Electronic Supplementary Material (ESI) for Chemical Communications

Modulation of Breathing Behavior of Layered Coordination Polymers *via* Solid Solutions: The Influence of Metal Ions on Sorption Behavior

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Supporting Information

Details of synthesis procedures and characterizations of complexes by elemental analyses, IR spectra, PXRD and TGA data, and gas isotherms.

General. Fourier transform IR (FTIR) spectra were recorded with an Perkin-Elmer instrument. Elemental analyses were obtained with a Perkin-Elmer instrument, series II, CHNS/O analyzer 2400. Thermogravimetric analysis (TGA) data were recorded under an Ar atmosphere at a heating rate of 5ºCmin^{-1} with a Perkin-Elmer instrument, Pyris Diamond TG/DTA. Powder X-ray diffraction (XRD) data were recorded with a Bruker APEX-2 diffractometer at room temperature.

The adsorption isotherms of N_2 (77K), H_2 (77K) and H_2O (298K) were measured in the gaseous state by using Quantachrome Autosorb iQ.

For Scanning Electron Microscopy Imaging (SEM) and Energy Dispersive X-ray (EDX) analyses, samples were dispersed over a sticky carbon surface adhered to a flat aluminum platform sample holder and then gold coated. Samples were analyzed using a JEOL JSM5800 Scanning Microscope equipped with Oxford EDS detector was used to evaluate the ratio between Cd(II) and Zn(II). Multiple samples of complex **5** and **6** were surveyed, without significant variation of Cd(II)/ Zn(II) ratio. Further, EDS analyses on ten randomly chosen crystals from bulk samples of **5** and **6** were carried out and the results did not vary notably from the proposed formulae, suggesting homogeneity of the bulk samples.

Benzene-1,3,5-triyltriisonicotinate (L)

The ligand was prepared according to the previously reported method.[1]

Synthesis of Complex by Direct Reactions:

Complex **1**: Methanolic solution (1 mL) of $Cd(ClO_4)_2\cdot$(0.01 mmol) was added to a stirred solution of ligand (0.009 g, 0.02 mmol) in 2 mL of $CHCl_3$. This solution was

filtered after stirring of few minutes and kept for slow evaporation. Crystals were formed after few hours.

All the complexes were prepared in a similar way by using the ligand, and corresponding metal salts.

The reactions with $M(PF_6)_2$ were prepared by mixing methanolic solution of $M(NO_3)_2$ in $(NH_4)_2PF_6$ in 1:1 ratio.

Complexes **5** and **6** were prepared by taking $Cd(ClO_4)_2$ and $Zn(ClO_4)_2$ in 1:1.5 and 1:2.5 ratios, respectively.

Complex **1**: Yield: 58%. Elemental analysis for $CdC_{52}H_{52}Cl_8N_6O_{28}$; calc (%) C 38.91, H 3.27, N 5.24; obs (%) C 38.85, H 3.00, N 5.57.

Complex **2**: Yield: 50%. Elemental analysis for $CdC_{52}H_{52}Cl_6N_6O_{20}P_2F_{12}$; calc (%) C 36.82, H 3.09, N 4.96; obs (%) C 38.87, H 2.90, N 5.58.

Complex **3**: Yield: 55%. Elemental analysis for $ZnC_{52}H_{52}Cl_8N_6O_{28}$; calc (%) C 40.09, H 3.36, N 5.39; obs (%) C 42.80, H 3.30, N 5.57.

Complex **4**: Yield: 30%. Elemental analysis for $ZnC_{52}H_{52}Cl_6N_6O_{20}P_2F_{12}$; calc (%) C 37.87, H 3.18, N 5.10; obs (%) C 40.68, H 2.95, N 5.69.

Complex **5**: Yield: 52%. Elemental analysis for $Cd_{0.60}Zn_{0.40}C_{52}H_{52}Cl_8N_6O_{28}$; calc (%) C 39.37, H 3.31, N 5.29; obs (%) C 37.83, H 2.75, N 5.25.

Complex **6**: Yield: 50%. Elemental analysis for $Cd_{0.32}Zn_{0.68}C_{52}H_{52}Cl_8N_6O_{28}$; calc (%) C 39.72, H 3.34, N 5.35; obs (%) C 38.29, H 2.52, N 5.42.

Crystal Structure Determinations (1, 2, 3 and 5)

The single crystal data was collected on Bruker APEX-2 CCD X-ray diffractometer that uses graphite monochromated MoKα radiation (λ =0.71073 Å) by hemisphere method. The structures are solved by direct methods and refined by least square methods on F^2

using SHELX-97.[2] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model.. The single crystal data for **2** was determined at low temperature (100K) while the others were determined at room temperature by coating crystal surface with silicone oil. As a result, the CH_3OH, $CHCl_3$ and other free water molecules were located and refined only in **2** without any problems, whereas in other structures, although they (anions+ solvents) were located, they were found to exhibit distortions and high thermal parameters. Therefore, in the final refinement the contribution of solvents and anions was removed by using the PLATON squeeze option.[3] Also PLATON was used for the calculation of guest available volumes.

Table S1: Crystallographic parameters for the complexes 1, 2, 3 and 5.

Compound	**1**(CCDC-965128)	**2**(CCDC-965129)	**3**(CCDC-965130)	**5**(CCDC-965131)
Formula	$CdC_{52}H_{52}Cl_8N_6O_{28}$	$CdC_{52}H_{52}Cl_6F_{12}N_6O_{20}P_2$	$ZnC_{52}H_{52}Cl_8N_6O_{28}$	$Cd_{0.60}Zn_{0.40}C_{52}H_{52}Cl_8N_6O_{28}$
M. Wt.	1605.00	1696.04	1557.97	1586.18
Temperature (K)	293	100	293	293
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	10.4535(19)	10.3591(4)	10.321(3)	10.391(2)
b(Å)	18.918(4)	19.0085(8)	18.735(5)	18.819(4)
c(Å)	17.278(3)	16.9399(7)	17.405(4)	17.351(4)
α(°)	90	90	90	90
β(°)	100.905(5)	101.516(1)	99.987(7)	100.537(6)
γ(°)	90	90	90	90
Vol. (Å^3)	3355.1(11)	3268.5(2)	3314.5(14)	3335.8(12)
Z	2	2	2	2
D_{calc}(g/cm^3)	1.589	1.723	1.497	1.579
R_1 ($I>2\sigma(I)$)	0.0584	0.0842	0.0911	0.0758
wR_2 (on F^2, all data)	0.0880	0.0912	0.1516	0.1174
independent reflns	4173	6572	3208	4075
reflns used[$I>2\sigma(I)$]	6217	7414	6078	6436
R_{int}	0.0989	0.0336	0.1640	0.1081

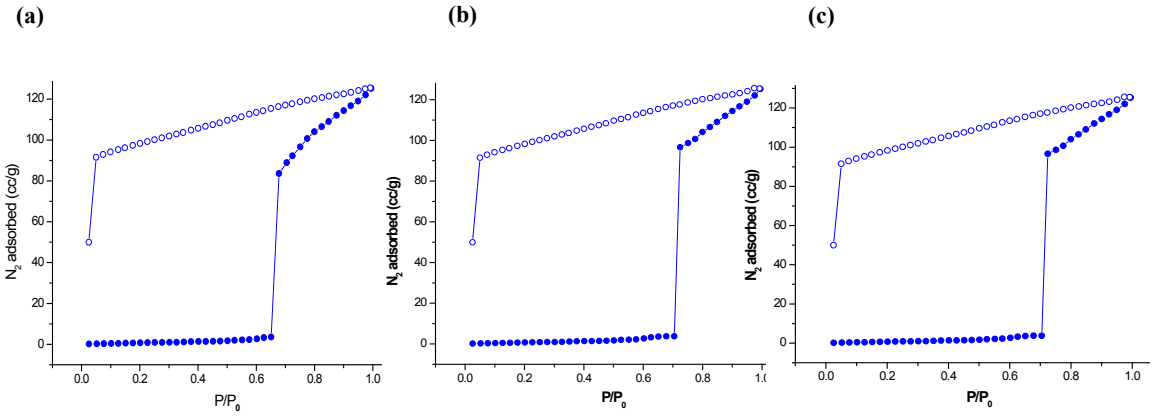

Figure S1. N_2 sorption profiles of sample **1**: (a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle. Filled and open symbols represent adsorption and desorption, respectively.

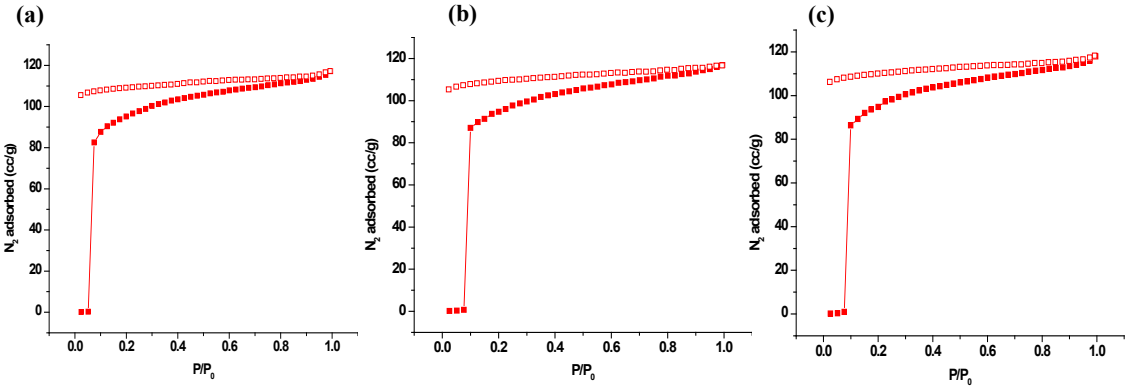

Figure S2. N_2 sorption profiles of sample **3**: (a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle. Filled and open symbols represent adsorption and desorption, respectively.

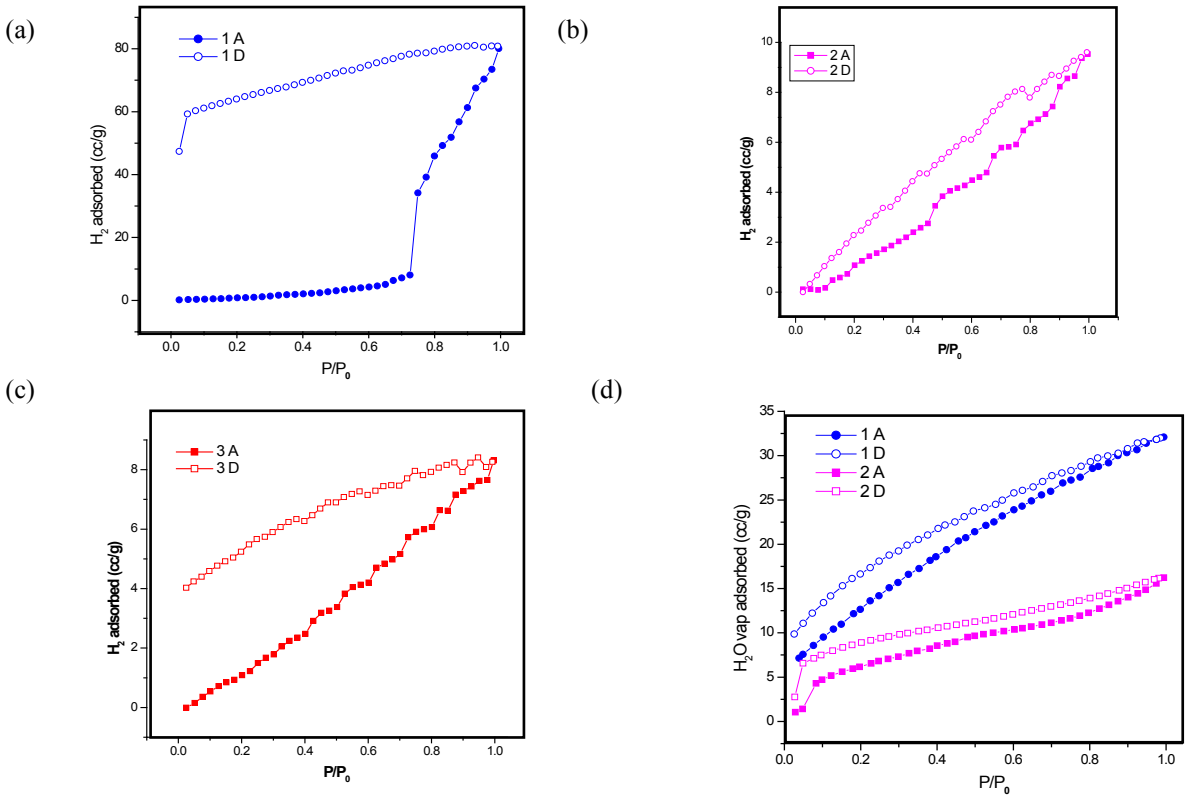

Figure S3. H_2 sorption profiles of: (a) sample **1**, (b) sample **2** (c) sample **3**; (d) water vapor sorption profile of sample **1** (blue) and **2** (pink). Filled and open symbols represent adsorption and desorption, respectively.

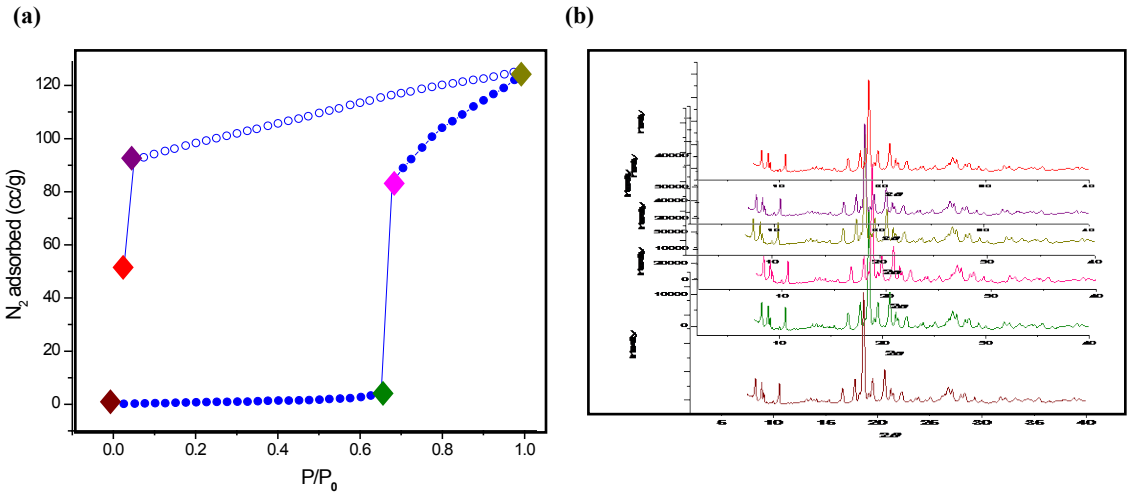

Figure S4. PXRD patterns of degassed sample **1** at different stages of N_2 sorption recorded at room temperature by interrupting the analysis at desired points.

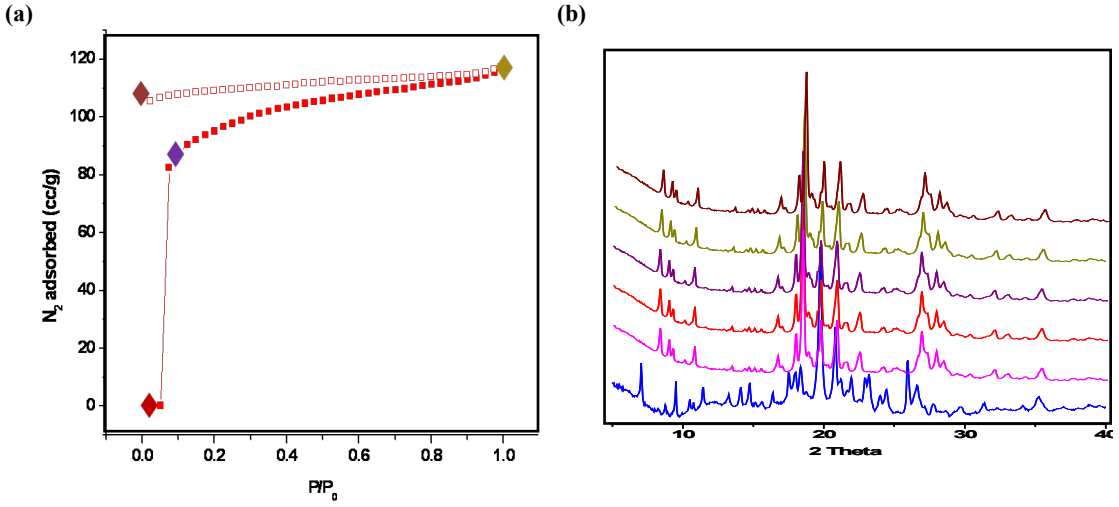

Figure S5. PXRD patterns of degassed sample **3** at different stages of N_2 sorption recorded at room temperature by interrupting the analysis at desired points. Blue: as-synthesized; pink: activated sample.

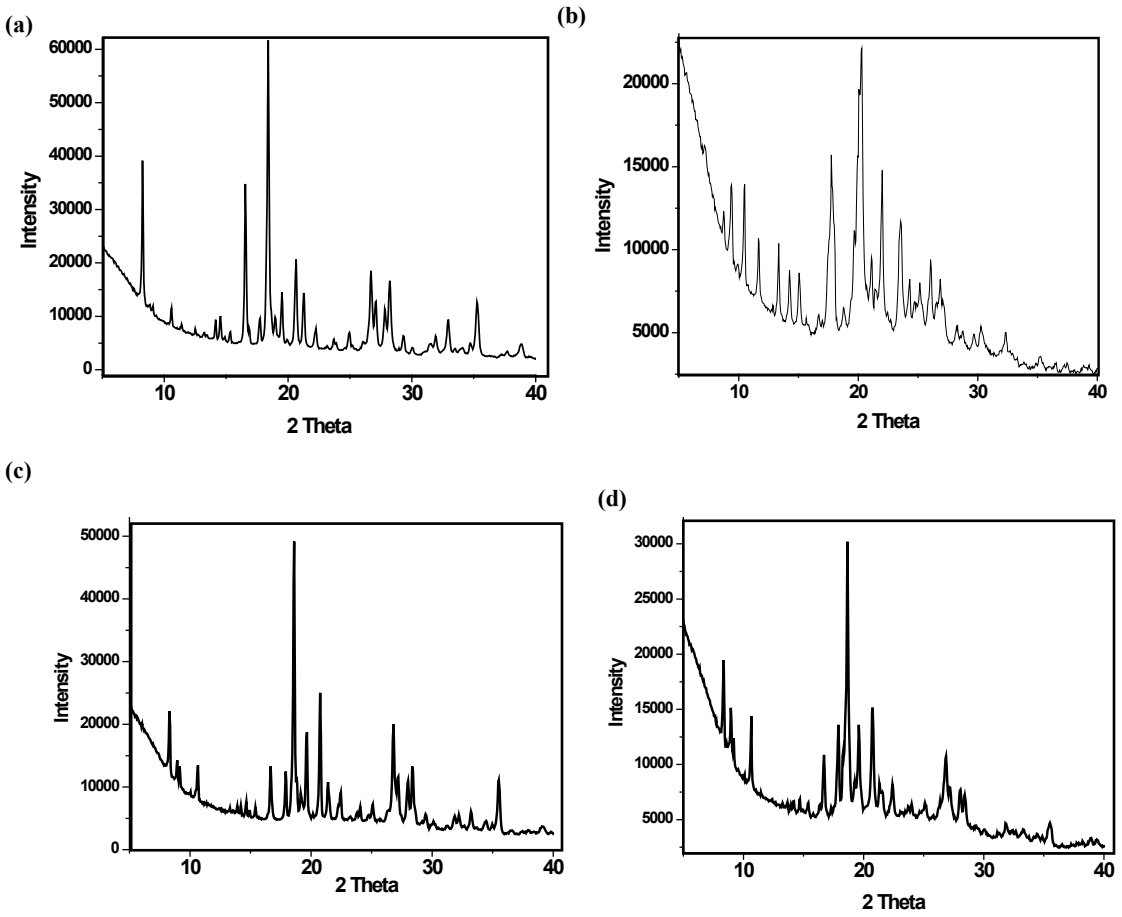

Figure S6. PXRD patterns of sample (a) **2,** (b) **4,** (c) **5,** (d) **6** at different stages of N_2 sorption recorded at ambient condition remain same.

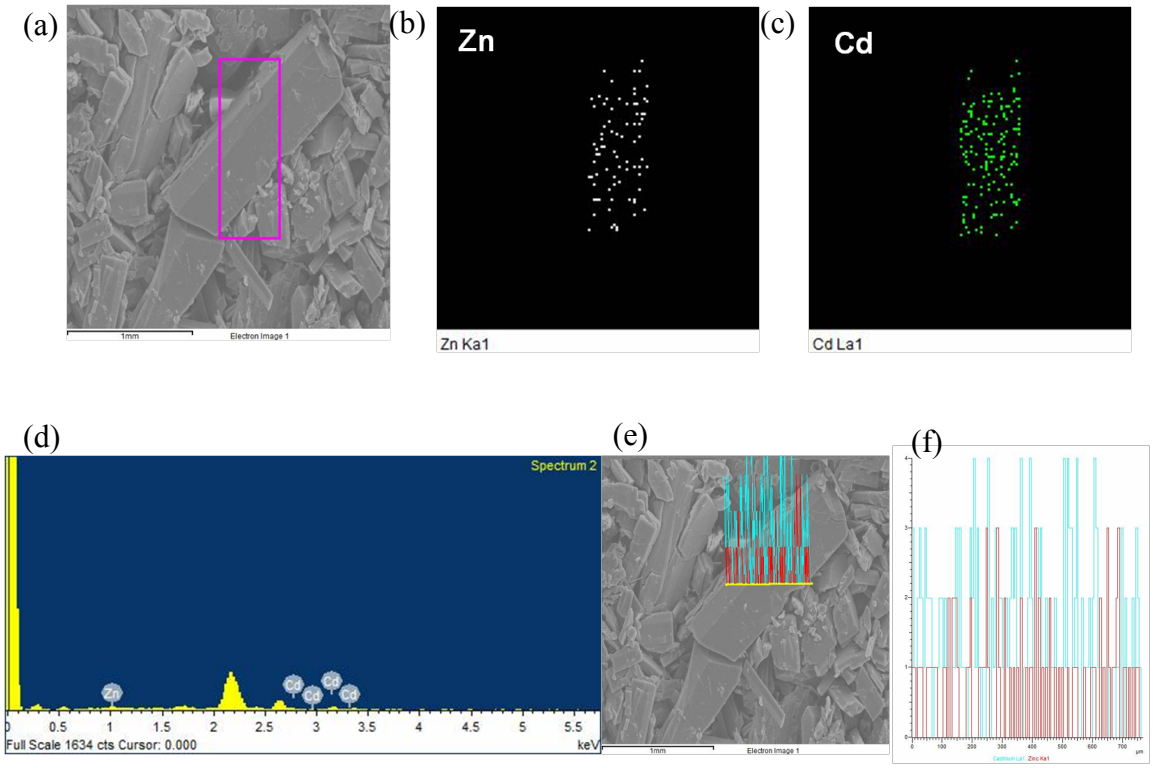

Figure S7. SEM-EDS images of **5** (a) SEM image of gold coated crystal; elemental images of (b) Zn(II) and (c) Cd(II); (d) EDS spectra; (e) and (f) show the line mapping for Cd(II) (red color) and Zn(II) (cyan color) suggesting homogeneous distribution of the metal ions

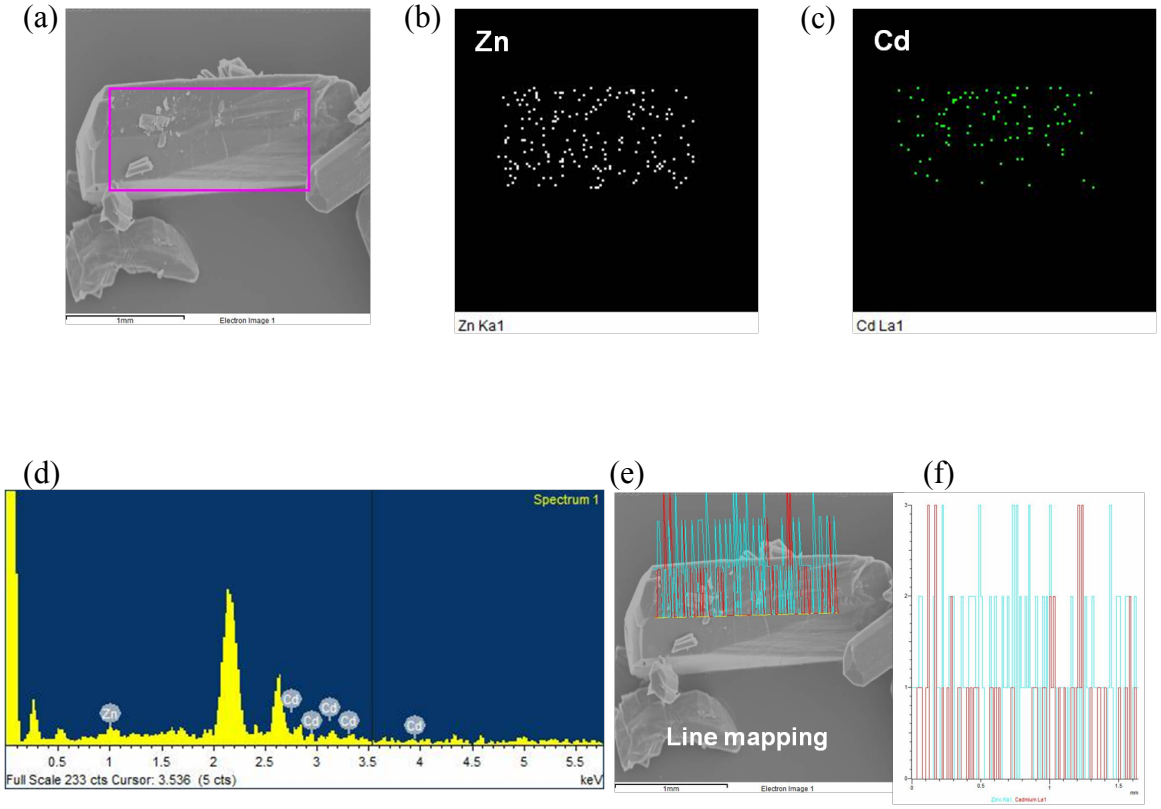

Figure S8. SEM-EDS images of **6** (a) SEM image of gold coated crystal; elemental images of (b) Zn(II) and (c) Cd(II); (d) EDS spectra; (e) and (f) show the line mapping for Cd(II) (red color) and Zn(II) (cyan color) suggesting homogeneous distribution of the metal ions

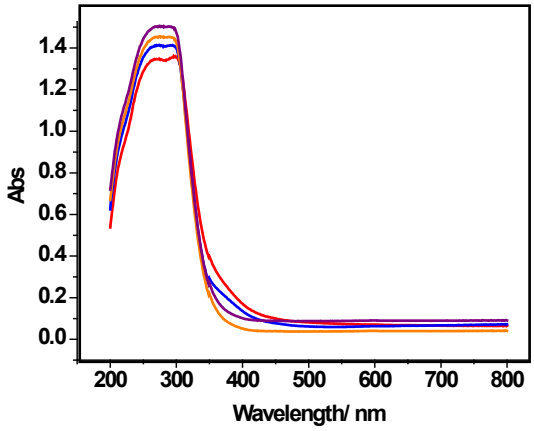

Figure S9. DRS spectra of **1** (blue), **3** (red), **5** (purple), **6** (orange). Spectra of the solid solutions **5** and **6** found to exhibit higher intensities than the single metal complexes **1** and **3**.

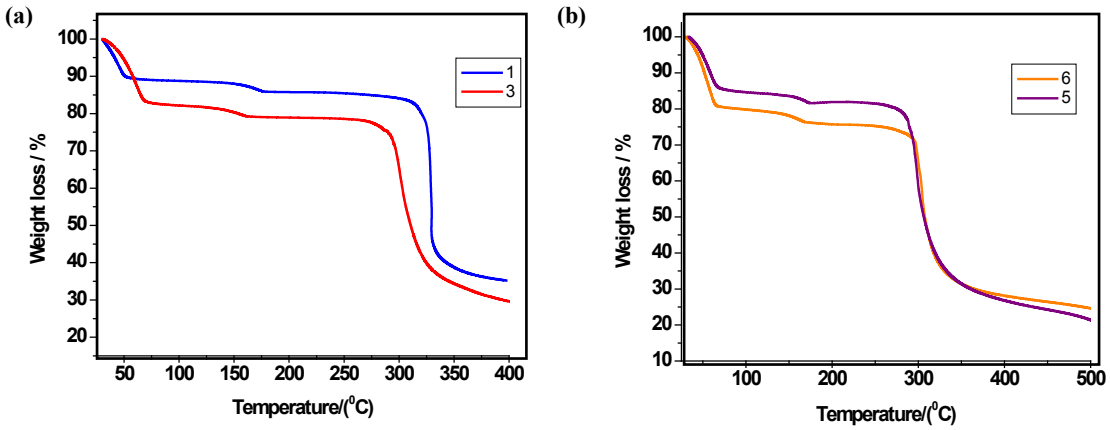

Figure S10. TGA profiles of (a) **1** and **3** (b) **5** and **6**.

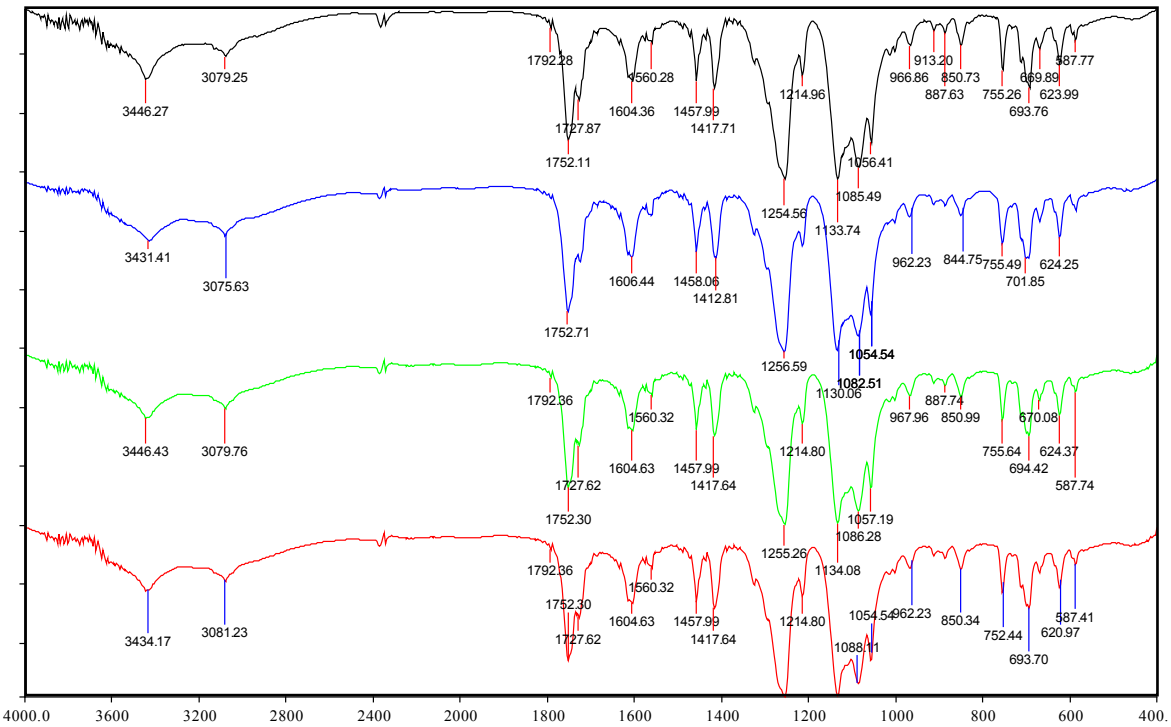

Figure S11. FT-IR spectra for as-synthesized **1** (black), **2** (blue), **3**(green), **4** (red).
3075 cm^{-1} (aromatic C-H str); 1752-1756 cm^{-1} (ester C=O); 1608- 1420 cm^{-1}(C=C, C=N pyridine ring str); 1110-1141 cm^{-1} (ClO_4).

References:

(1) Noh, T. H.; Kim, S. A.; Lee, S. Y; Jung, O. –S. *Eur. J. Inorg. Chem.* **2009**, 4518.

(2) G. M. Sheldrick, SHELX-97, *Program for the Solution and Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997.

(3) A. L. Spek, *PLATON-A Multi Purpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2002.