

# Reversible structural transformations in a Co(II)-based 2D dynamic metal-organic framework showing selective solvent uptake

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**Abstract.** A Co(II)-based two-dimensional (2D) metal-organic framework (MOF) [Co(pca)(bdc)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1**) {pca = pyrazine carboxylic acid, and bdc = 1,4-benzene dicarboxylic acid} was synthesized solvothermally. The compound loses the coordinated lattice water molecules on heating which is accompanied by solid-state structural transformation to yield dehydrated phase [Co(pca)(bdc)<sub>0.5</sub>] (**1'**). The hydrated structure can be regained by exposing **1'** to water vapour (**1''**). These reversible solid-state structural transformations are accompanied by a visible colour change in the material. The dehydrated compound also shows highly selective water uptake over other solvents like MeOH, EtOH, THF. This selective water uptake can be ascribed to the high affinity of polar water molecule towards the open metal site created on heating. The present report provides important insights into the reversible structural transformations observed due to variable coordination number of the central metal ion and transformability of the framework. The selective water uptake over alcohols along with visible colour change demonstrates the potential of the present compound in bio-alcohol purification.

**Keywords.** Metal-organic frameworks; coordination polymers; selective uptake; dynamic framework.

## 1. Introduction

The limited natural resources like gas and oil have accelerated the research in the field of alternate sustainable energy resources.<sup>1–3</sup> Bio-alcohols are getting increased attention as sustainable energy resource which are expected to be commercialized in the near future. Despite its high potential, water as an unavoidable impurity present in the bio-alcohols restricts its extensive use.<sup>4–6</sup> The conventional distillation approach for separation of water from alcohols is energy intensive and ineffective.<sup>7–9</sup> Adsorption-based separation methods are more promising in this respect as they are energy efficient processes.<sup>10</sup> Thus, the effective and efficient separation of water from water-alcohol mixture by adsorption methods is highly anticipated.

The metal-organic frameworks (MOFs) and coordination polymers (CP) are well known for their designable architecture and porous properties, which along with the ease of material fabrication, feasibility of hybridization with other materials make MOFs significant materials.<sup>11–13</sup> Since their discovery, these materials have been extensively studied for storage, separation, magnetism, sensing, biomedical and very recently for ion conduction applications.<sup>14–21</sup> Hydrogen

bonding and van der Waals interactions have been explored especially to get selective separation through host guest interaction like  $\pi-\pi$ .<sup>22–24</sup> In this regard, the soft, porous crystals or dynamic frameworks have attracted much attention owing to the framework flexibility in addition to designable nature of the framework.<sup>25–27</sup> The flexibility provides an additional tool to control the guest uptake and gives rise to unusual phenomena like gate opening and selective adsorption.<sup>24–29</sup> These solid state transformations are triggered by external stimuli like heat, light, pressure, etc., and these are more attractive compared to rigid frameworks.<sup>30–32</sup> Despite these promising properties, reports of dynamic MOFs are limited due to the difficulties in the characterization of such solid-state structural transformations. Thus, the design and synthesis of dynamic MOF with high affinity for water becomes handy in separation applications. Also, for a material to be smart sorbent, in addition to selective and efficient sorption it should also show some change in properties like colour, magnetism, etc., so that it can be a self-indicator to identify the extent of saturation of sorbent.

Herein, we report a Co(II)-based dynamic metal-organic framework [Co(pca)(bdc)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1**) synthesized solvothermally. The compound exhibits reversible solid-state structural transformations as confirmed by

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PXRD and TGA analysis, accompanied by distinct colour change. The solvent sorption isotherms of the activated compound shows highly selective uptake of H<sub>2</sub>O over other solvents like MeOH, EtOH, THF, toluene, etc. This highly selective H<sub>2</sub>O uptake can be ascribed to the open metal sites generated on dehydration and the highly polar nature of water. The highly selective H<sub>2</sub>O uptake over EtOH and the colour change associated with it shows potential of the present compound to separate water from alcohol-water mixture.

## 2. Experimental

### 2.1 Materials

All the reagents were commercially available and used as supplied without further purification. Pyrazine carboxylic acid and 1,4-benzene dicarboxylic acid were purchased from Aldrich Chemical Co. Cobalt(II) nitrate and NaOH were purchased from Merck India. All other solvents used were purchased locally.

### 2.2 Synthesis of [Co(pca)(bdc)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1**)

The reaction between Co(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O (1 mmol), pyrazine carboxylic acid (pcaH, 1 mmol), 1,4-benzene dicarboxylic acid (bdcH<sub>2</sub>, 1 mmol) and NaOH (1 mmol), in 6 mL of H<sub>2</sub>O at 160°C for 3 days in a Teflon-lined vessel gave wine red single crystals of **1** in ~60 % yield.

### 2.3 Dehydration [Co(pca)(bdc)<sub>0.5</sub>] (**1'**)

The wine red single crystals of **1** were grinded to get fine powder which then was heated at 140°C for 8 h under reduced pressure. The dehydrated phase was obtained as brown powder.

### 2.4 Rehydration [Co(pca)(bdc)<sub>0.5</sub>(H<sub>2</sub>O)<sub>2</sub>] (**1''**)

The glass vial containing dehydrated sample was kept in a slightly bigger screw cap bottle containing water. After exposing to water vapour for 3 days at room temperature, the rehydrated phase was obtained. Rehydration can also be achieved by exposing the dehydrated sample to air, but complete rehydration takes a long time (~30 days).

### 2.5 X-Ray crystallography

Single-crystal X-ray data on **1** were collected at 200 K on a Bruker KAPPA APEX II CCD Duo diffractometer

(operated at 1500 W power: 50 kV, 30 mA) using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The crystal was on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The data integration and reduction were processed with SAINT<sup>33</sup> software. A multi-scan absorption correction was applied to the collected reflections. The structure was solved by the direct method using SHELXTL<sup>34</sup> and was refined on F<sup>2</sup> by full matrix least-squares technique using the SHELXL-97<sup>35</sup> program package within the WINGX<sup>36</sup> program. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in successive difference Fourier maps, and they were treated as riding atoms using SHELXL default parameters. The structures were examined using the Adsym subroutine of PLATON<sup>37</sup> to ensure that no additional symmetry could be applied to the models (table 1).

### 2.6 Physical measurements

FT-IR spectra were measured on a Nicolet 6700 FT-IR spectrophotometer by making KBr pellets (400–4000 cm<sup>-1</sup>), X-ray powder patterns were recorded on a Bruker D8 advanced X-ray diffractometer using Cu

**Table 1.** Crystal data and structure refinement for compound **1**.

Compound	<b>1</b>
Empirical formula	C9 H9 Co N2 O6
Formula weight	297.09
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pbc</i>
<i>a</i> (Å)	11.8920(15)
<i>b</i> (Å)	11.1027(14)
<i>c</i> (Å)	15.673(2)
Volume (Å <sup>3</sup> )	2069.4(5)
<i>Z</i>	8
Calculated density (mg m <sup>-3</sup> )	1.906
Absorption coefficient (mm <sup>-1</sup> )	1.941
<i>F</i> (000)	1224
Theta range (°)	2.85–29.31
Reflections collected/unique	11385/2746
Completeness to $\theta$ /%	99.10
Max./Min. transmission	0.8296/0.6975
Data/restraints parameters	2746/0/175
Goodness-of-fit on F <sup>2</sup>	1.058
Final R indices $I > 2\sigma(I)$ <sup>(a)</sup>	0.0213
R indices (all data) <sup>(b)</sup>	0.0570

$${}^a R_1 = \frac{\sum ||F_0| - |F_c||}{\sum |F_0|}$$

$${}^b wR_2 = [\frac{\sum (w(F_0^2 - F_c^2)^2)}{\sum w(F_0^2)^2}]^{1/2}$$

$K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) with scan rate  $0.4 \text{ s/step}$  and step size  $0.01^\circ$ , and thermogravimetric analyses were recorded with heating rate of  $10^\circ\text{C/min}$  under  $\text{N}_2$  atmosphere on a Perkin-Elmer STA 6000 TGA analyzer.

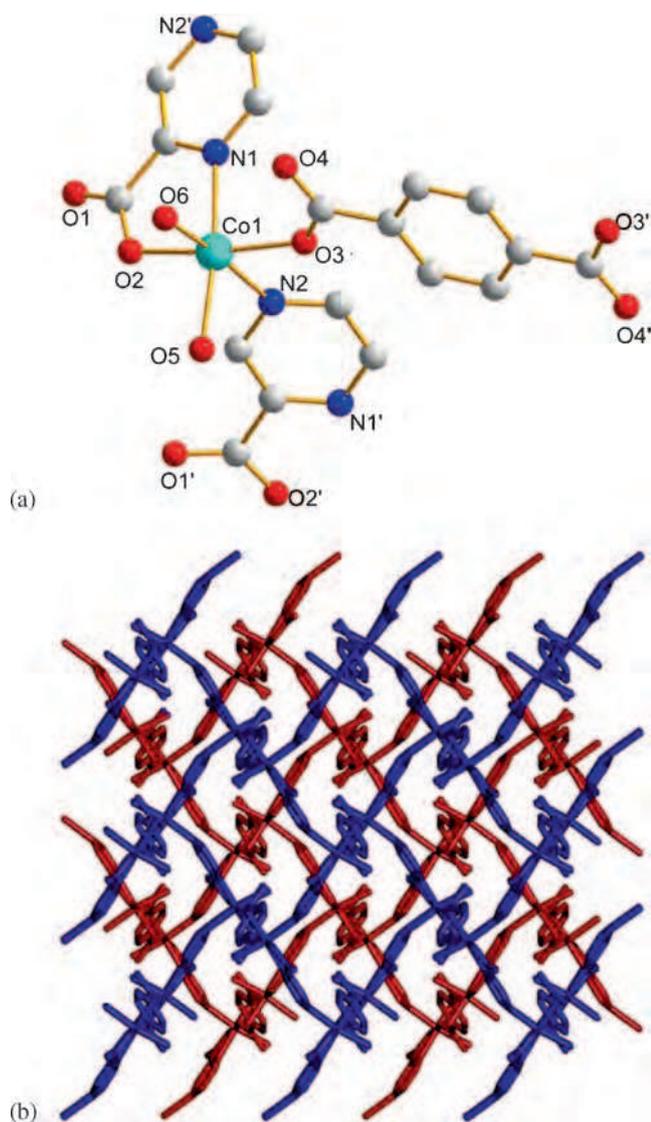
### 2.7 Low pressure sorption measurement

Low pressure gas and solvent sorption measurements were measured using BelSorp-max (Bel Japan). The sample **1** was heated at  $140^\circ\text{C}$  for 2 h in oil bath prior to adsorption measurement to activate the sample. The activated sample was further heated at  $120^\circ\text{C}$  under vacuum for 5 h using BelPrepvacII and purged with  $\text{N}_2$  on cooling. The sample was out-gassed similarly

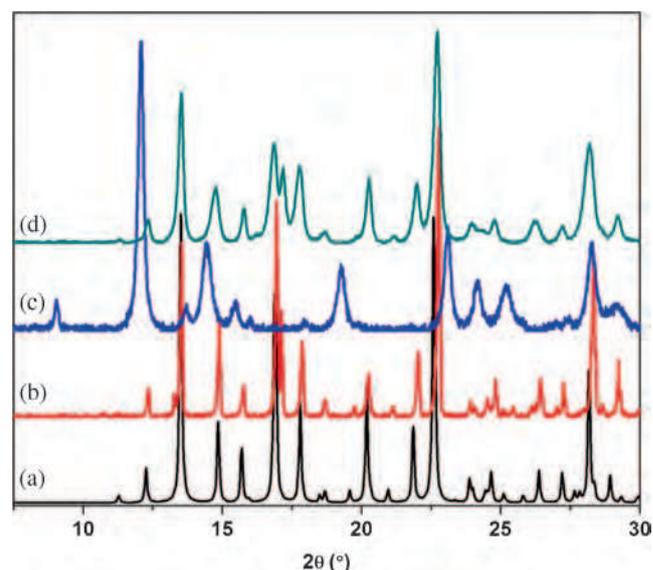
before each measurement for 5 h. All the solvent sorption isotherms were measured at 298 K while the gas measurements were performed at 195 K.

## 3. Results and Discussion

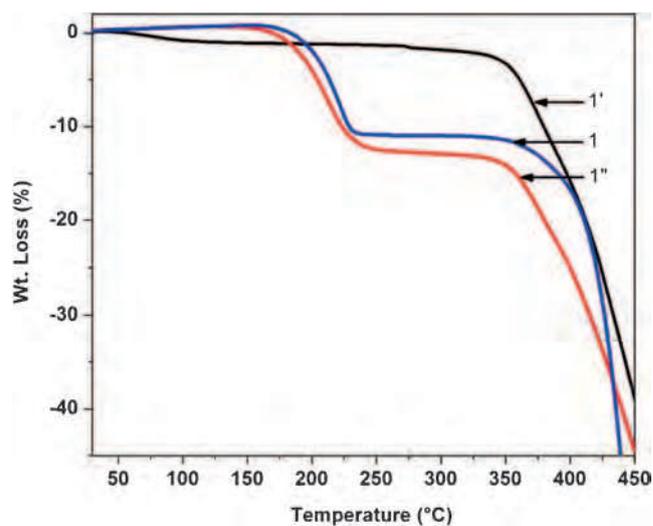
The solvothermal reaction between pyrazine carboxylic acid (pcaH), 1,4-benzene dicarboxylic acid (bdcH<sub>2</sub>), NaOH, and  $\text{Co}(\text{NO}_3)_2$  in  $\text{H}_2\text{O}$  at  $160^\circ\text{C}$  for 3 days gave wine red coloured crystals of  $[\text{Co}(\text{pca})(\text{bdc})_{0.5}(\text{H}_2\text{O})_2]$  (**1**). Single crystal X-ray analysis (SC-XRD) of compound **1** revealed that the compound crystallizes in



**Figure 1.** (a) Coordination environment of compound **1**; (b) ABAB arrangement of 2D sheets of compound **1** along 'c' axis.

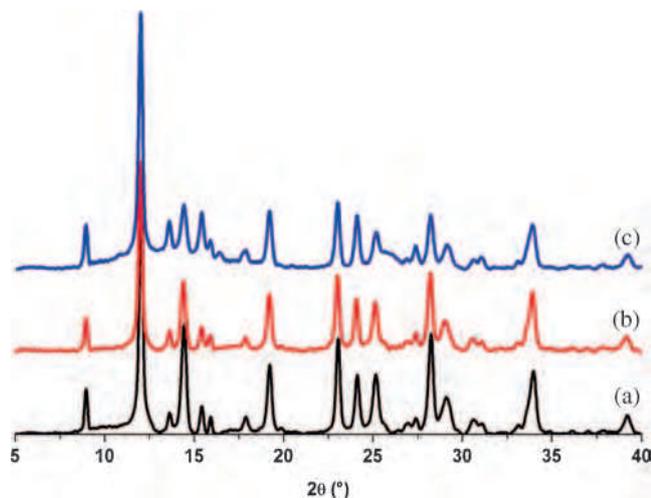


**Figure 2.** Powder X-ray diffraction patterns of different phases of compound **1**. [(a) Simulated, (b) As-synthesized, (c) Dehydrated, (d) Rehydrated].

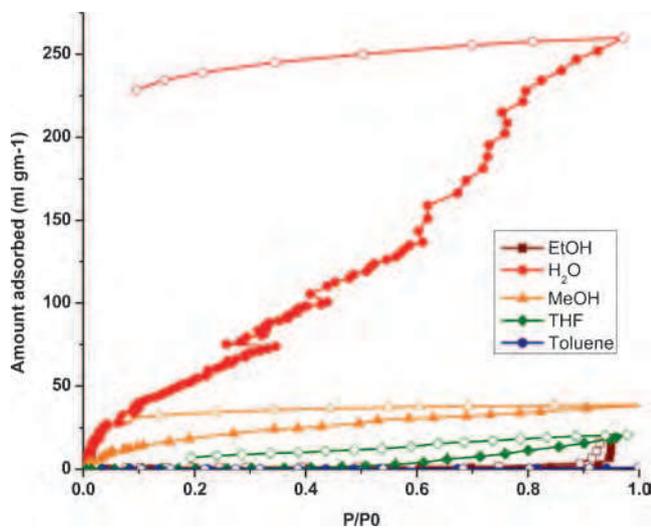


**Figure 3.** Thermogravimetric analysis of different phases of compound **1**. (**1** as-synthesized, **1'** dehydrated, **1''** rehydrated).

orthorhombic crystal system with space group *Pbca*. One *pca* ligand and half *bdc* ligand are connected to the central Co(II) metal ion to make the overall framework neutral. Two water molecules coordinate to the metal centre from the opposite sides of *pca* nitrogen atoms.



**Figure 4.** Powder X-ray diffraction (PXRD) patterns of compound **1'**. a) de-solvated phase (**1'**), b) **1'**, exposed to THF for 8 days, c) **1'**, exposed to MeOH for 8 days.



**Figure 5.** Selective solvent sorption isotherms for **1'** at 298 K. (Filled symbols indicate adsorption, and open symbols indicate desorption.)

The metal ions adopt octahedral environment with  $N_2O_4$  donor set (figure 1a). The adjacent Co(II) centres are connected by pyrazine nitrogens forming 1D Zigzag chain along *b* axis. The *bdc* ligand with mono-dentate coordination mode connect these 1D zigzag chain of Co(II) pyrazine to give rise to 2D sheet structure along '*c*' axis. The sheets are arranged one above the other in ABAB fashion and formed hydrogen bonded pseudo-3D interpenetrated structure (figure 1b). The free carboxylate oxygen from both *pca* and *bdc* ligands form hydrogen bonds with the water molecules from adjacent A layers present above and below it. Also, the B layer form hydrogen bonds with neighbouring B layer present above and below it.<sup>38</sup> The phase purity of the bulk sample was confirmed by overlapping Powder X-ray diffraction patterns (PXRD) of as-synthesized material with simulated PXRD pattern from SC-XRD (figure 2).

The thermogravimetric analysis (TGA) of compound **1** in  $N_2$  atmosphere revealed that the compound is stable up to 160°C (figure 3). Above 160°C, the compound starts losing coordinated water molecules and complete water loss occurred at ~230°C forming dehydrated phase  $[Co(pca)(bdc)_{0.5}]$  (**1'**). The dehydrated phase **1'** is stable up to 360°C after which it starts decomposing. The formation of dehydrated phase was also confirmed by TGA and PXRD analysis. To get the dehydrated phase, compound **1** was heated at 140°C under vacuum for 12 h. The TGA analysis of dehydrated sample showed negligible weight loss till 160°C which confirmed the complete removal of coordinated water molecules. The comparison between PXRD patterns of as-synthesized and dehydrated form showed that on dehydration the original structure transforms to a new structure. But interestingly, upon exposure to the water vapour, the dehydrated phase again transforms back to original hydrated structure (**1''**) as was evident from the PXRD analysis (figure 2). Also, the TGA of this rehydrated form shows weight loss corresponding to two water molecules. We also exposed the dehydrated phase **1''** to other polar coordinating solvents MeOH and THF. Surprisingly, we did not observe any structural change in **1''** upon exposure to MeOH or THF (figure 4). The



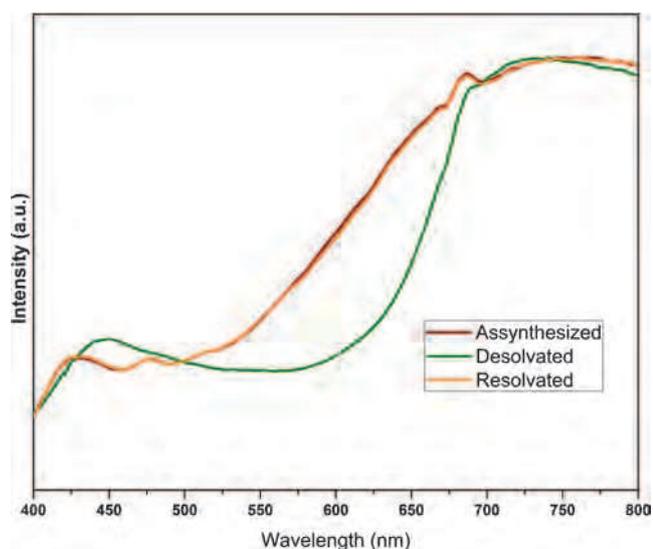
**Figure 6.** Photograph showing visible colour changes in compound **1**.

above results demonstrate that the reversible structural change observed in the compound is highly selective for water.

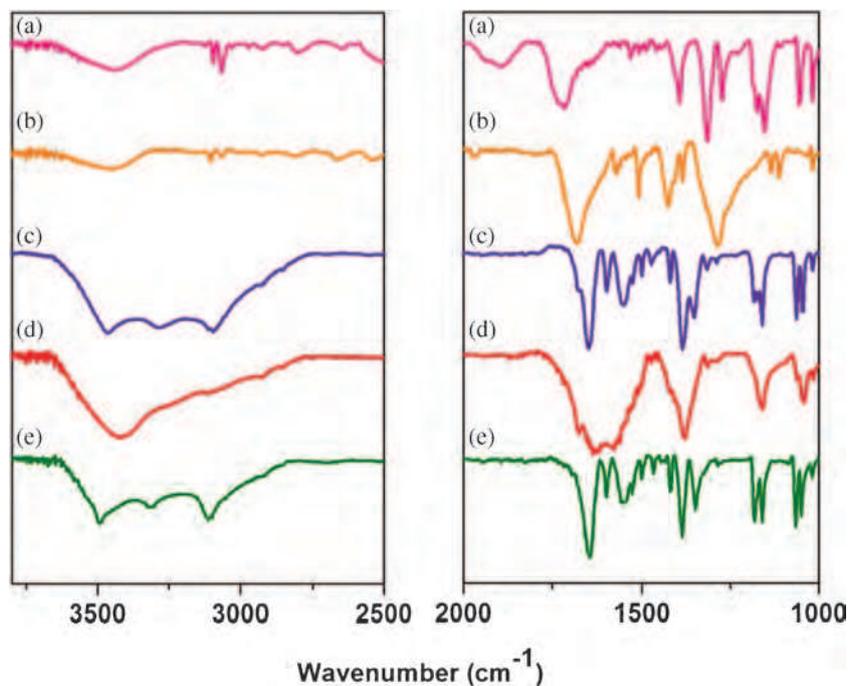
To further confirm the selective uptake of water, we measured sorption isotherms of different adsorbates ( $\text{H}_2\text{O}$ , MeOH, EtOH, THF, Toluene) having varying polarities with compound **1'** volumetrically. As expected, the compound **1'** showed non-porous behaviour towards gas molecules. The sorption profile

of water showed linear increase in water uptake with increasing pressure with a maximum uptake of 200 mL per gram (figure 5). This  $\text{H}_2\text{O}$  uptake corresponds to uptake of two water molecules per formula unit. Desorption profile showed a large hysteresis with negligible weight loss even at reduced pressure. On the other hand, the sorption profiles of polar coordinating solvents like MeOH, EtOH, THF showed insignificant uptakes. These results are in good agreement with structural rigidity of **1'** towards MeOH and THF as mentioned above. The selective water uptake can be assigned to the smaller size and polar nature of water molecule along with the flexible nature of the compound driven by host-guest interaction. The above results confirm the selective water sorption behaviour of compound **1**.

In addition to reversible structural transformation, we observed that the compound shows reversible visible colour change corresponding to hydrated and dehydrated phases (figure 6). This prompted us to measure the solid-state UV-Vis spectra of different phases of compound **1** to ensure the complete structural transformation (figure 7). The as-synthesized pink compound (**1**) shows absorbance maximum at 425 nm which on dehydration shifts to 450 nm with change in colour from pink to dark purple (**1'**). On rehydration, the dark purple coloured dehydrated phase again changes to pink coloured rehydrated phase showing absorbance maximum again at 425 nm (**1''**).



**Figure 7.** Solid-state UV spectrum of as-synthesized, desolvated and resolvated phases of compound **1**.



**Figure 8.** Comparison between the selected area of FT-IR spectra for (a) pca, (b) bdc, (c) as-synthesized, (d) desolvated and (e) resolvated phases of compound **1**.

To gain insights into the reversible structural transformation on water exposure and associated colour change, we tried to get the structure of desolvated phase **1'** by SC-XRD analysis. We heated the single crystals of **1** under reduced pressure and collected the SC-XRD data. Unfortunately, after several attempts we could not get the structure of desolvated phase. We recorded IR spectra of both the pure ligands, as-synthesized, desolvated and resolvated compounds to get the hint of possible structural changes around central metal ion (figure 8).

The peak corresponding to the coordinated water molecule ( $3110\text{ cm}^{-1}$ ) is present in both as-synthesized and rehydrated compound but absent in dehydrated phase.<sup>38</sup> This clearly indicates that on heating, both the water molecules are removed from as-synthesized compound which are regained upon rehydration in **1''**. Also, the peak corresponding to free carboxylates ( $1648\text{ s}$  and  $1596\text{ w cm}^{-1}$ ) become broad on dehydration which can be recovered on hydration indicating change in the coordination ability of the free carboxylates.<sup>38</sup> Hence, we propose that on heating, compound **1** loses both the coordinate molecules and transforms to dehydrated phase **1'** creating open metal sites. This change in coordination environment around central metal atom leads to a change in visible colour. On rehydration owing to small size and polar nature of water, the original structure can be recovered.

#### 4. Conclusion

We have synthesized 2D metal organic frameworks with formula  $[\text{Co}(\text{pca})(\text{bdc})_{0.5}(\text{H}_2\text{O})_2]$ . The compound shows reversible, dynamic structural transformations between two states with visible change in colour. The reversible structural transformation between as-synthesized  $[\text{Co}(\text{pca})(\text{bdc})_{0.5}(\text{H}_2\text{O})_2]$  and dehydrated  $[\text{Co}(\text{pca})(\text{bdc})_{0.5}]$  states was confirmed by IR spectroscopy, TGA and PXRD data. The desolvated compound shows selective sorption of water. The selective uptake of  $\text{H}_2\text{O}$  over other organic solvents like MeOH, EtOH, THF and toluene by desolvated phase is ascribed to the strong affinity of polar solvent to the open metal sites and H-bonding interaction between the host and guest. This 2D framework has the potential to separate water in alcohols and can be used in bio-alcohol purification.

#### Supplementary Information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

data Centre, CCDC 870178 for complex **1**. Copies of the data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: (internet) +44-1223-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)

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#### References

1. Yoon M, Suh K, Natarajan S and Kim K 2013 *Angew. Chem. Int. Ed.* **52** 2688
2. Li S-L and Xu Q 2013 *Energy Environ. Sci.* **6** 1656
3. Laberty-Robert C, Valle K, Pereira F and Sanchez C 2011 *Chem. Soc. Rev.* **40** 961
4. Hill G J, Nelson E, Tilman D, Polasky S and Tiffany D 2006 *Proc. Natl. Acad. Sci. U. S. A.* **103** 11206
5. Gnansounou E and Dauriat A 2010 *Bioresour. Technol.* **101** 4980
6. Luque R, Herrero-Davila L, Campelo J M, Clark J H, Hidalgo J M, Luna D, Marinas J M and Romero A A 2008 *Energy Environ. Sci.* **1** 542
7. Sano T, Yanagishita H, Kiyozumi Y, Mizukami F and Haraya K J 1994 *Membr. Sci.* **95** 221
8. Okamoto K, Kita H, Horii K and Tanaka K 2001 *Ind. Eng. Chem. Res.* **40** 163
9. Tuan V A, Li S, Falconer J L and Noble R D 2002 *J. Membr. Sci.* **196** 111
10. Nagarkar S S, Chaudhari A K and Ghosh S K 2012 *Inorg. Chem.* **51** 572
11. Kitagawa S and Matsuda R 2007 *Coord. Chem. Rev.* **251** 2490
12. Yaghi O M, O'Keeffe M, Ockwig N W, Chae H K, Eddaoudi M and Kim J 2003 *Nature* **423** 705
13. Horike S, Umeyama D and Kitagawa S 2013 *Acc. Chem. Res.* **46** 11
14. Nagarkar S S, Joarder B, Chaudhari A K, Mukherjee S and Ghosh S K 2013 *Angew. Chem. Int. Ed.* **52** 2881
15. Czaja A U, Trukhan N and Mueller U 2009 *Chem. Soc. Rev.* **38** 1284
16. Stock N and Biswas S 2012 *Chem. Rev.* **112** 933
17. Zhao D, Meek S T, Greathouse J A and Allendorf M D 2011 *Adv. Mater.* **23** 249
18. Perry J J, Perman J A and Zaworotko M J 2009 *Chem. Soc. Rev.* **38** 1400
19. Cui Y, Yue Y, Qian G and Chen B 2011 *Chem. Rev.* **112** 1126
20. Tanabe K K and Cohen S M 2011 *Chem. Soc. Rev.* **40** 498

21. Kuppler R J, Timmons D J, Fang Q R, Li J R, Makal T A, Young M D, Yuan D Q, Zhao D, Zhuang W J and Zhou H C 2009 *Coord. Chem. Rev.* **253** 3042
22. Ling Y, Chen Z-X, Zhai F-P, Zhou Y-M, Weng L-H and Zhao D-Y 2011 *Chem. Commun.* **47** 7197
23. Shimomura S, Horike S, Matsuda R and Kitagawa S 2007 *J. Am. Chem. Soc.* **129** 10990
24. Maji T K, Matsuda R and Kitagawa S 2007 *Nature Mat.* **6** 142
25. Horike S, Shimomura S and Kitagawa S 2009 *Nature Chem.* **1** 695
26. Manna B, Chaudhari A K, Joarder B, Karmakar A and Ghosh S K 2013 *Angew. Chem. Int. Ed.* **52** 998
27. Joarder B, Chaudhari A K, Nagarkar S S, Manna B and Ghosh S K 2013 *Chem. Eur. J.* **19** 11178
28. Li J-R, Kuppler R J and Zhou H-C 2009 *Chem. Soc. Rev.* **38** 1477
29. Zhang J and Chen X-M 2008 *J. Am. Chem. Soc.* **130** 6010
30. Yanai N, Umera T, Inoue M, Matsuda R, Fukushima T, Tsujimoto M, Isoda S and Kitagawa S 2012 *J. Am. Chem. Soc.* **134** 4501
31. Gagnon K J, Beavers C M and Clearfield A 2013 *J. Am. Chem. Soc.* **135** 1252
32. Coronado E and Espallargas G M 2013 *Chem. Soc. Rev.* **42** 1525
33. SAINTPlus (Version 7.03) 2004 (Madison, WI: Bruker AXS Inc.
34. Sheldrick G M 1997 *SHELXTL, Reference Manual, Version 5.1* (Madison, WI: Bruker AXS)
35. Sheldrick G M 2008 *Acta Crystallogr. Sect. A* 112
36. Farrugia L J 2009 *WINGX version 1.80.05* (Glasgow: University of Glasgow)
37. Spek A L and PLATON A 2005 *Multipurpose Crystallographic Tool* (Utrecht, The Netherlands: Utrecht University)
38. Nagarkar S S, Das R, Poddar P and Ghosh S K 2012 *Inorg. Chem.* **51** 8317