Supplementary material for:

Methanol Mediated Crystal Transformations in a Solvatochromic Metal Organic Framework constructed from Co(II) ions and 4-(4-pyridyl) benzoate spacer

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The structural transformations of compound **1** $\{[Co(44pba)_2]_4\cdot(DMF)_3\cdot(EtOH)_{0.25}\cdot(H_2O)_4\}_n$ [44pba = 4-(4-pyridyl) benzoate] were followed during exchange of DMF and ethanol molecules by methanol at room temperature. The new phases obtained **2** $\{[Co(44pba)_2]\cdot(MeOH)_{2.5}\cdot(H_2O)\}_n$, **3** $\{[Co(44pba)_2(MeOH)_2]_2\cdot(MeOH)_{2.5}\cdot(H_2O)_2\}_n$ and **4** $\{[Co(44pba)_2(MeOH)_2]\cdot(MeOH)_{0.5}(H_2O)_{0.5}\}_n$ were studied using differential scanning calorimetry, thermogravimetric analysis and X-ray diffraction methods. The final phase **4** reverts back to **1** upon soaking **4** in dry DMF/ethanol mixture as evidenced by powder diffraction data and infrared spectra.

(a) (b)

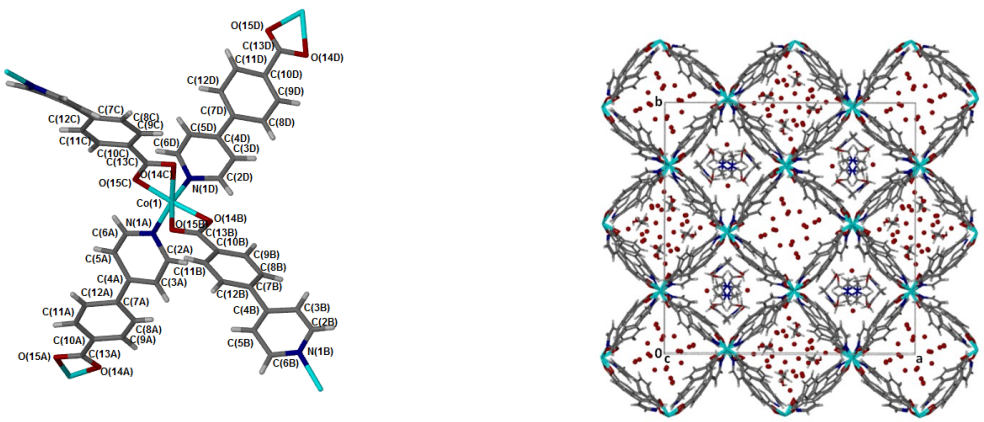

Fig. S1(a)Co^{II} environment in **1**, showing atom labels used. Further ligands are labelled with suffices E-H. (b) Crystal packing in **2**, viewed down [001]. The framework and DMF and ethanol guests are shown in stick form while water molecules are shown as red spheres.[1]

[1] G. Mehlana, S. A. Bourne, G. Ramon, *Dalton Trans.*, **2012**, *41*, 4224.

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Table S1 Bond lengths for **2**

Bond type	Bond distance	Bond type	Bond distance
Co1-O14A	2.048(4)	Co1-O15B	2.038(4)
Co1-O14B	2.302(4)	Co1-N1A	2.062(4)
Co1-O15A	2.279(4)	Co1-N1B	2.069(4

Table S2. Bond angles for **2**

	Angle		Angle
O14A-Co1-O14B	97.49(16	O14B-Co1-O15A	84.89(16)
O14A-Co1-O15A	60.87(15)	O14B-Co1-O15B	60.46(14)
O14A-Co1-O15B	150.51(17)	O14B-Co1-N1A	89.73(17)
O14A-Co1-N1A	95.93(16)	O14B-Co1-N1B	158.00(15)
O14A-Co1-N1B	100.83(17)	O15A-Co1-O15B	95.68(15)
O15A-Co1-N1A	155.07(15)	O15B-Co1-N1A	102.78(17)
O15A-Co1-N1B	93.46(17)	O15B-Co1-N1B	98.02(16)
N1A-Co1-N1B	100.32(18)		

Table S3. Bond lengths for **3**

Bond type	Bond distance	Bond type	Bond distance
Co1-O1	2.161(5)	Co1-O15D	2.036(5)
Co1-O2	2.153(5)	Co1-N1A	2.126(6)
Co1-O15C	2.059(5)	Co1-N1B	2.131(6)
Co2-O4	2.149(6)	Co2-O15B	2.029(4)
Co2-O6	2.163(6)	Co2-N1C	2.144(5)
Co2-O15A	2.035(5)	Co2-N1D	2.179(5)

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Table S4. Bond angles for **3**

	Angle(°)		Angle(°)
O1-Co1-O2	89.2(2)	O15D-Co1-N1B	91.4(2)
O2-Co1-O15D	91.4(2	O1-Co1-O15D	86.9(2)
O15D-Co1-N1A	88.3(2)	O2-Co1-O15C	87.0(2)
O1-Co1-O15C	93.1(2)	O15C-Co1-N1B	90.2(2)
O1-Co1-N1B	91.9(2)	N1A-Co1-N1B	87.1(2)
O2-Co1-N1A	92.1(2)	O4-Co2-N1C	89.3(2)
O15C-Co1-N1A	91.8(2)	O6-Co2-O15B	91.7(2)
O15A-Co2-O15B	179.4(2)	O15B-Co2-N1D	89.6(2)
O15B-Co2-N1C	91.4(2)	O15A-Co2-N1C	88.1(2)
O6-Co2-O15B	91.7(2)	O4-Co2-O15B	89.3(2)
O6-Co2-N1C	91.2(2)	O6-Co2-O15A	88.7(2)
O4-Co2-N1D	91.2(2)	O6-Co2-N1D	88.4(2)
O4-Co2-O15A	90.3(2)	O15A-Co2-N1D	90.9(2)

Table S5. Bond lengths for **4**

Bond type	Bond distance	Bond type	Bond distance
Co1-O2C	2.128(17)	Co1-N1B	2.131(10)
Co1-O2D	2.132(14)	Co1-O14B	2.071(17)
Co1-N1A	2.142(16)	Co1-O15A	2.063(14)

Table S6. Bond Angles for **4**

	Angle(°)		**Angle**(°)
O2C-Co1-O2D	89.9(4)	O2D-Co1-N1A	91.6(4)
O2C-Co1-N1A	177.5(4)	O2D-Co1-O14B	91.4(4)
O2C-Co1-N1B	87.3(4)	O2D-Co1-O15A	87.9(4)
O2C-Co1-O14B	88.1(4)	N1A-Co1-N1B	91.3(4)
O2C-Co1-O15A	90.2(5)	N1A-Co1-O14B	89.9(4)
N1A-Co1-O15A	91.9(5)	N1B-Co1-O15A	89.3(4)
N1B-Co1- O14B	91.3(3)		

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Table S7. Dihedral angle between the benzene and pyridyl rings in **1** and **2**

		Torsion angle/°			Torsion angle/°
Compound 1					
Ligand A	C12-C7A-C4A-C5A	-33.9	Ligand B	C12B-C7B-C4B-C5B	15.7
	C8A-C7A-C4A-C3A	-20.5		C8B-C7B-C4B-C3B	39.3
Ligand C	C12C-C7C- C4C-C5C	-31.3	Ligand D	C12D-C7D-C4D-C5D	11.6
	C8C-C7C-C4C-C3C	-26.8		C8D-C7D-C4D-C3D	8.5
Ligand E	C12E-C7E-C4E-C5E	-27.3	Ligand F	C12F-C7F-C4F-C5F	40.9
	C8E-C7E-C4E-C3E	-33.6		C8F-C7F-C4F-C3F	40.0
Ligand G	C12G-C7G-C4G-C5G	-21.3	Ligand H	C12H-C7H-C4H-C5H	24.6
	C8G-C7G-C4G-C3G	-30.5		C8H-C7H-C4H-C3H	24.9
Compound 2					
Ligand A	C12-C7A-C4A-C5A	33.4			
	C8A-C7A-C4A-C3A	32.9			
Ligand B	C12B-C7B-C4B-C5B	-27.3			
	C8B-C7B-C4B-C3B	-27.6			

(a) (b)

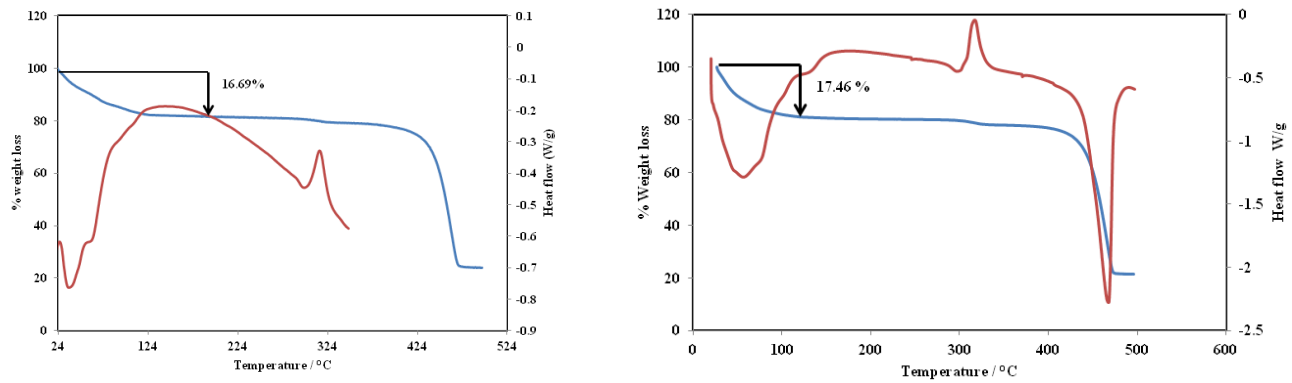

Fig S2 (a) TGA (blue) and DSC (red) of **2.** (b) TGA (blue) and DSC (red) of **4**

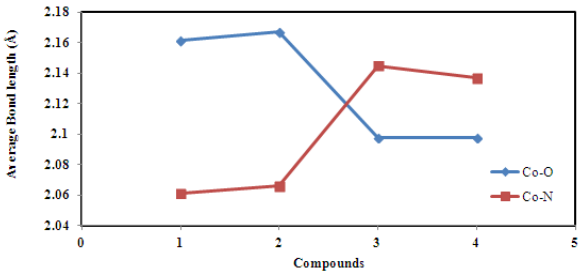

Fig S3. Average bond length analysis of compound **1-4**

Table S8. Torsion angles of the benzene ring and carboxyl groups in **3** and **4**

		Torsion angle/°			Torsion angle/°
Compound 3					
Ligand A	O15A-C13A-C10A-C9A	26.6	Ligand B	O15B-C13B-C10B-C11B	-21.3
	O15A-C13A-C10A-C11A	153.8		O15B-C13B-C10B-C9B	153.4
Ligand C	O15C-C13C-C10C-C9C	-26.9	Ligand D	O15D-C13D-C10D-C9D	-26.6
	O15C-C13C-C10C-C11C	153.7		O15D-C13D-C10D-C11D	-145.4
Compound 4					
Ligand A	O15A-C13A-C10A-C11A	-9.9			
	O15A-C13A-C10A-C9A	179.6			
Ligand B	O15B-C13B-C10B-C11B	177.5			
	O15B-C13B-C10B-C9B	-0.61			

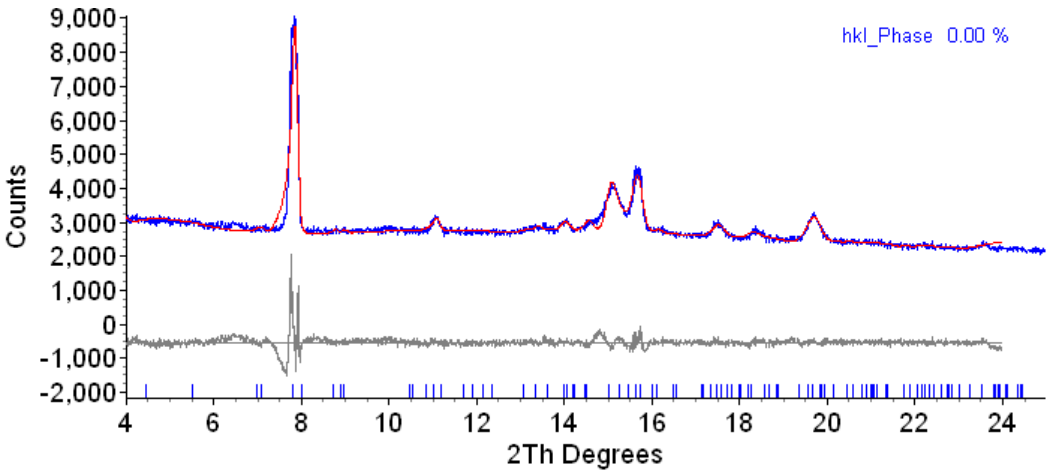

Fig. S4. Pawley fitting profile of powder data collected after immersing **4** in DMF/ethanol mixture at room temperature. The unit cell dimensions of **1** were used for this profile fitting. The blue pattern corresponds to the observed peak intensities and positions and the red pattern is the computed data. The difference between the two is depicted in grey. By viewing the observed and calculated patterns graphically, it is very clear that the two patterns match well; thus the proposed model is chemically plausible. The discrepancies observed at about 7.8° and from 14.5- 15.8° are caused by the failure of the integration used for R_{Bragg} indices when peaks have significant unmodeled asymmetry.

Topology out files

Compound 2

```
################################################
4:C26.50 H27.50 Co N2 O7.50/clusters at rings>6
################################################

Topology for Cr1
----------
Atom Cr1 links by bridge ligands and has
Common vertex with                    R(A-A)
Cr 1   0.2598   0.7894  -0.2532  ( 0 0 0)   13.036A      1
Cr 1   0.2598  -0.2106  -0.2532  ( 0-1 0)   13.036A      1
Cr 1  -0.2598   0.2106   0.7468  (-1 0 1)   13.072A      1
Cr 1   0.7402   0.2106   0.7468  ( 0 0 1)   13.072A      1
-------------------------
Structural group analysis
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Structural group No 1
-------------------------
Structure consists of 3D framework with Cr
There are 4 interpenetrating nets
TIV: Translating interpenetration vectors
----------------------------------------
[0,0,1] (12.70A)
----------------------------------------
NISE: Non-translating interpenetration symmetry elements
--------------------------------------------------------
1: 2[1,-1,0]
2: 2[1,1,0]
--------------------------------------------------------
PIC: [0,0,2][0,1,0][1,0,0] (PICVR=2)

Zt=2; Zn=2


Class IIIa  Z=4[2*2]

Coordination sequences
----------------------
Cr1:  1  2  3  4   5   6   7   8   9  10
Num   4 12 24 42  64  92 124 162 204 252
Cum   5 17 41 83 147 239 363 525 729 981
----------------------
TD10=981

Vertex symbols for selected sublattice
--------------------------------------
Cr1 Point symbol:{6^6}
Extended point symbol:[6(2).6(2).6(2).6(2).6(2).6(2)]
--------------------------------------
Point symbol for net: {6^6}
4-c net; uninodal net

Topological type: dia Diamond; 4/6/c1; sqc6 (topos&RCSR.ttd)
{6^6} - VS [6(2).6(2).6(2).6(2).6(2).6(2)] (73689 types in 11
databases)
Elapsed time: 1.41 sec.
```

Compound 3

```
################################################
3:C55 H57.90 Co2 N4 O16.35/clusters at rings>6
################################################

Topology for V1
---------------
Atom V1 links by bridge ligands and has
Common vertex with                    R(A-A)
V  2  -0.1186   0.3642  -0.6028  (-1 0-1)   13.257A      1
V  2   0.3814   0.6358   0.8972  (-1 1 0)   13.301A      1
V  2  -0.1186  -0.6358   0.3972  (-1-1 0)   13.934A      1
V  2   0.3814   1.6358  -0.1028  (-1 2-1)   13.978A      1
Topology for V2
---------------
Atom V2 links by bridge ligands and has
Common vertex with                    R(A-A)
V  1   1.1304   0.4974   1.1462  ( 1 0 1)   13.257A      1
V  1   0.6304   0.5026  -0.3538  ( 0 1-1)   13.301A      1
V  1   1.1304   1.4974   0.1462  ( 1 1 0)   13.934A      1
V  1   0.6304   1.5026   0.6462  ( 0 2 0)   13.978A      1
-------------------------
Structural group analysis
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Structural group No 1
-------------------------
Structure consists of 3D framework with V
There are 2 interpenetrating nets
FIV: Full interpenetration vectors
----------------------------------
[0,1,0] (10.60A)
----------------------------------
PIC: [0,2,0][1,1,0][0,1,1] (PICVR=2)

Zt=2; Zn=1

Class Ia  Z=2

Coordination sequences
----------------------
V1:  1  2  3  4   5   6   7   8   9  10
Num  4 10 24 42  64  92 124 162 204 252
Cum  5 15 39 81 145 237 361 523 727 979
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V2:  1  2  3  4   5   6   7   8   9  10
Num  4 10 24 42  64  90 124 162 204 250
Cum  5 15 39 81 145 235 359 521 725 975
----------------------
TD10=977

Vertex symbols for selected sublattice
--------------------------------------
V1 Point symbol:{4^2.8^4}
Extended point symbol:[4.4.8(2).8(2).8(8).8(8)]
--------------------------------------
V2 Point symbol:{4^2.8^4}
Extended point symbol:[4.4.8(7).8(7).8(7).8(7)]
--------------------------------------
Point symbol for net: {4^2.8^4}
4,4-c net with stoichiometry (4-c)(4-c); 2-nodal net
```

Topological type: pts PtS, Cooperite; sqc183 (topos&RCSR.ttd)
{4^2.8^4} - VS [4.4.8(7).8(7).8(7).8(7)] [4.4.8(2).8(2).8(8).8(8)]
(73689 types in 11 databases)
Elapsed time: 14.51 sec.

Compound 4

##
5:C26.80 H25.20 Co N2 O7.11/clusters at rings>6
##

Topology for Cr1

Atom Cr1 links by bridge ligands and has
Common vertex with R(A-A)

Cr 1	1.4063	1.8127	-0.0106	(2 2-1)	14.256A	1
Cr 1	0.1873	1.5936	0.6560	(0 2 0)	14.256A	1
Cr 1	-0.5937	0.8127	-0.0106	(0 1-1)	14.257A	1
Cr 1	-0.8127	-0.4064	0.6560	(-1 0 0)	14.257A	1

Structural group analysis

Structural group No 1

Structure consists of 3D framework with Cr
There are 3 interpenetrating nets
FIV: Full interpenetration vectors

[0,1,0] (10.70A)
[1,0,0] (10.70A)
[1,1,0] (10.70A)

PIC: [0,3,0][1,-1,0][0,0,1] (PICVR=3)

Zt=3; Zn=1

Class Ia Z=3

Coordination sequences

Cr1: 1 2 3 4 5 6 7 8 9 10
Num 4 12 30 52 80 116 156 204 258 318
Cum 5 17 47 99 179 295 451 655 913 1231

TD10=1231

Vertex symbols for selected sublattice

Cr1 Point symbol:{6^4.8^2}
Extended point symbol:[6.6.6(2).6(2).8(9).8(9)]

Point symbol for net: {6^4.8^2}
4-c net; uninodal net

Topological type: qtz Quartz; 4/6/h1 (topos&RCSR.ttd)
{6^4.8^2} - VS [6.6.6(2).6(2).8(7).8(7)] (73689 types in 11
databases)
Elapsed time: 1.58 sec.