Electronic Supporting Information (ESI)

Tuning of Thermal Expansion Properties of Mixed-Ligand MOF by Ligand Variation

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1. Experimental Section

Synthesis of Co[(Bpy)(TPA)] (2)

All the chemicals were purchased from commercial sources and used as received without further purification. The solvent used *i.e.* Methanol has been distilled before use after receiving from commercial source. The synthesis of **2** has been done by a slightly modified method from reported literature.[1] 8ml Methanolic solution of $CoCl_2.6H_2O$ (119mg, 0.5 mmol), 4,4'-Bipyridine (**Bpy**) (78mg, 0.5 mmol), and terephthalic acid (**TPA**) (83mg, 0.5 mmol) was stirred for 3 hrs. Then the solution was transferred to a Teflon lined autoclave and heated at 200°C for 72 hrs and then cooled to room temperature slowly to get pink needle shaped crystals. The crystals came along with the precipitate, from which the crystals have been separated manually. Then the crystals were washed thoroughly with methanol and dried in air.

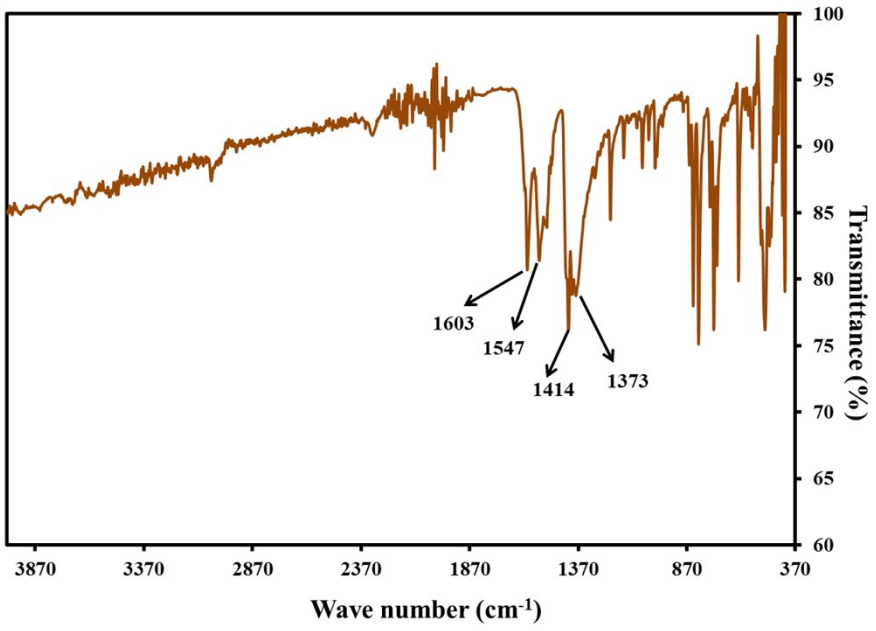


Figure S1 FT-IR Spectra of **2** recorded in Shimadzu (IR Affinity-1SWL).

2. Powder X-Ray Diffraction Study

The powder X-Ray diffraction data was taken in Rigaku powder X-ray diffractometer (Miniflex-600 with CuKα radiation, λ= 1.54059Å) to confirm the purity of the

compound. The crystals of the compound **2** were crushed to form powder and this powder was placed in a quartz holder and data was taken at room temperature from 5°C to 40°C (2θ value) at a scan rate of 2°/min.

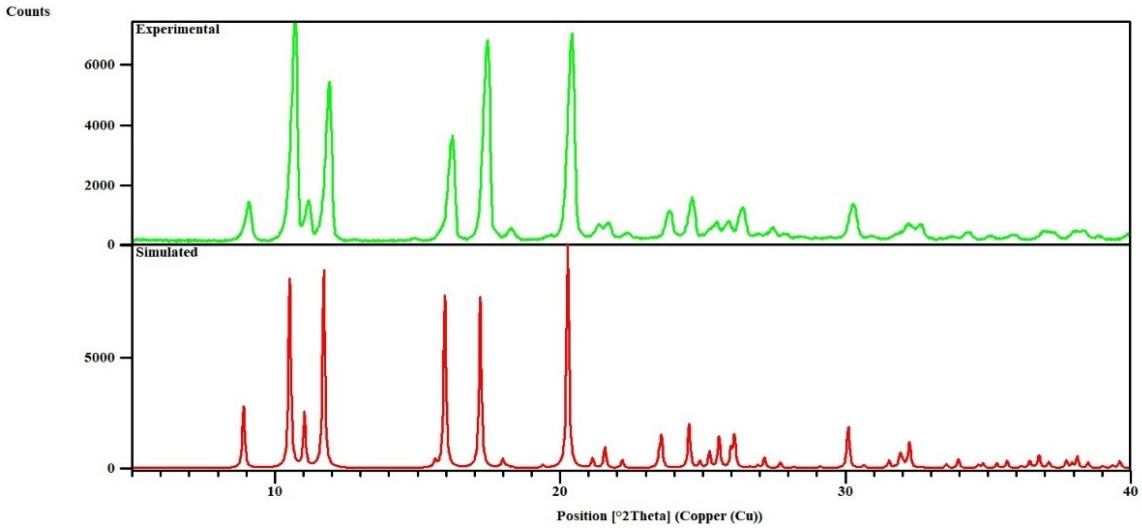


Figure S2 PXRD pattern of **2** in which comparison of experimental (Green) and simulated obtained from crystal structure (Red) PXRD pattern has been done.

3. Thermogravimetric Analysis

TGA analysis showed the starting point of mass loss is 355°C that continues till 500°C, which implies that the thermal decomposition of compound starts at 355°C and till that point compound is stable. TGA measurement was done in Mettler Toledo instrument supported with StarRe software version 13.00 with heating rate 10°C/min.

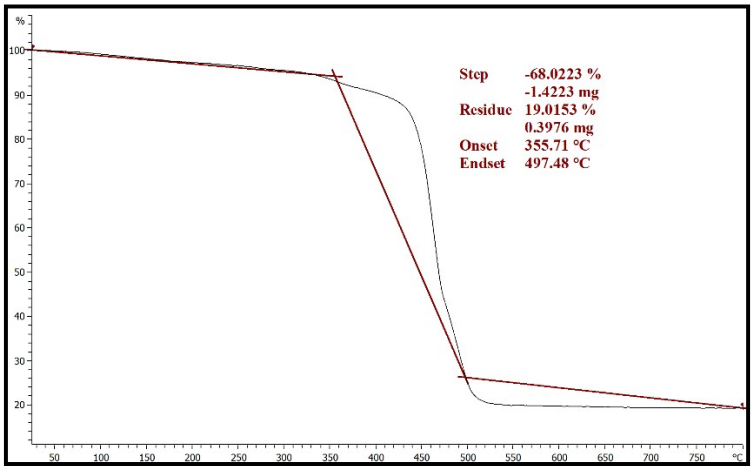


Figure S3 TGA thermogram that shows mass loss after 350°C.

4. Single Crystal X-Ray Diffraction Study

A suitable single crystal of **2** was mounted on goniometer head using nylon loop and single crystal X-Ray diffraction data has been taken on Bruker D8 Quest single crystal X-ray diffractometer equipped with a microfocus anode (MoKα) and a PHOTON 100 CMOS detector. The data was integrated and scaled using the Bruker suite programs.[1] Structure was solved by direct method and refined using SHELXL.[3, 4]

5. Variable Temperature X-Ray Diffraction Study

For variable temperature single crystal X-Ray diffraction study a suitable single crystal was glued with epoxy glue on top of a glass fiber. The single-crystal data was initially recorded at 100K and then successive data sets were collected at intervals of 50K till 450K. Although the crystal was stable up to 600K but data was collected up to 450K due to the limitations of cryostat attached with the diffractometer. All the data at each temperature was integrated and scaled using the Bruker suite programs.[2] Structure was solved by direct method and refined using SHELXL[3, 4] and X-Seed software.[5] Crystallographic data and final refinement details are given in Table S1.

Table S1: Crystallographic data of **2** from 100K to 450K.

Compound	**2_100K**	**2_150K**	**2_200K**	**2_250K**
Moiety formula	$C_{18}H_{12}CoN_2O_4$	$C_{18}H_{12}CoN_2O_4$	$C_{18}H_{12}CoN_2O_4$	$C_{18}H_{12}CoN_2O_4$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*
a/Å	20.777(3)	20.720(3)	20.676(3)	20.634(2)
b/Å	10.2704(15)	10.2647(14)	10.2639(13)	10.2655(12)
c/Å	16.306(2)	16.365(2)	16.439(2)	16.4990(19)
α/(°)	90	90	90	90
β/(°)	105.520(5)	105.495(5)	105.457(4)	105.415(4)
γ/(°)	90	90	90	90

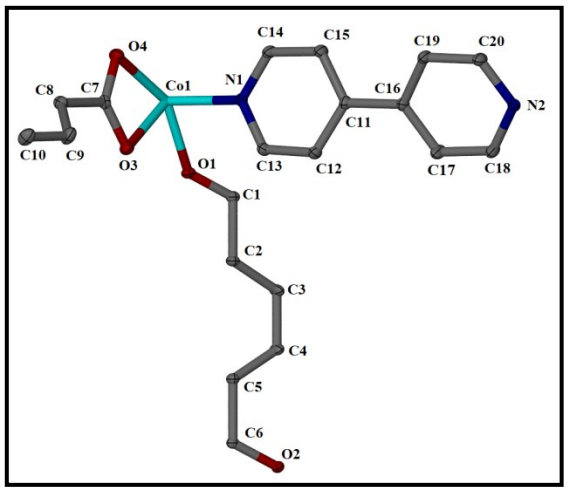
V/Å^3	3352.7(8)	3354.0(8)	3362.5(7)	3369.0(7)
Z	8	8	8	8
D_{cal}/g cm^{-3}	1.503	1.502	1.498	1.495
T/K	100	150	200	250
μ/mm^{-1}	1.048	1.048	1.045	1.043
F_{000}	1544	1544	1544	1544
Reflections measured	42019	42235	42334	42653
Unique reflections	4175	4177	4186	4201
Observed reflections	3712	3670	3593	3240
Parameters	228	228	228	237
R_{int}	0.0325	0.0317	0.0325	0.0336
final R (I >2σ(I))	0.0251	0.0256	0.0293	0.0357
final R (all data)	0.0300	0.0315	0.0365	0.0494
GOF on F ^{2}	1.089	1.078	1.074	1.070
CCDC No.	2253955	2253956	2253957	2253958

Compound	**2_300K**	**2_350K**	**2_400K**	**2_450K**
Moiety formula	C_{18} H_{12} Co N_2 O_4	C_{18} H_{12} Co N_2 O_4	C_{18} H_{12} Co N_2 O_4	C_{18} H_{12} Co N_2 O_4
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*C2/c*	*C2/c*	*C2/c*	*C2/c*
a/Å	20.570(2)	20.504(3)	20.439(3)	20.376(3)
b/Å	10.2665(12)	10.2634(13)	10.2687(17)	10.2653(14)
c/Å	16.5997(18)	16.711(2)	16.814(3)	16.928(2)
α/(°)	90	90	90	90
β/(°)	105.387(4)	105.360(5)	105.349(6)	105.342(5)
γ/(°)	90	90	90	90
V/Å^3	3380.0(7)	3391.0(7)	3403.0(9)	3414.6(8)

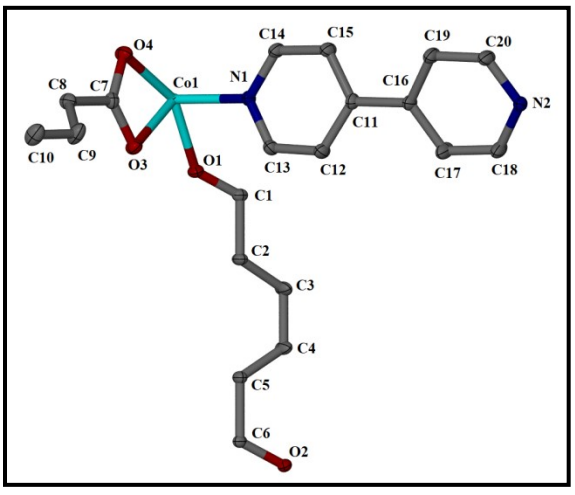
Z	8	8	8	8
D_{cal}/g cm^{-3}	1.490	1.486	1.480	1.475
T/K	300	350	400	450
μ/mm^{-1}	1.040	1.037	1.033	1.029
F_{000}	1544	1544	1544	1544
Reflections measured	43116	43290	38018	43465
Unique reflections	4211	4233	3499	4271
Observed reflections	2176	2129	1773	2021
Parameters	257	267	247	247
R_{int}	0.0350	0.0365	0.0358	0.0499
final R (I >2σ(I))	0.0331	0.0317	0.0296	0.0344
final R (all data)	0.0561	0.0560	0.0517	0.0664
GOF on F ^{2}	1.087	1.054	1.051	1.049
CCDC No.	2253959	2253960	2253961	2253962

Note. All parameters are calculated in PLATON.[6]

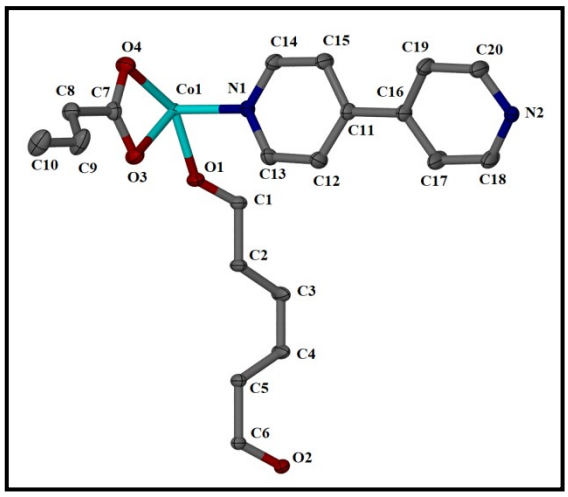
6. Thermal Ellipsoid Plots of Asymmetric Units at Different Temperature



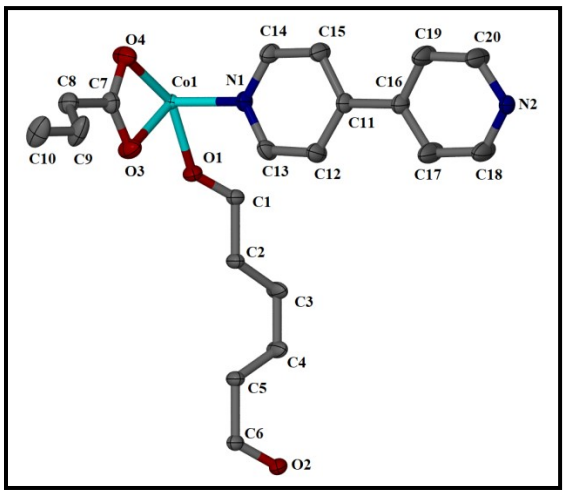
100K



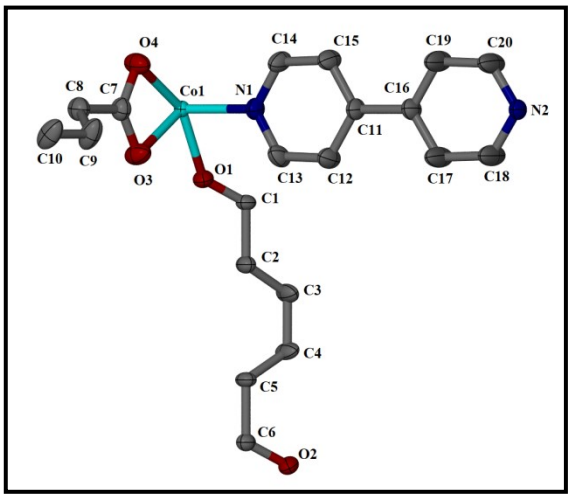
150K



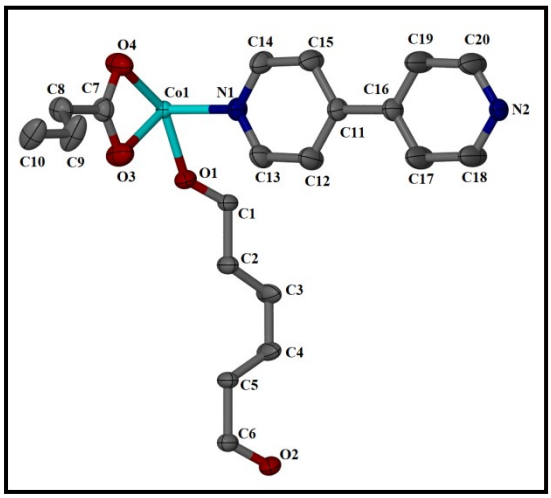
200K



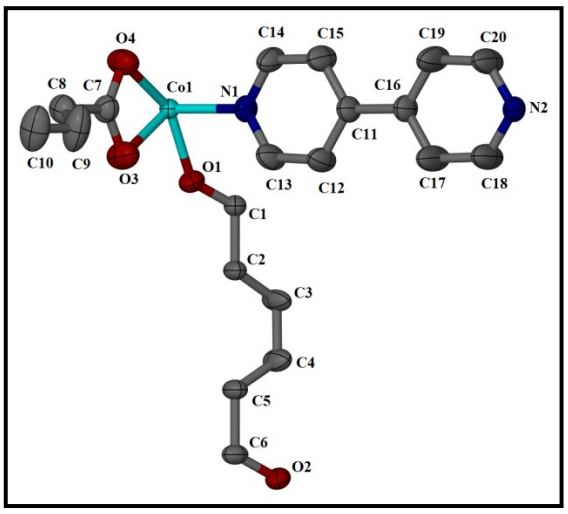
250K



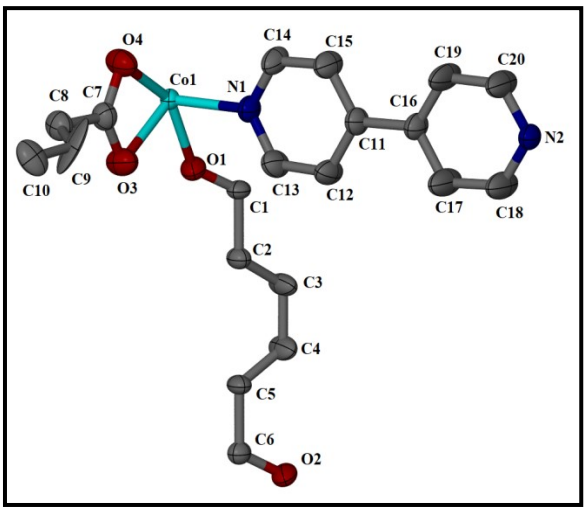
300K



350K



400K



450K

Figure S4 Thermal ellipsoid plots of asymmetric units of the crystal structure of **2** at different temperatures (100 K – 450 K) shown in 50 % probability.

7. Change in Unit Cell Parameters of the Crystal Structures of Co[(Bpy)(TPA)] (2) with Temperature

Table S2 Change of unit cell parameters of the crystal structures of **2** at different temperature.

Temperature (K)	*a* (Å)	*b* (Å)	*c* (Å)	α= γ (°)	β(°)	Volume(Å^3)
100	20.7774	10.2704	16.3059	90	105.520	3352.68
150	20.7198	10.2647	16.3648	90	105.495	3354.00
200	20.6758	10.2639	16.4394	90	105.457	3362.49
250	20.6336	10.2655	16.4990	90	105.415	3369.00
300	20.5705	10.2665	16.5997	90	105.387	3379.98
350	20.5038	10.2634	16.7108	90	105.36	3390.99
400	20.439	10.2687	16.814	90	105.349	3403.00
450	20.3762	10.2653	16.9277	90	105.342	3414.55

Note. NTE along *a* axis and ZTE along *b* axis are highlighted in olive green and maroon colour respectively.

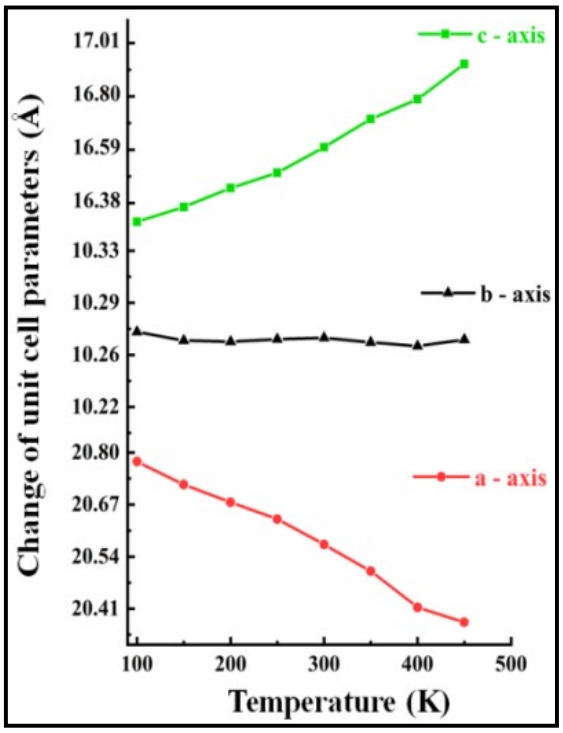


Figure S5 Change of the length of unit cell axes with increasing temperature from 100K to 450K in case of **2.**

8. Calculation of Thermal Expansion Coefficient by PASCal Program

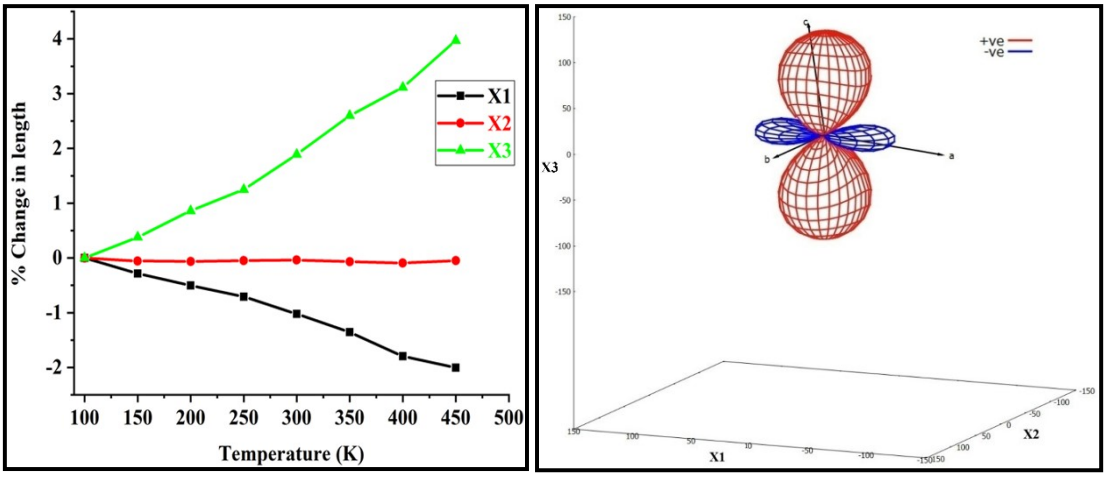
Table S3 Thermal expansion coefficient of **2** from temperature range 100K to 450K.

			Direction		
Axes	**α (MK^{-1})**	**σα (MK^{-1})**	***a***	***b***	***c***
X_1	-56.8766	1.5398	-0.9934	0.0000	-0.1150
X_2	-0.3756	0.7674	0.0000	1.0000	-0.0000
X_3	114.2622	5.0633	0.1408	-0.0000	0.9900
V	56.5803	3.5441			

Note. Thermal expansion coefficients were calculated using the PASCal program.[7]

Table S4 Percentage change in length with change in temperature.

Temperature (K)	**X_1**	**X_2**	**X_3**
100	0.0000	0.0000	0.0000
150	-0.2840	-0.0555	0.3801
200	-0.5010	-0.0633	0.8610
250	-0.7071	-0.0477	1.2496
300	-1.0220	-0.0380	1.8915
350	-1.3560	-0.0682	2.5985
400	-1. 6829	-0.0166	3. 2513
450	-2.0020	-0.0497	3.9685



(a) (b)

Figure S6 (a) Percentage change in length with change in temperature. (b) Expansivity indicatrix plot**.**

9. Schematic Representation of Fencing Motion

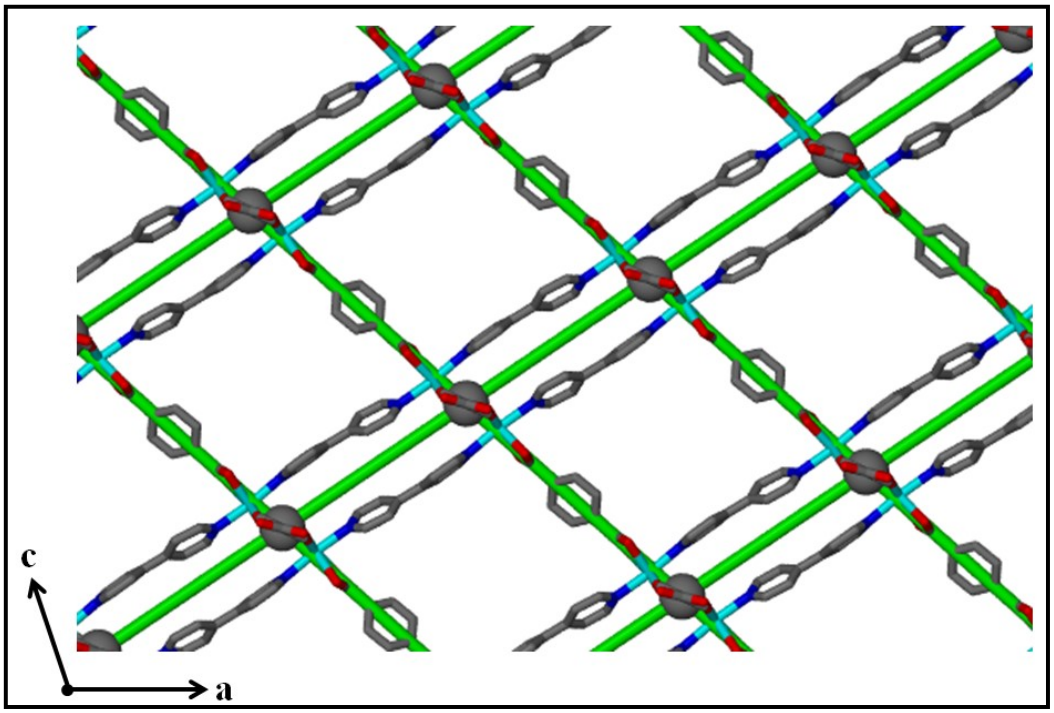
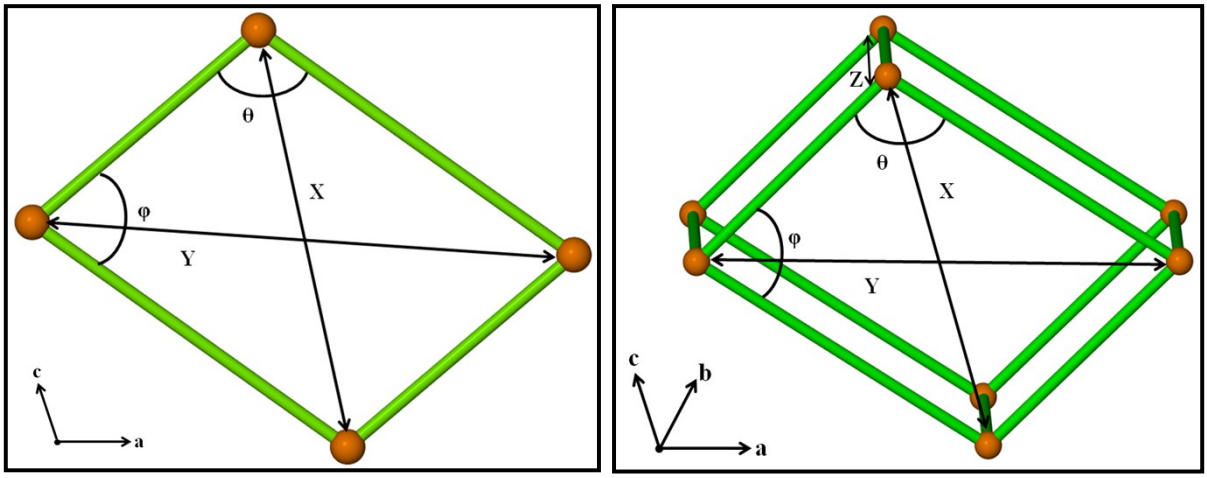


Figure S7 Fence like motion in 3D Network of **2** (Centroids of SBUs shown by '●' are hinges of the fence).



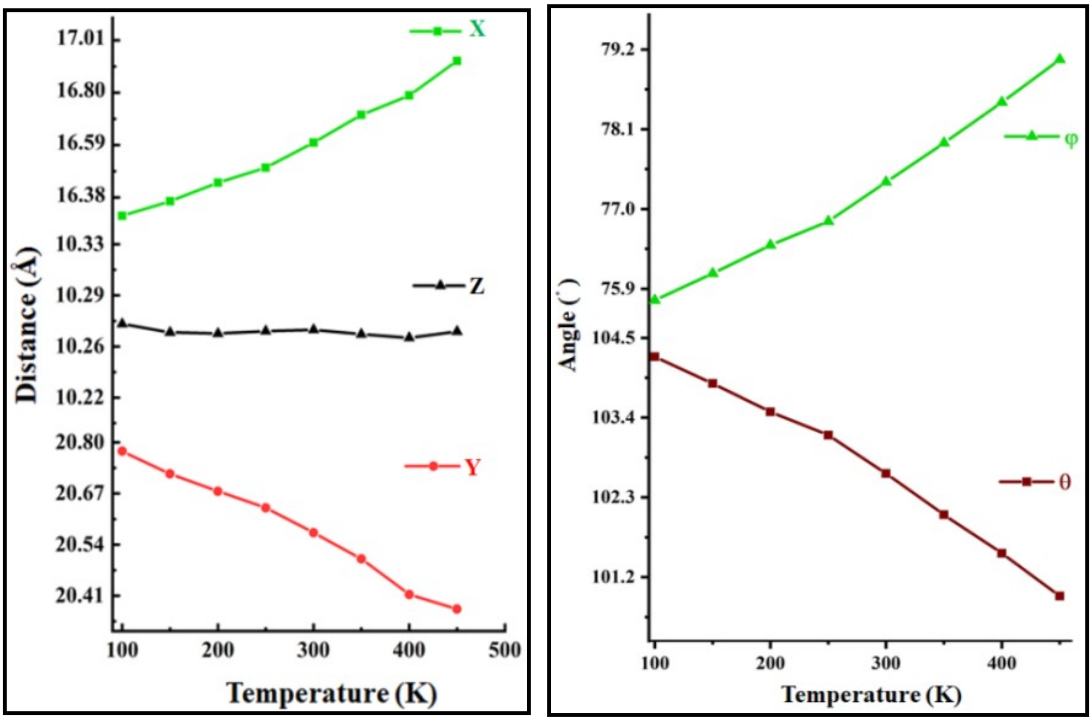
(a) (b)

Figure S8 Schematic representation of 2D rectangular grid. (a) Representing diagonal distance X, Y and angle θ and φ. (b) Representing distance Z that is responsible for ZTE.

10. Change of Distance X, Y and Z and Angle θ, φ with Change in Temperature

Table S5 Change of Distance X, Y and Z and angle θ, φ with change in temperature from 100K to 450K.

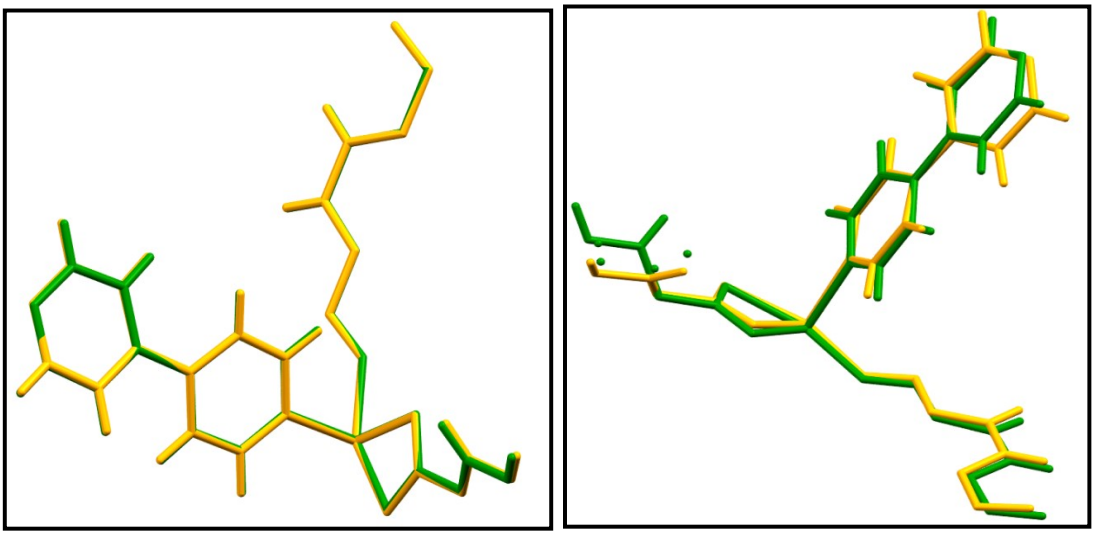
Temperature(K)	X	Y	Z	θ	φ
100	16.306	20.777	10.270	104.24	75.74
150	16.365	20.720	10.265	103.87	76.11
200	16.439	20.676	10.264	103.48	76.50
250	16.499	20.634	10.265	103.16	76.83
300	16.600	20.571	10.267	102.63	77.37
350	16.711	20.504	10.263	102.06	77.94
400	16.789	20.413	10.261	101.53	78.47
450	16.928	20.376	10.265	100.94	79.06



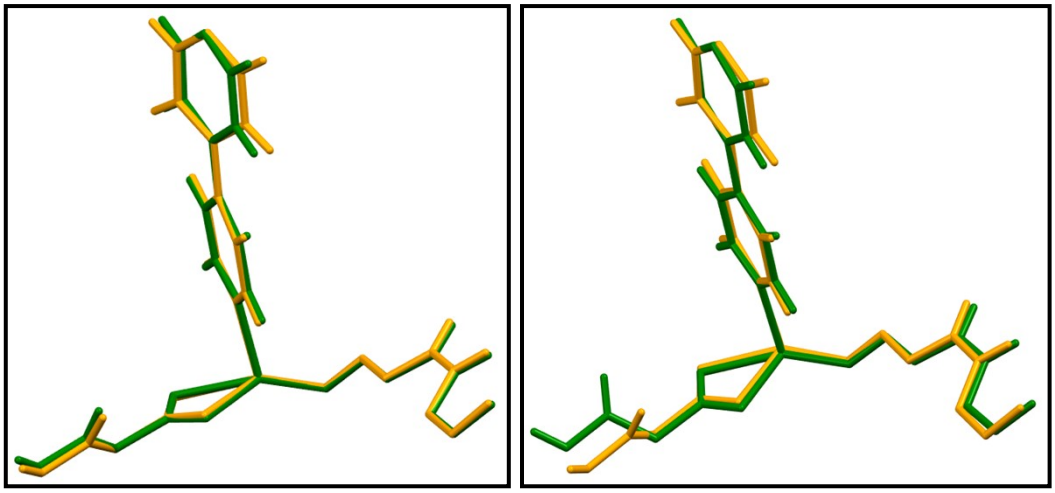
(a) (b)

Figure S9 (a) Change in length X, Y and Z with temperature (b) Change in angle θ and ϕ with temperature for **2.**

11. Change in Tilt Angle of Pyridyl Rings of 4,4'-Bipyridine (Bpy)



(a) (b)



(c) (d)

Figure S10 (a) Molecular Overlay of asymmetric units at 100K and 200K. (b) Molecular Overlay of asymmetric units at 100K and 450K. (c) Molecular Overlay of asymmetric units at 100K and 250K. (d) Molecular Overlay of asymmetric units at 250K and 450K.

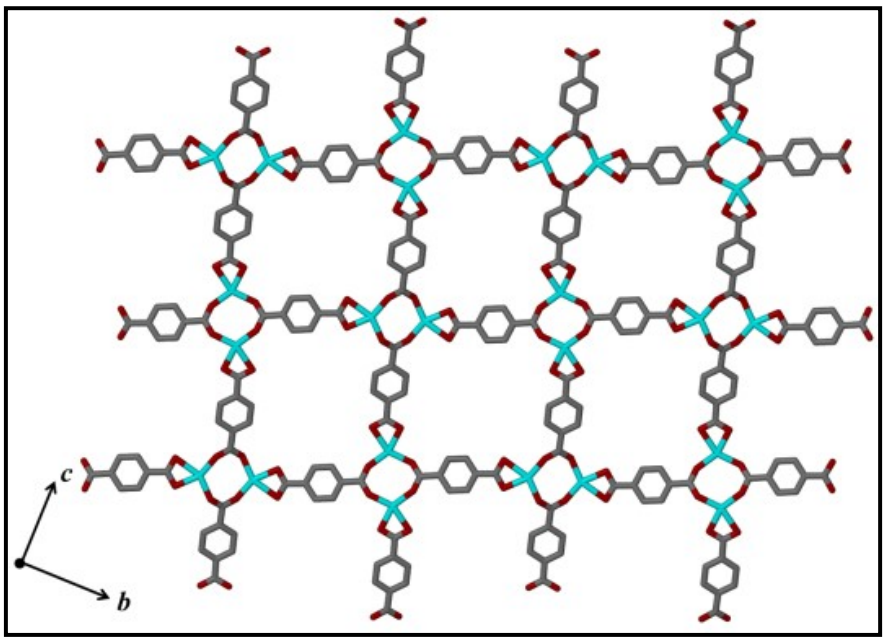
Table S6 Change in angle between two pyridyl rings of **Bpy** ligand with change in temperature.

Temperature (K)	**Angle between two pyridyl rings of Bpy ligand (°)**	**Rate of change of angle with temperature (°)**
100	26.28	0
150	25.44	0.84
200	23.46	1.98
250	14.34	9.12
300	6.23	8.11
350	5.92	0.31
400	5.67	0.25
450	5.50	0.17

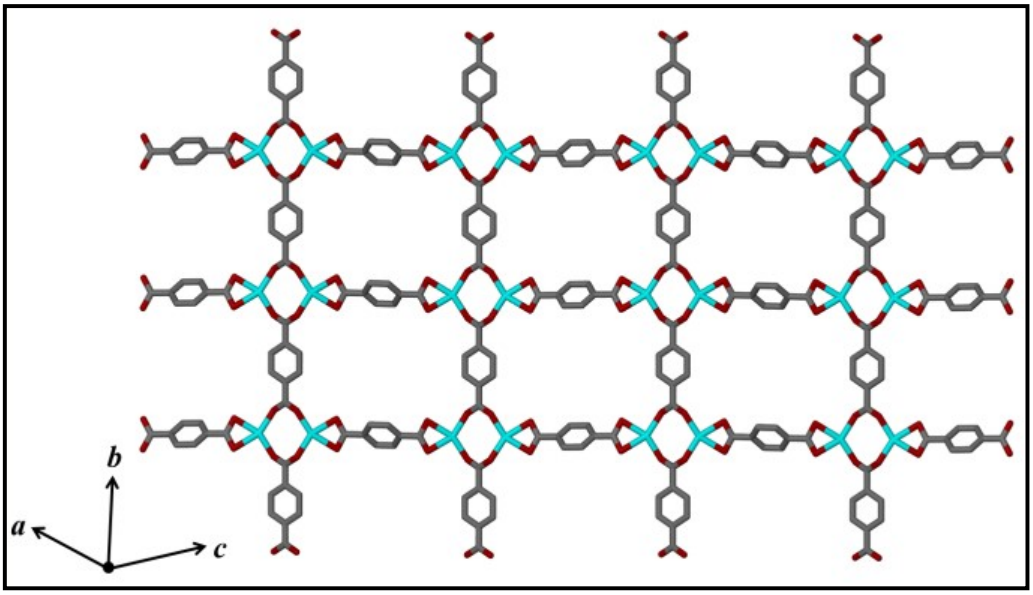
Table S7 RMSD values of Molecular Overlay of asymmetric units of crystal structure of 2 at each temperature.

Temperature (K)	RMSD	Max. D
100-150	0.0152	0.0376
150-200	0.0223	0.0547
200-250	0.0710	0.1810
250-300	0.2703	0.8249
300-350	0.0375	0.1334
350-400	0.1277	0.4325
400-450	0.2002	0.6386

12. Comparison of the Packing Arrangement of Co[(Pz)(TPA)] (1)[8] and Co[(Bpy)(TPA)] (2)

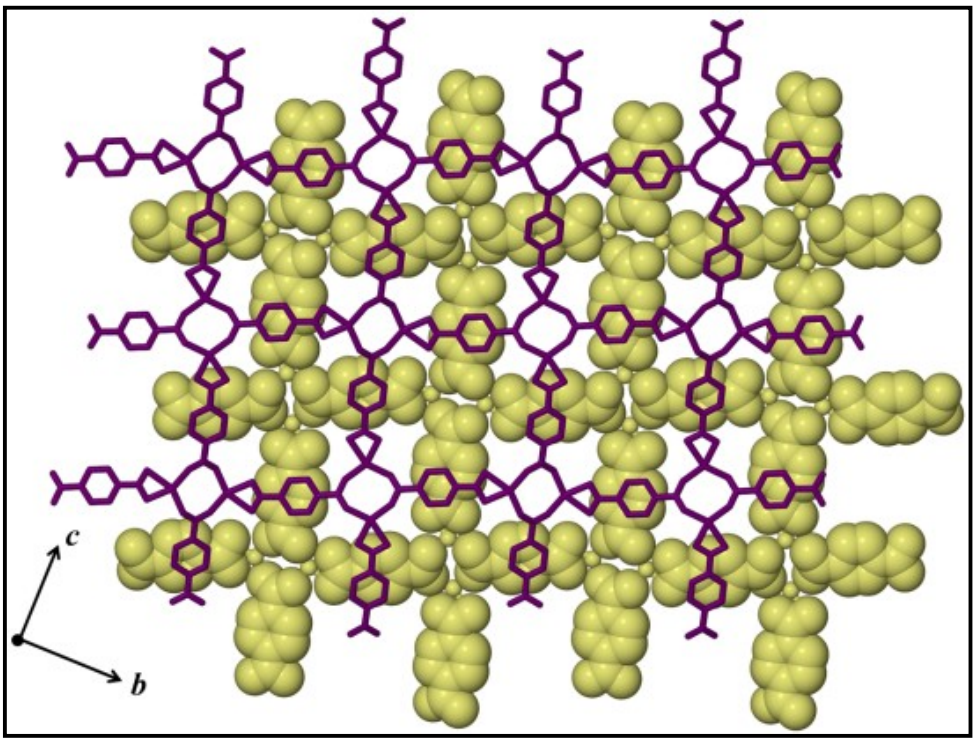


(a)

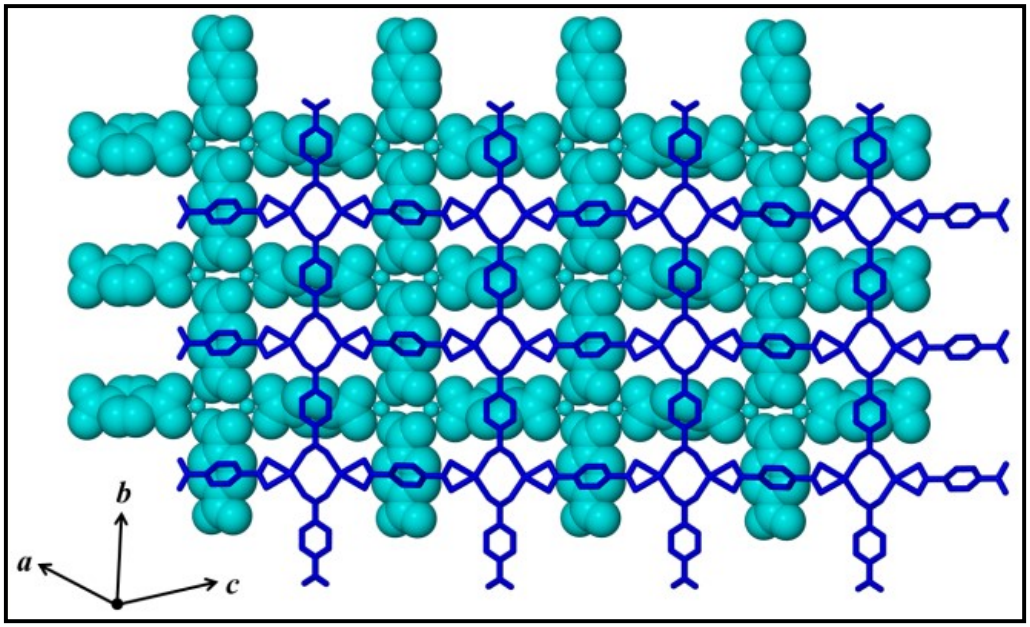


(b)

Figure S11 (a) 2D square grid parallel to *bc* plane formed in the crystal structure of **1**. (b) 2D rectangular grid parallel to (2 0 1) plane formed in the crystal structure of **2**.



(a)



(b)

Figure S12 Interpenetrated 3D framework in the crystal structure of compound **1** and **2** in which A and B layers are shown in two different colours (a) **1** viewed in *bc* plane. (b) **2** viewed in (2 0 1) plane.

13. References

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