05
-3	1	2	0.042522	0.042556	-0.010	23.801	23.810	3.7354	0.09
0	-3	1	0.045220	0.045233	-0.004	24.555	24.559	3.6223	0.06
0	3	0	0.046787	0.046811	-0.006	24.984	24.991	3.5611	0.03

-1	0	3	0.051331	0.051434	-0.027	26.190	26.217	3.3999	0.02
1	1	2	0.053956	0.053917	0.010	26.863	26.853	3.3161	0.03
-2	-2	2	0.055404	0.055401	0.001	27.228	27.227	3.2725	0.09
0	3	1	0.061516	0.061494	0.005	28.721	28.716	3.1057	0.22
3	0	1		0.061577			28.736		
2	0	2		0.061579			28.736		
-1	-2	3	0.064339	0.064282	0.013	29.387	29.374	3.0368	0.06
-2	2	3	0.073931	0.073861	0.015	31.555	31.540	2.8329	0.06
3	-2	2	0.078571	0.078568	0.001	32.557	32.556	2.7480	0.03
3	-1	2	0.080785	0.080839	-0.011	33.025	33.037	2.7101	0.09
				0.083429			33.577	2.6668	
-5	1	1	0.092010	0.091970	0.008	35.316	35.308	2.5394	0.06
0	2	3	0.096088	0.096032	0.011	36.116	36.105	2.4849	0.02
-1	-4	1		0.096194			36.137		
				0.103622			37.556	2.3929	

Number of obs. lines = 27

Number of calc. lines = 28

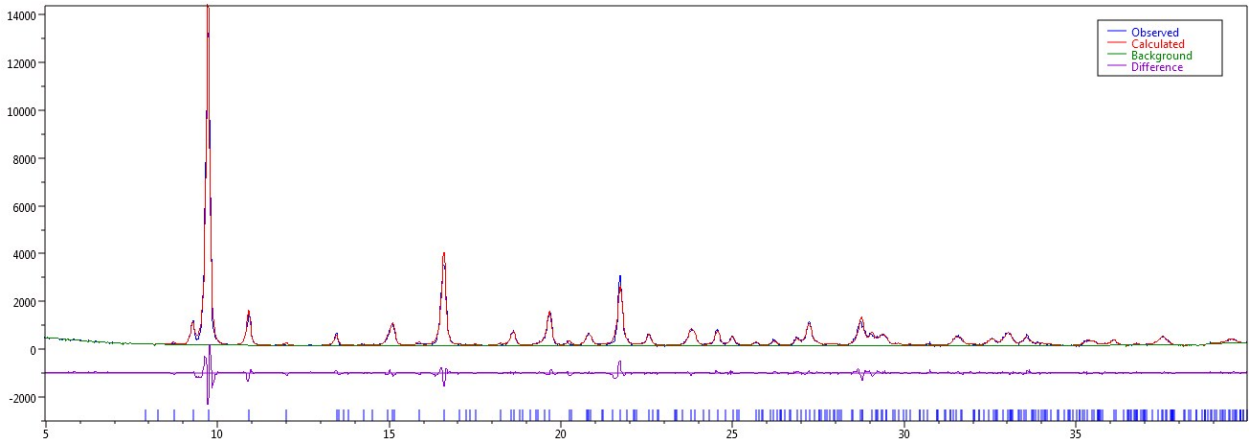

Fig. S7 LeBail fitting of powder pattern of **2′**.

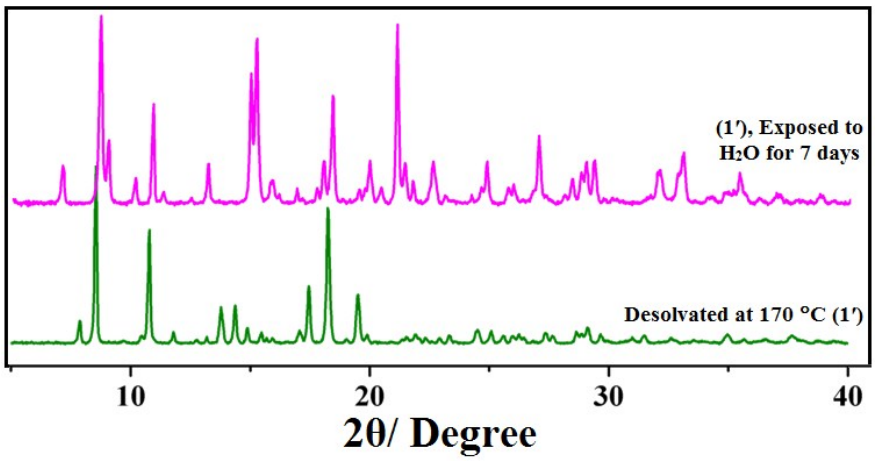

Fig. S8 Powder X-ray diffraction patterns of compound **1** in desolvated phaes and desolvated phase exposed to water for 7 days.

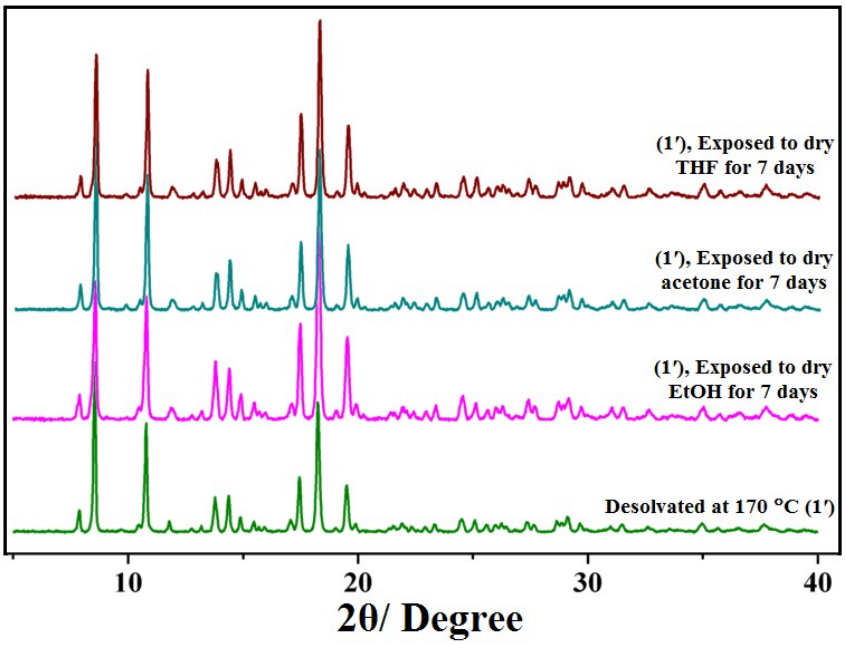

Fig. S9 Powder X-ray diffraction patterns of compound **1** in desolvated phase and desolvated phase exposed to different dry solvents for 7 days.

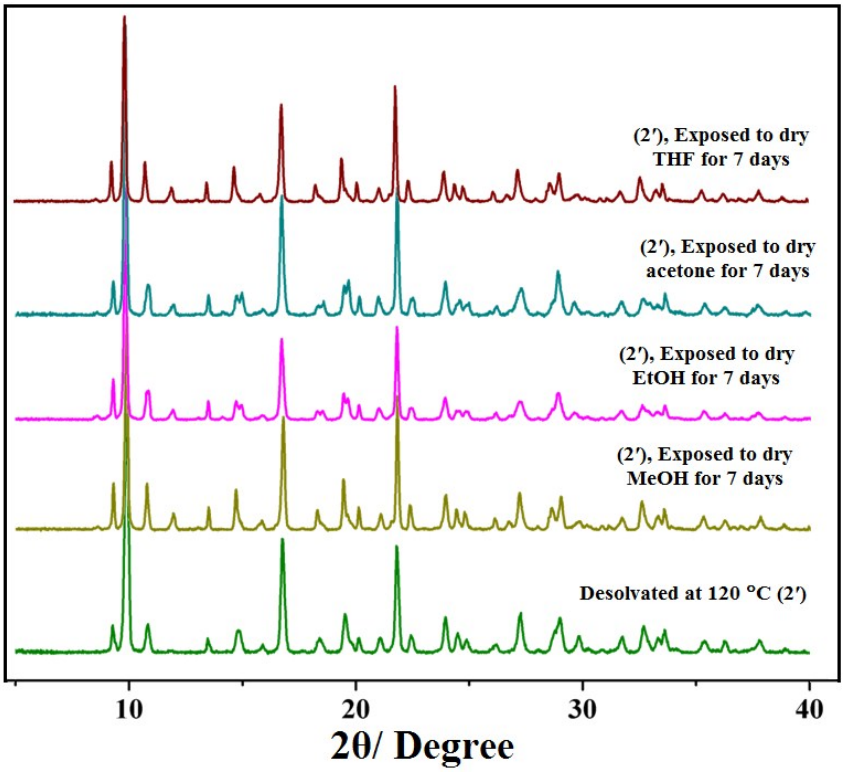

Fig. S10 Powder X-ray diffraction patterns of compound **2** in desolvated phase and desolvated phase exposed to different dry solvents for 7 days.

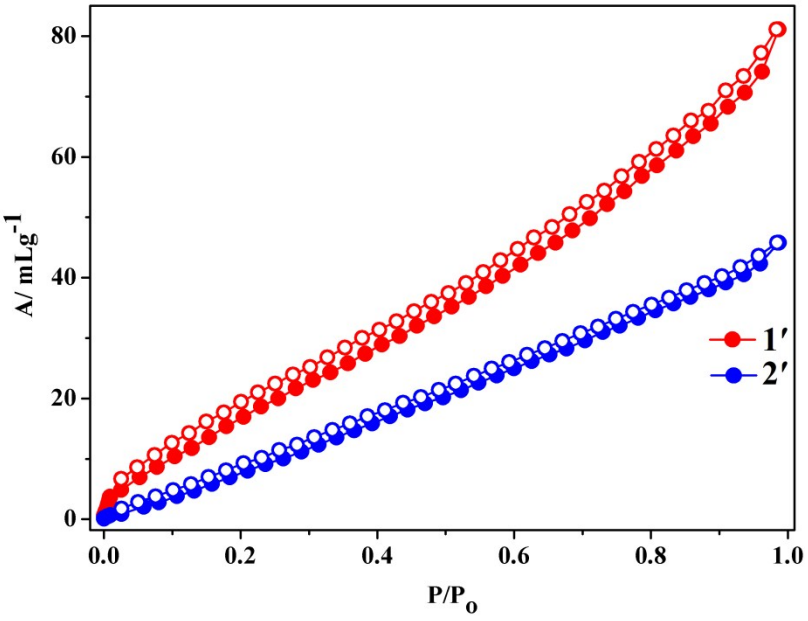

Fig. S11 N_2 adsorption isotherms of **1′** (red) and **2′** (blue) measured at 77 K. Filled and open circles represent adsorption and desorption respectively.

GC-MS study supporting the mechanism of 2D to 3D conversion:

Pure crystalline compound of **1** was isolated and treated at 170°C to prepare desolvated frameworks of **1** (**1′**). 50 mg of **1′** was immersed in water and kept undisturbed for seven days. After this, the slightly turbid mixture was filtrated and a white compound is separated. It was washed three times taking 10 ml of methanol each. The whole filtrate along with washing extract was then evaporated to get a white compound which was subjected to GC-MS study.

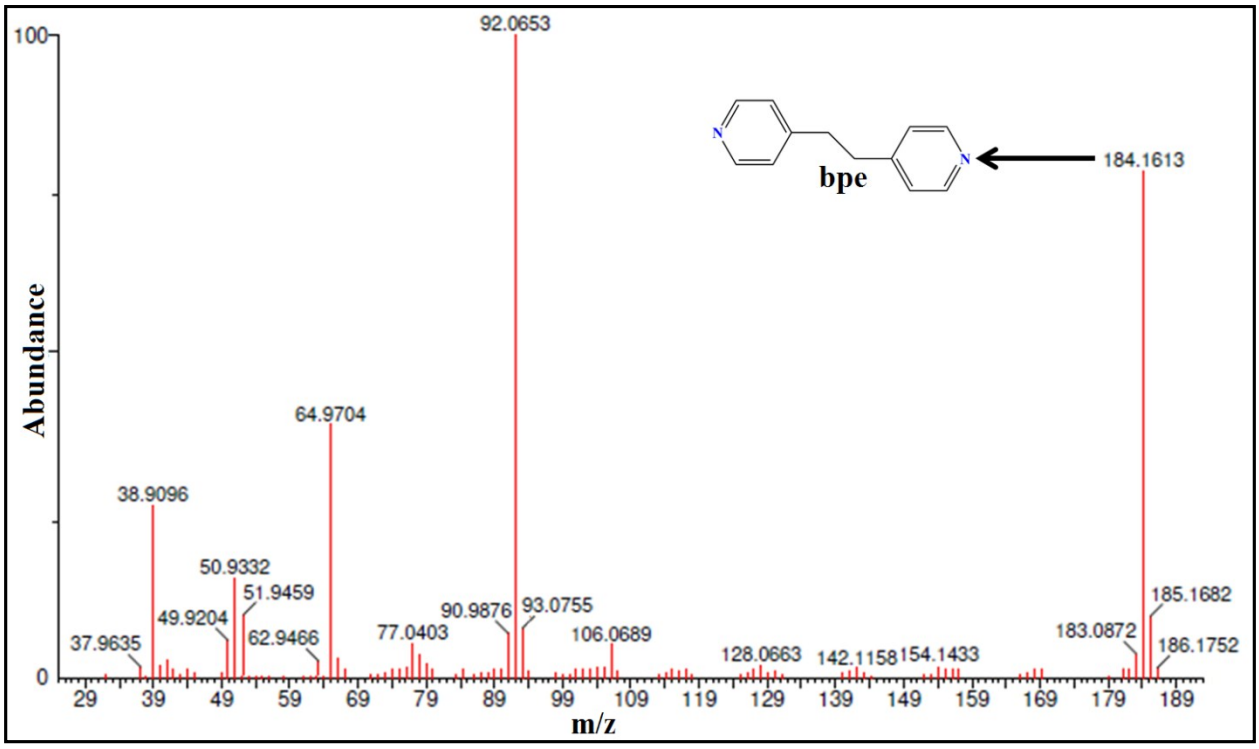

Fig. S12 Mass spectra of the peak at 11.06 min. from the GC trace for the remaining solid residue obtained by evaporating water-methanol combined filtrate.

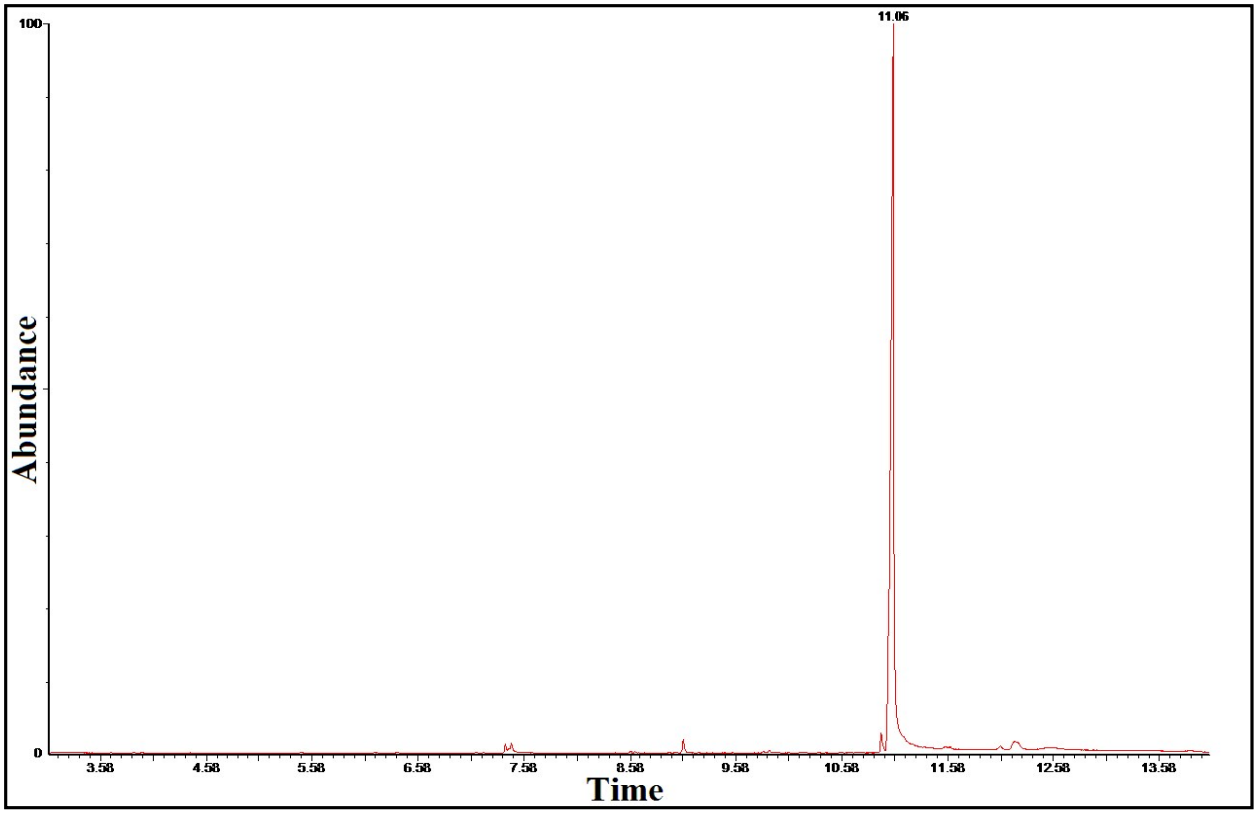

Fig. S13 GC trace for the remaining solid residue obtained by evaporating water-methanol combined filtrate.