Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Selective carbon dioxide uptake and crystal-to-crystal transformation: Porous 3D framework to 1D chain triggered by conformational change of the spacer

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Table S1. Selected bond lengths (Å) and angles (°) for $\{[Zn(bpe)_2(N(CN)_2)](N(CN)_2)(5H_2O)\}_n$ **(1).**

Zn1-N1	2.162(3)	Zn1-N3	2.153(3)
Zn1 -N1_b	2.162(3)	Zn1-N3_b	2.153(3)
Zn1-N2_c	2.213(3)	Zn1-N2_e	2.213(3)
N1-Zn1-N3	91.95(13)	N1-Zn1-N1_b	86.38(11)
N1-Zn1-N3_b	94.23(13)	N1-Zn1-N2_c	176.04(12)
N1-Zn1-N2_e	90.11(12)	N1_b-Zn1-N3	94.23(13)
N3-Zn1-N3_b	171.52(13)	N2_c-Zn1-N3	86.47(13)
N2_e-Zn1-N3	87.72(13)	N1_b-Zn1-N3_b	91.95(13)
N1_b-Zn1-N2_c	90.11(12)	N1_b-Zn1-N2_e	176.04(12)
N2_c-Zn1-N3_b	87.72(13)	N2_e-Zn1-N3_b	86.47(13)
N2_c-Zn1-N2_e	93.45(12)	Zn1-N1-C1	124.1(3)
Zn1-N1-C5	118.7(3)	Zn1_d-N2-C11	122.8(3)
Zn1_d-N2-C12	120.8(3)	Zn1-N3-C13	168.3(3)

Symmetry code: b = 2-x,y,3/2-z; c = -1/2+x,-1/2+y,z; e = 5/2-x,-1/2+y,3/2-z.

Table S2. Selected bond lengths (Å) and angles (°) for $\{[Co(bpe)_2(N(CN)_2)](N(CN)_2)(4H_2O)\}_n$ **(2).**

Co1 -N1	2.113(3)	Co1-N3	2.189(2)
Co1 -N4	2.149(2)	Co1-N1_b	2.113(3)
Co1 -N3_b	2.189(2)	Co1-N4_b	2.149(2)
N1-Co1-N3	86.95(8)	N1-Co1-N4	91.83(8)
N1-Co1-N1_b	172.45(9)	N1-Co1-N3_b	87.90(8)
N1-Co1-N4_b	93.69(8)	N3-Co1-N4	175.67(8)
N1_b-Co1-N3	87.90(8)	N3-Co1-N3_b	93.95(8)
N3-Co1-N4_b	90.16(8)	N1_b-Co1-N4	93.69(8)
N3_b-Co1-N4	90.16(8)	N4-Co1-N4_b	85.78(8)
N1_b-Co1-N3_b	86.95(8)	N1_b-Co1-N4_b	91.83(8)
N3_b-Co1-N4_b	175.67(8)		

Symmetry code: b = 2-x,y,3/2-z

Table S3. Selected bond lengths (Å) and angles (°) for $\{[Zn(bpe)_2(N(CN)_2)](N(CN)_2)(H_2O)\}_n$ **(1′).**

Zn1-N1	2.174(4)	Zn1-N2	2.217(4)
Zn1-N3	2.162(5)	Zn1-N1_a	2.174(4)
Zn1-N2_a	2.217(4)	Zn1-N3_a	2.162(5)
N1-Zn1-N2	176.47(15)	N1-Zn1-N3	91.92(17)
N1-Zn1-N1_a	87.05(15)	N1-Zn1-N3_a	93.92(17)
N1-Zn1-N2_a	89.74(14)	N2-Zn1-N3	86.86(17)
N1_a-Zn1-N2	89.74(14)	N2-Zn1-N2_a	93.51(15)
N2-Zn1-N3_a	87.50(17)	N1_a-Zn1-N3	93.92(17)
N2_a-Zn1-N3	87.63(17)	N3-Zn1-N3_a	171.96(16)
N1_a-Zn1-N2_a	176.47(15)	N1_a-Zn1-N3_a	91.92(17)
N2_a-Zn1-N3_a	86.86(17)		

Symmetry code: a = 1-x, y, 1/2-z

Table S4. Selected bond lengths (Å) and angles (°) for $\{[Zn(bpe)_2(N(CN)_2)](N(CN)_2)(5H_2O)\}_n$ **(1″).**

Zn1-N1	2.217(4)	Zn1-N2	2.168(4)
Zn1-N3	2.158(4)	Zn1-N1_a	2.217(4)
Zn1-N2_a	2.168(4)	Zn1-N3_a	2.158(4)
N1-Zn1-N2	175.93(15)	N1-Zn1-N3	86.69(17)
N1-Zn1-N1_a	93.57(15)	N1-Zn1-N2_a	90.07(14)
N1-Zn1-N3_a	87.26(17)	N2-Zn1-N3	91.66(17)
N1_a-Zn1-N2	90.07(15)	N2-Zn1-N2_a	86.36(15)
N2-Zn1-N3_a	94.83(17)	N1_a-Zn1-N3	87.47(17)
N2_a-Zn1-N3	94.78(17)	N3-Zn1-N3_a	171.16(16)
N1_a-Zn1-N2_a	175.93(15)	N1_a-Zn1-N3_a	86.69(17)
N2_a-Zn1-N3_a	91.66(17)		

Symmetry code: a = 1-x, y, 1/2-z

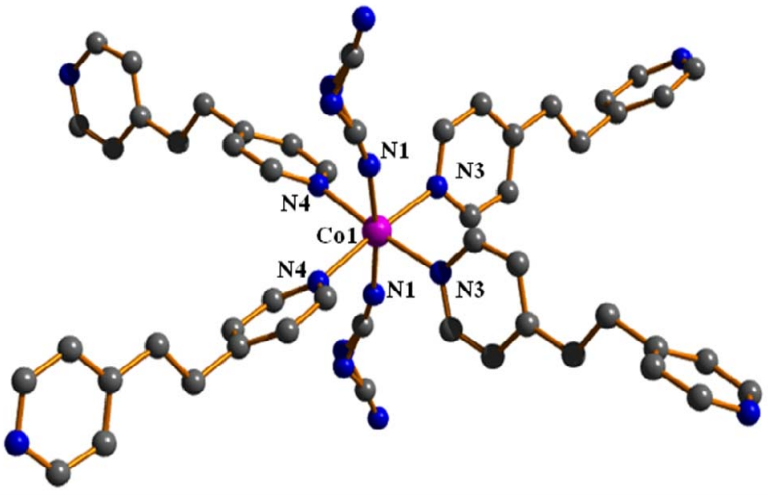

Fig. S1 View of the coordination environment of Co(II) in compound **1**.

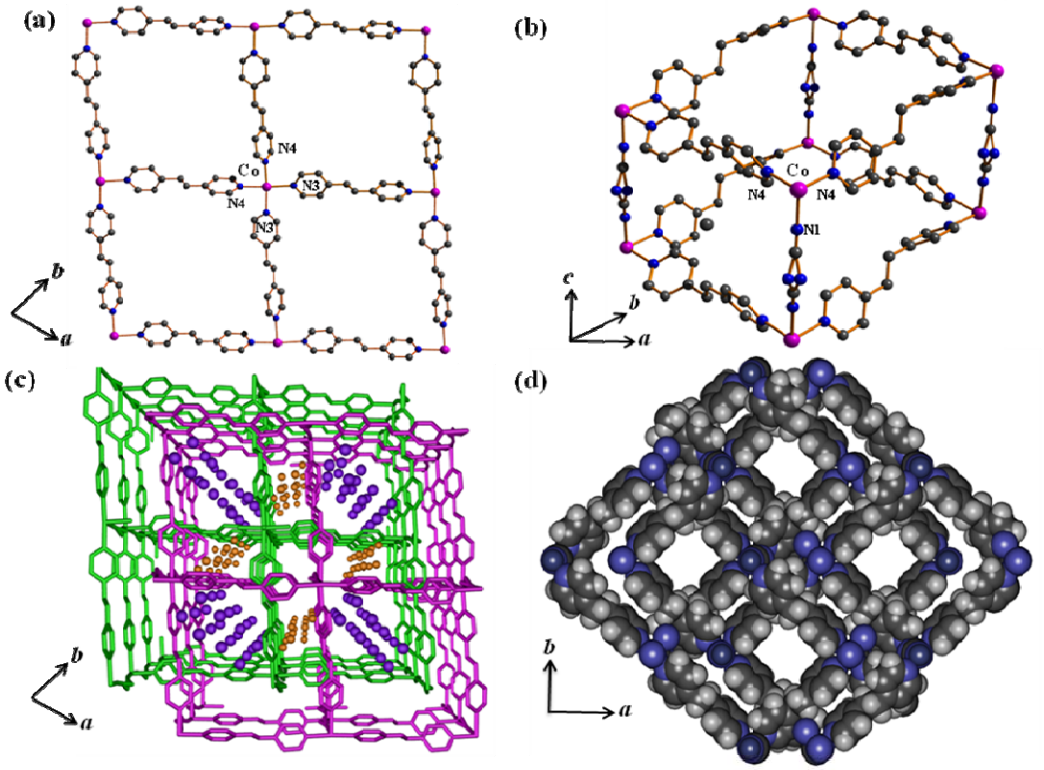

Fig. S2 (a) 2D sheet of $\{Co(bpe)_2\}^{2+}$ along crystallographic *ab* plane, (b) α-Po type 3D building unit of compound **2**, (c) View of 3D framework along crystallographic *c*-axis showing two fold interpenetrated bimodal channel structure, (d) CPK diagram showing two types of pores along *c* axis.

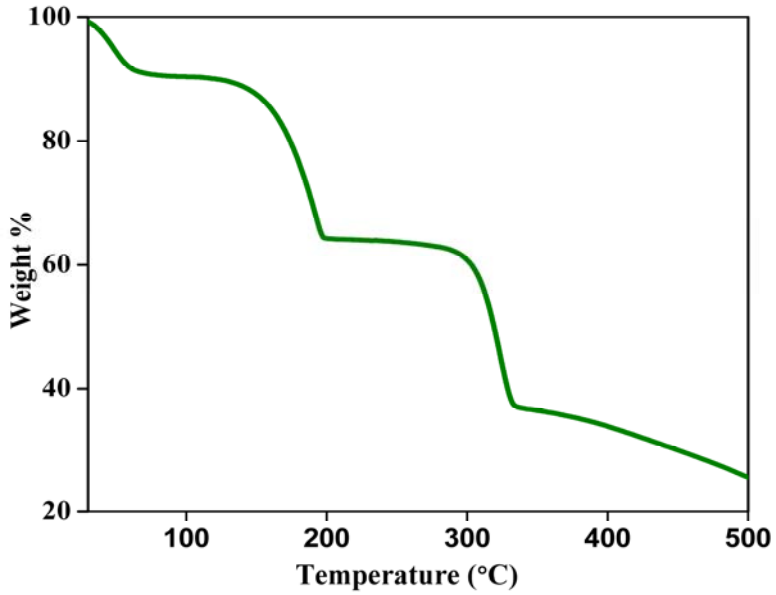

Fig. S3 TGA of compound **1** in the temperature range of 30-500 °C at heating rate of 3 °C/min under N_2 atmosphere.

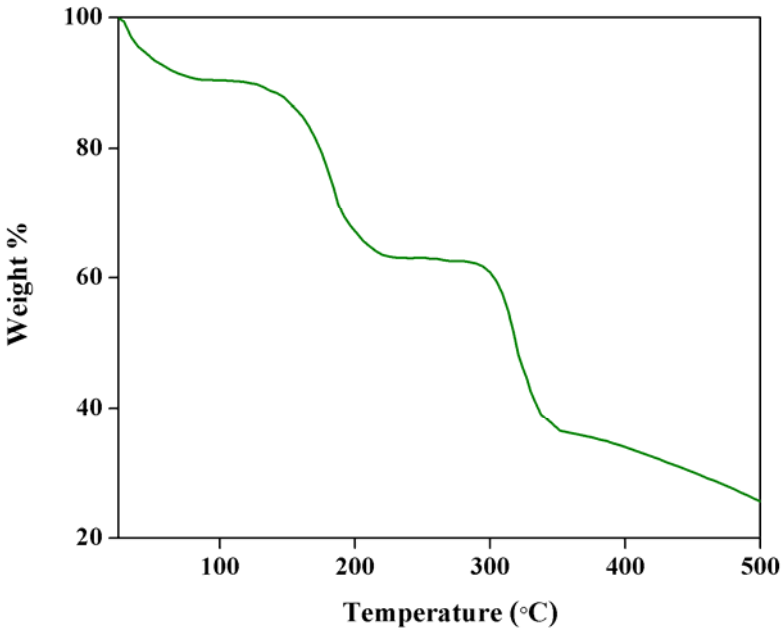

Fig. S4 TGA of compound **2** in the temperature range of 30-500 °C at heating rate of 3 °C/min under N_2 atmosphere.

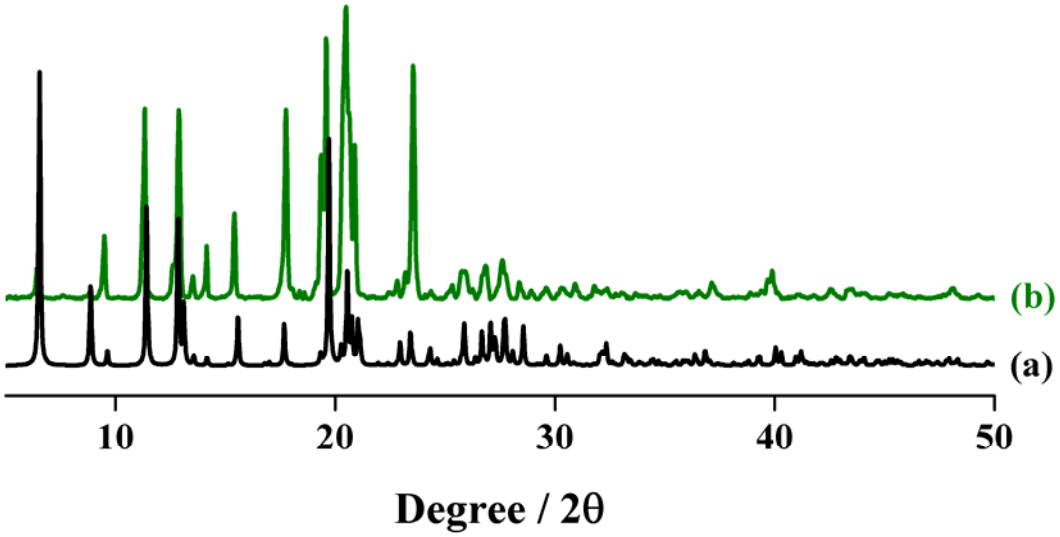

Fig. S5 PXRD patterns of $\{[Zn(bpe)_2(N(CN)_2)](N(CN)_2)(5H_2O)\}_n$ (**1**). (a) simulated, (b) as-synthesized.

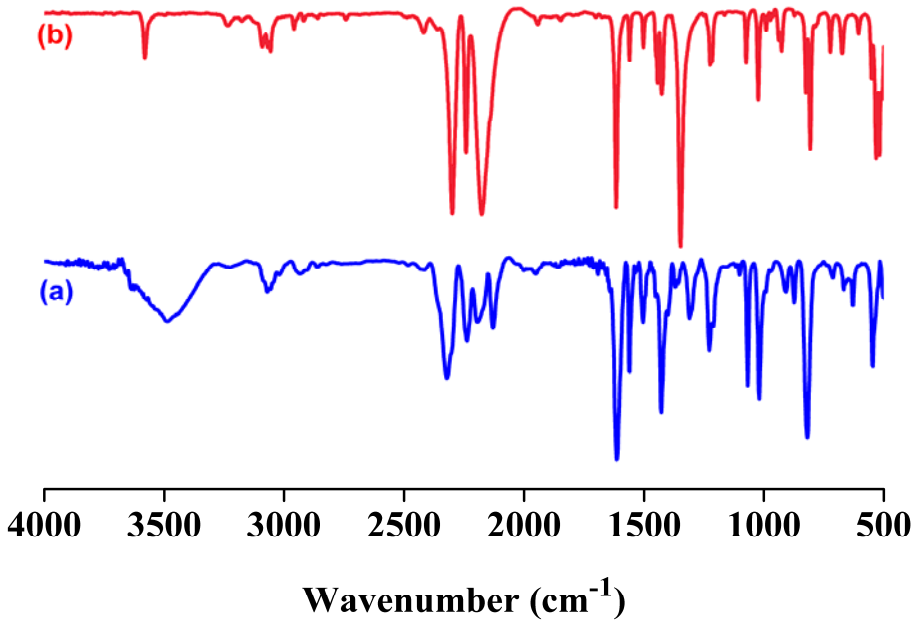

Fig. S6 FT-IR spectra (a) compound $\{[Zn(bpe)_2(N(CN)_2)](N(CN)_2)(5H_2O)\}_n$ **(1)** and (b) $\{Zn(bpe)(N(CN)_2)_2\}_n$ **(1b).**

Synthesis of $\{[M(bpe)(N(CN)_2)_2]\}_n$ (M= Zn(II) (1b) / Co(II) (2b)).

An aqueous solution (25 mL) of $NaN(CN)_2$ (1mmol, 0.089 gm) was mixed with an ethanolic solution (25 mL) of bpe (0.5 mmol, 0.092 gm) and stirred for 30 min to mix well. $Zn(NO_3)_2 \cdot 6H_2O$ (0.5 mmol, 0.146 gm) (for compound **2**, $Co(NO_3)_2 \cdot 6H_2O$) was dissolved in 50 mL of water and added to the ligand solution drop wise. White powder sample was isolated after 1-2 days of continuous stirring. Just by keeping the filtrate solution in room temperature for 4-5 days beautiful colorless block shaped crystals of compound **1** (pink colored crystals for compound **2**) were obtained. Crystals were separated, washed with water and dried. Good quality single crystals were picked up from the mother liquor and immediately covered with paraffin oil and crystal data was collected at 293 K. Compound **1b**:Yield: 50%, relative to Zn. Compound **1b**: FT-IR (KBr pellet, 4000-500 cm^{-1}): 3237(w), 3057(w), 2298(s), 2240(s), 2180(s), 1616(s), 1561(s), 1503(s), 1423(s), 1349(s), 1216(s), 1074(s), 1024(s), 928(m), 807(s). Anal. Calcd. for $C_{16}H_{12}ZnN_8$: C, 50.39; H, 3.14; N, 29.39. Found: C, 50.82; H, 3.54; N, 29.75. Compound **2b:** Yield: 61%, relative to Co. FT-IR (KBr pellet, 4000-500 cm^{-1}): similar to **1b**. Anal. Calcd. for $C_{16}H_{12}CoN_8$: C, 51.16; H, 3.31; N, 29.84. Found: C, 51.51; H, 3.39; N, 29.09.

Synthesis of $\{[Co(bpe)_2(N(CN)_2)](N(CN)_2)\}_n$ (2a) :

As-synthesized compound **2** (~ 0.100 g) was taken in a glass tube and heated at 100 °C under dynamic vacuum (10^{-1} pa) for about 10 hours to remove all the guest water molecules. This dehydrated compound **2a** is characterized by PXRD (see Fig. 5 in manuscript) and elemental analysis. Anal. Calcd. for $C_{28}H_{24}CoN_{10}$: C, 60.05; H, 4.28; N, 25.22. Found: C, 60.51; H, 4.39; N, 26.09.

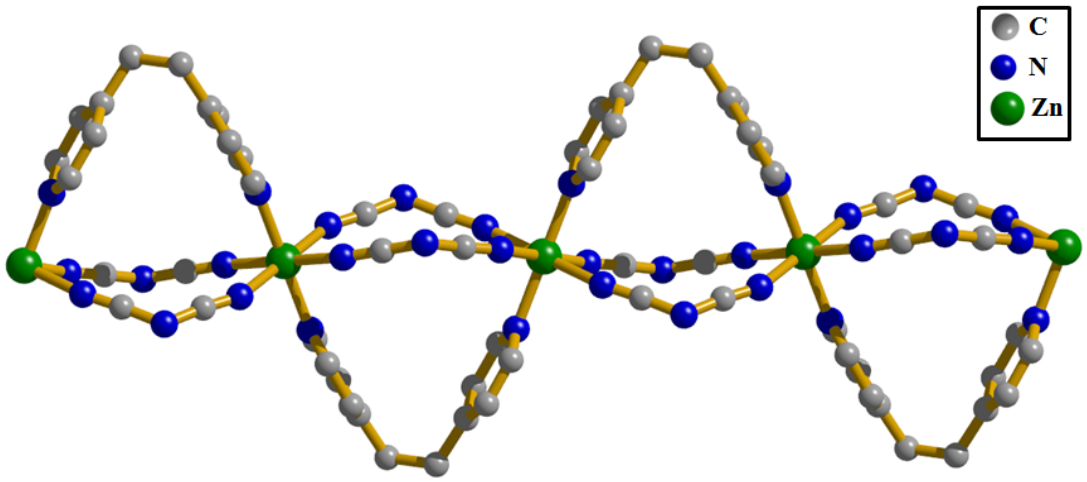

Fig. S7 View of the 1D coordination chain of $\{[Zn(bpe)(N(CN)_2)_2]\}_n$ (**1b)** showing octahedral Zn(II) centers connected by doubly bridged $N(CN)_2^-$ and bpe linkers.

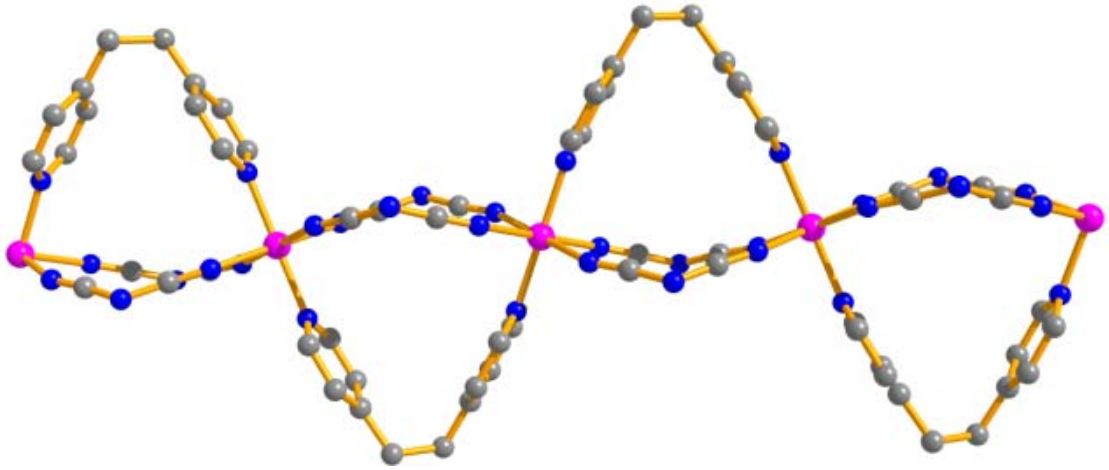

Fig. S8 View of the 1D coordination chain of $\{[Co(bpe)(N(CN)_2)_2]\}_n$ (**2b)** showing octahedral Co(II) centers connected by doubly bridged $N(CN)_2^-$ and bpe linkers.

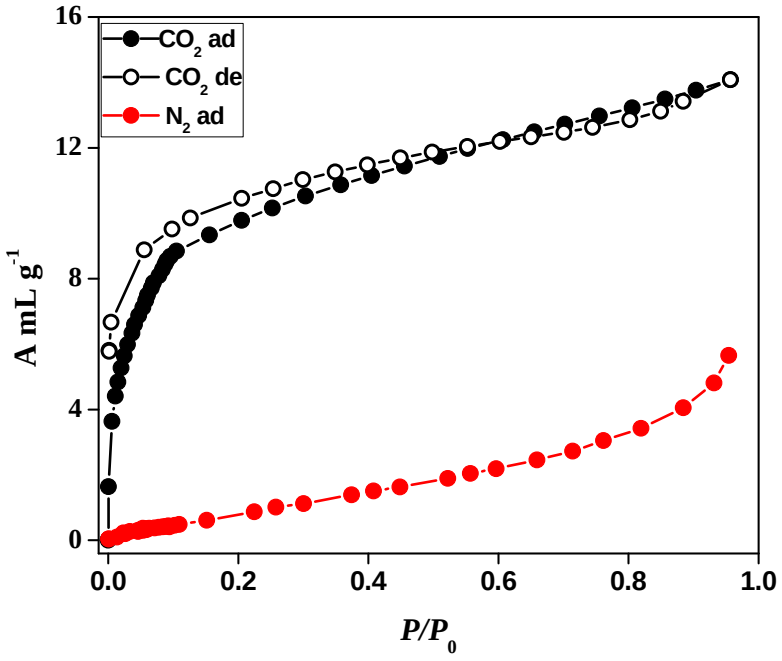

Fig. S9: CO_2 adsorption profile of compound **1a** at 195 K.

Indexing result of the powder pattern of the compound 1b after heating at 200 °C

Cell parameters: a = 16.5107(4) Å, b = 9.5342(5) Å, c = 12.8793(7) Å , β = 123.444(7)°, V = 1699.39 (9) Å

H	K	L	SST-OBS	SST-CALC	DELTA	2TH-OBS	2TH-CALC	D-OBS	FREE PARAM.
0	1	1	.010318	.010320	-.000002	11.660	11.661	7.5834	0
			.011795			12.470		7.0926	0
0	0	2	.015535	.015538	-.000003	14.320	14.321	6.1802	0
2	1	0		.018730			15.732		
-2	1	1	.018844	.018845	-.000001	15.780	15.781	5.6115	0
-2	0	2	.020294	.020293	.000001	16.380	16.380	5.4073	0
-1	1	2	.021290	.021278	.000012	16.780	16.775	5.2793	0
2	1	1	.026395	.026384	.000011	18.700	18.696	4.7413	0
1	2	0	.028796	.028817	-.000021	19.540	19.547	4.5394	0
1	1	2		.028817			19.547		
-1	2	1	.030814	.030816	-.000003	20.220	20.221	4.3882	0
3	1	0	.034091	.034097	-.000006	21.280	21.282	4.1720	0
2	0	2	.035369	.035371	-.000002	21.680	21.680	4.0959	0
-2	2	1		.038152			22.527		
-3	1	2	.038261	.038327	-.000066	22.560	22.580	3.9381	0
-2	1	3	.042379	.042382	-.000002	23.760	23.761	3.7418	0
-3	2	1		.051635			26.268		
-4	1	1	.051912	.051957	-.000045	26.340	26.352	3.3809	0
-3	1	3		.052095			26.387		
0	3	0		.057922			27.852		
-1	2	3	.058117	.058123	-.000006	27.900	27.901	3.1953	0
0	2	3		.060703			28.527		
3	1	2		.060943			28.584		
1	3	0	.061009	.060996	.000013	28.600	28.597	3.1186	0
2	2	2		.061114			28.625		
2	1	3	.064994	.064998	-.000004	29.540	29.541	3.0215	0
1	3	1		.066765			29.949		
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LOUER, D. & LOUER, M. (1972). J. APPL. CRYST. 5, 271-275.

BOULTIF, A. & LOUER, D. (1991). J. APPL. CRYST. 24, 987-993.

Indexing result of the powder pattern of the compound 2b after heating at 200 °C

Cell parameters : a = 16.5034(9) Å, b = 9.5213(4) Å, c = 12.8964(6) Å , β = 123.484(3)°, V = 1690.15(6)Å^3

H	K	L	DOBS	DCAL	DOBS-DCAL	QOBS	QCAL	2TH.OBS	2TH.CAL	DIF.2TH.
1	1	-1	7.53190	7.55937	-.02747	.01763	.01750	11.740	11.697	.043
1	0	1	6.84653	6.83994	.00659	.02133	.02137	12.920	12.932	-.012
2	0	-2	6.20604	6.21669	-.01065	.02596	.02588	14.260	14.235	.025
2	1	-1		6.21595	-.00991		.02588		14.237	.023
1	1	1	5.56247	5.55510	.00737	.03232	.03241	15.920	15.941	-.021
2	1	0		5.57768	-.01521		.03214		15.876	.044
0	0	2	5.36822	5.37807	-.00985	.03470	.03457	16.500	16.470	.030
1	1	-2	5.26680	5.27214	-.00533	.03605	.03598	16.820	16.803	.017
0	2	0	4.76152	4.76064	.00088	.04411	.04412	18.620	18.623	-.003
3	1	-2	4.53936	4.54588	-.00652	.04853	.04839	19.540	19.512	.028
0	2	1	4.35835	4.35331	.00504	.05264	.05277	20.360	20.384	-.024
3	1	0	4.12976	4.13328	-.00352	.05863	.05853	21.500	21.481	.019
1	1	2	3.89715	3.89875	-.00160	.06584	.06579	22.800	22.791	.009
1	1	-3	3.73871	3.73348	.00523	.07154	.07174	23.780	23.814	-.034
3	1	1	3.34347	3.34195	.00151	.08946	.08954	26.640	26.652	-.012
5	0	-3	3.19752	3.19516	.00236	.09781	.09795	27.880	27.901	-.021
4	0	-4	3.10376	3.10834	-.00458	.10381	.10350	28.740	28.697	.043
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LOUER, D. & LOUER, M. (1972). J. APPL. CRYST. 5, 271-275.
BOULTIF, A. & LOUER, D. (1991). J. APPL. CRYST. 24, 987-993.