Electronic Supplementary Information for Dalton Transactions

Supplementary Information

Single-crystal to single-crystal transformations in discrete hydrated dimeric copper domplexes

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Experimental

Materials and Instrumentation. The commercially available starting materials, Cu(OC(=O) $CH_3)_2.2H_2O$, 2-(2-hydroxyethyl)pyridine (hep-H), n-propionic acid and reagent grade solvents: methanol, ethanol, isopropanol, acetonitrile, dichloromethane and N N$^/$-dimethylformamide were used as received. Elemental analyses were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra of complexes as KBr pellets and DTA/TGA experiments were done on a Nicolet spectrophotometer and Perkin Elmer Instrument, respectively. X-ray (powder) diffraction data were collected on a Philips X'Pert Pro X-ray diffraction system using monochromated CuKα1 radiation (λ = 1.5406 Å). The magnetic susceptibility measurements at 298 K were performed using a Faraday balance (Cahn Instruments Inc., serial no. 76240).

Synthesis of [(OAc)Cu(μ-hep)$_2$Cu(OAc)]·2H$_2$O (1.2H$_2$O). A solution of hep-H (0.123 g, 1 mmol) in methanol (25 cm^3) was added to a solution of $Cu(OC(=O)CH_3)_2 \bullet 2H_2O$ (0.199 g, 1 mmol) in methanol (25 cm^3) and the resultant solution in a 100 cm^3 beaker was stirred magnetically for 6 h at 298 K. The solution was then passed through the filter paper (Whatman filter paper, 70 mm) in order to remove any unreacted materials. The filtrate was then allowed to stand at 298 K for crystallization. On slow evapouration of the solvent the dark blue single crystals of **1**.2H$_2$O were obtained after a week. M.P.: 223-225°C. Yield: 0.165 g (80%). Elemental Analalysis (%) calculated for $C_9H_{15}N_1O_5Cu_1$, (Mr = 280.77): C, 43.42; H, 4.97; N, 4.61. Found: C, 43.57; H, 5.01; N, 4.66. IR (KBr, cm^{-1}): 3448(br), 3080(vw), 2951(vw), 2876(w), 2830(w), 2380(vw), 2681(vw), 1590(vs), 1484(s), 1394(s), 1335(s), 1160(w), 1380(vs), 1340(m), 1315(w), 1220(w), 1112(m), 1081(s), 1056(m), 1080(m), 880(w), 779(m), 680(m), 623(m), 579(w). TGA: Temperature range °C (% Weight loss): 50-130 (5.0); 130-270 (60.5).

SCSC-transformation of [(OAc)Cu(μ-hep)$_2$Cu(OAc)]·2H_2O (1.2H_2O**) to [(OAc)Cu(μ-hep)$_2$Cu(OAc)] (1)**. Blue coloured single crystal of **1**.2H_2O was exposed to heating at 110 °C for 3 h. Subsequently the crystal was subjected to X-ray analysis which confirmed the identity of the crystal as a dehydrated [(OAc)Cu(μ-hep)$_2$Cu(OAc)] (**1**). Similar thermal method was followed to prepare the bulk sample of **1**. M.P.: 217-219^{o}C. Elemental Analalysis (%) calculated for $C_{18}H_{22}N_2O_6Cu_2$, (Mr = 489.46): C, 44.26; H, 4.54; N, 5.74. Found: C, 44.37; H, 4.64; N, 5.67. IR (KBr, cm^{-1}): 3084(m), 2953(m), 2876(m), 2829(m), 2687(w), 1616(vs), 1584(vs), 1474(s), 1386(s), 1332(s), 1244(m), 1079(s), 1041(s), 876(s), 767(s), 690(s), 614(s). TGA: Temp. range ^{o}C (% Weight loss): 130-265 (64.7).

Backward SCSC-transformation of [(OAc)Cu(μ-hep)$_2$Cu(OAc)] (1) **to [(OAc)Cu(μ-hep)$_2$Cu(OAc)]·2H_2O (1.2H_2O)**. Single-crystal of (**1**) was taken in a small vial (3 inches length and 0.5 inch width) which was then placed inside one bigger vial (3.5 inches length and 1 inch width) containing 2 cm^3 water and the outer vial was closed. The crystal was allowed to stand in presence of water vapour at 298K for 24 h. The crystal was then subjected to X-ray diffraction data collection which confirmed the regeneration of the dihydrated **1.**2H_2O. The Bulk.sample was then prepared by following the same above method. M.P.: 223-225^{o}C. Yield: 165 mg (80%). Elemental Analalysis (%) calculated for $C_9H_{15}N_1O_5Cu_1$, (Mr = 280.77): C, 43.42; H, 4.97; N, 4.61. Found: C, 43.50; H, 5.04; N, 4.56. IR (KBr, cm^{-1}): 3448(br), 3082(vw), 2951(vw), 2876(w), 2830(m), 2360(vw), 1591(vs), 1484(s), 1396(vs), 1336(s), 1248(w), 1198(w), 1168(w), 1117(m), 1081(s), 925(vw), 882(vw), 780(m), 680(m), 623(s), 580(vw). TGA: Temperature range ^{o}C (% Weight loss): 50-130 (5.3); 130-250 (57).

Synthesis of [(OAc)Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H_2O (2.2H_2O). A solution of **1**.2H_2O (0.250 g, 0.5 mmol) in 25 cm^3 methanol was taken in a 100 cm^3 beaker. Propionic acid (CH_3CH_2COOH, 0.02 cm^3, 0.25 mmol) was added to the above solution of **1**.2H_2O and the resultant solution was stirred for 6 h at room temperature. The solution was allowed to stand at room temperature for crystallization. Dark blue single crystals of **2**.2H_2O were obtained within 10 days by slow evapouration of the solvent. M.P.: 228-230^{o}C. Yield: 0.175 g (70 %). Elemental Analalysis (%) calculated for $C_{19}H_{28}N_2O_8Cu_2$, (Mr = 539.51): C, 42.38; H, 5.24; N, 5.21. Found: C, 42.47; H, 5.21; N, 5.26. IR (KBr, cm^{-1}): 3448(br), 3081(vw), 2955(vw), 2879(w), 2821(w), 2361(vw), 1608(vs), 1591(vs), 1485(s), 1447(vw), 1394(s), 1360(vw), 1334(vw), 1314(vw), 1281(w), 1248(w), 1115(m), 1081(s), 1051(w), 1028(vw), 880(m), 776(m), 680(w), 625(m), 579(w). TGA: Temperature range ^{o}C (% Weight loss): 25-90 (7.0); 90-272 (62.4).

SCSC-transformation of [(OAc)Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H_2O (2.2H_2O) to [(OAc)Cu(μ-hep)$_2$Cu(O^{n}Pr)] (2). Blue coloured single crystal of **2**.2H_2O was exposed to heating at 110 °C for 3 h. The crystal was then subjected to X-ray analysis which confirmed the identity of the crystal as a dehydrated [(OAc)Cu(μ-hep)$_2$Cu(O^{n}Pr)] (**2**). Similarly the bulk sample of **2** was prepared. M.P: 219-221^{o}C. Elemental Analalysis (%) calculated for $C_{19}H_{24}N_2O_6Cu_2$ (Mr = 503.48): C, 45.42; H, 4.82; N, 5.58. Found: C, 45.37; H, 4.64; N, 5.67. IR (KBr, cm^{-1}): 3081(vw), 2924(vw), 2879(vw), 2854(vw), 2360(m), 2341(m), 1609(vs), 1592(vs), 1485(m), 1394(s), 1360(vw), 1282(w), 1249(w), 1116(w), 1082(m), 1051(vw), 1028(vw), 879(m), 776(m), 679(w), 621(s). TGA: Temp. range ^{o}C (% Weight loss): 200-265 (55.7).

Backward SCSC-transformation of [(OAc)Cu(μ-hep)$_2$Cu(O^{n}Pr)] (2) to [(OAc)Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H_2O (2.2H_2O). Single-crystal of (**2**) inside one small vial (3 inches length and 0.5 inch width) was placed inside another bigger vial (3.5 inches length and 1 inch width) containing 2 mL water and the outer vial was closed. The single crystal was allowed to stand in presence of water vapour at 298K for 24 h and subsequently the crystal was subjected to X-ray diffraction study which established the regeneration of the parent dihydrated **2**.2H_2O. The same method was also followed to regenerate the bulk sample of the dihydrated **2**.2H_2O from **2**. M.P.: 228-230°C Elemental Analalysis (%) calculated for $C_{19}H_{28}N_2O_8Cu_2$, (Mr = 539.51): C, 42.38; H, 5.24; N, 5.21. Found: C, 42.43; H, 5.22; N, 5.24. IR (KBr, cm^{-1}): 3447(br), 2953(vw), 2929(w), 2878(w), 2851(w), 2820(w), 2356(m), 2334(w), 1611(vs), 1588(vs), 1483(s), 1395(s), 1333(vw), 1280(w), 1247(w), 1114(m), 1079(s), 1052(w), 882(m), 791(w), 777(m), 679(w), 622(m), 577(vw). TGA: Temperature range °C (% Weight loss): 25-90 (7.0); 170-272 (62.4).

The transformations of 1.2H_2O $\rightarrow$ 1 and 2.2H_2O $\rightarrow$ 2 were taken place without any change in colour.

Synthesis of [(O^nPr)Cu(μ-hep)$_2$Cu(O^nPr)]·2H_2O (3.2H_2O). Propionic acid (0.04 cm^3, 0.5 mmol) was added to the preformed **1**.2H_2O in 25 cm^3 MeOH (0.250 g, 0.5 mmol) and the resultant solution was stirred magnetically for 6 h at 298 K. The subsequent slow evapouration of the solution yielded the dark blue single crystals of **3**.2H_2O within 10 days. M.P.: 229-231°C. Yield: 0.140 g (70 %). Elemental Analalysis (%) calculated for $C_{20}H_{30}N_2O_8Cu_2$, (Mr = 553.54): C, 43.47; H, 5.48; N, 5.07. Found: C, 43.50; H, 5.42; N, 5.00. IR (KBr, cm^{-1}): 3404(br), 3082(w), 3036(vw), 2971(m), 2892(vw), 2837(m), 2687(vw), 1616(vs), 1586(s), 1474(m), 1414(s), 1392(s), 1271(s), 1123(m), 1068(s), 977(w), 880(s), 776(s), 626(s), 579(w). TGA: Temperature range °C (% Weight loss): 25-97 (7.0); 100-246 (60).

Irreversible SCSC-transformation of [(O^nPr)Cu(μ-hep)$_2$Cu(O^nPr)]·2H_2O (3.2H_2O) to [Cu_4($μ_3$-hep)$_2$(μ-hep)$_2$(μ-O^nPr)$_2$(O^nPr)$_2$] (4). *Blue* coloured single crystal of **3** was exposed to heating at 110 °C for 3 h which led to the distinct change in colour of the crystal from *blue* to *green* without the loss in crystallinity. X-ray analysis of the *green* crystal confirmed its identity as a *double open cubane* tetrameric structure of [Cu_4($μ_3$-hep)$_2$(μ-hep)$_2$(μ-O^nPr)$_2$(O^nPr)$_2$] (**4**).

Similar thermal method was subsequently followed to prepare the bulk sample of **4**. M.P: 237-238^{o}C. Elemental Analalysis (%) calculated for $C_{40}H_{52}N_4O_{12}Cu_4$, (Mr = 1035.02): C, 46.51; H, 5.08; N, 5.43. Found: C, 46.57; H, 5.04; N, 5.48. IR (KBr, cm^{-1}): 3129(vw), 3072(vw), 3037(vw), 2964(w), 2937(w), 2842(w), 1611(vs), 14856(m), 1445(m), 1370(vs), 1266(s), 1118(m), 1069(m), 871(m), 762(m). TGA: Temp. range ^{o}C (% Weight loss): 150-280 (68).

Alternative vapour diffusion method for the SCSC-transformation of [(O^{n}Pr)Cu(μ-hep)$_2$Cu(O^{n}Pr)]·2H$_2$O (3.2H$_2$O**) to [Cu$_4$(μ$_3$-hep)$_2$(μ-hep)$_2$(μ-O^{n}Pr)$_2$(O^{n}Pr)$_2$] (4).** Blue coloured single crystal of **3**.2H$_2$O was taken in a small sample glass vial (3 inches length and 0.5 inch width) which was placed inside a bigger bottle (3.5 inches length and 1 inch width) containing 2 mL methanol. The outer bottle was closed and the set up was left at room temperature over a period of 5 m which led to the distinct change in colour of the crystal from *blue* to *green* with retaining the crystallinity. The *green* crystal was then subjected to X-ray analysis which confirmed the identity of the crystal as a *double open cubane* tetrameric structure of [Cu$_4$(μ$_3$-hep)$_2$(μ-hep)$_2$(μ-O^{n}Pr)$_2$(O^{n}Pr)$_2$] (**4**). The SCSC transformation of **3**.2H$_2$O to **4** was also checked in presence vapour of different solvents (**Figure A**).

Similar vapour diffusion method was also followed to prepare the bulk sample of **4**. M.P: 237-238^{o}C. Elemental Analalysis (%) calculated for $C_{40}H_{52}N_4O_{12}Cu_4$, (Mr = 1035.02): C, 46.51; H, 5.08; N, 5.43. Found: C, 46.54; H, 5.03; N, 5.40. IR (KBr, cm^{-1}): 3129(vw), 3072(vw), 3037(vw), 2964(w), 2937(w), 2904(w), 2844(w), 1616(vs), 14896(m), 1441(m), 1392(vs), 1266(s), 1114(m), 1063(m), 1036(m), 877(m), 762(m), 603(m). TGA: Temp. range ^{o}C (% Weight loss): 150-280 (68).

Blue crystals of **3**.$2H_2O$

Vapour difussion technique

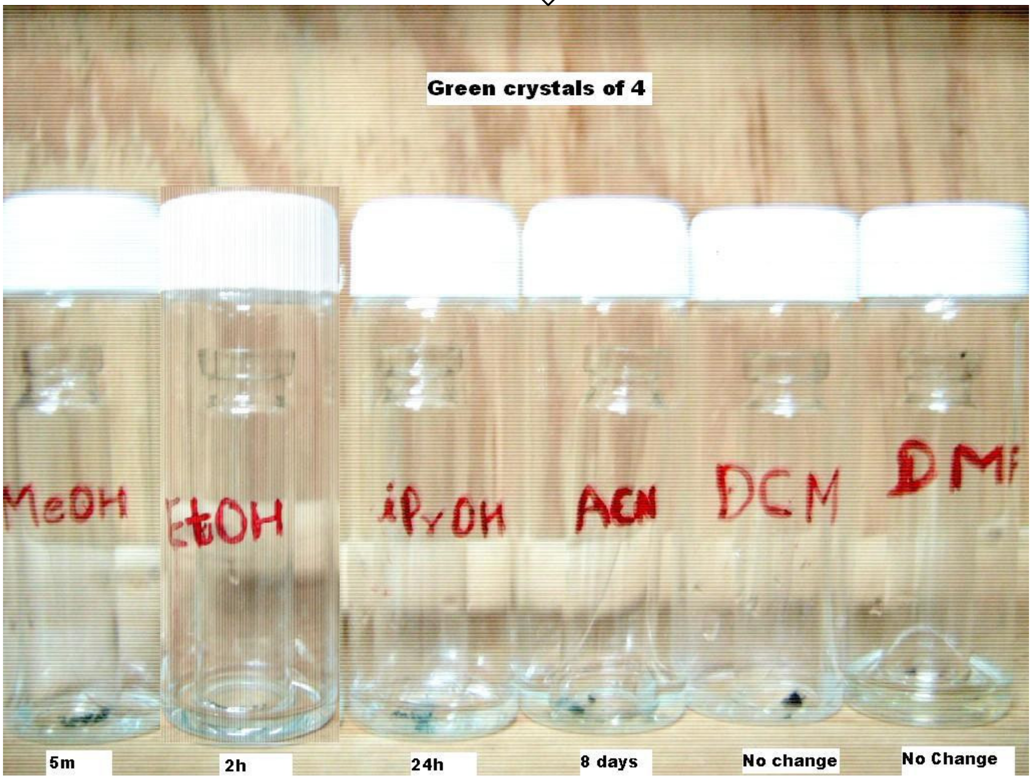


***Fig.* A** Photographs of the transformation of **3**.$2H_2O$ to **4** using vapour diffusion technique in different solvents

X-ray crystallography

Single crystal X-ray structural studies of all the crystals were performed on a CCD Oxford Diffraction XCALIBUR-S diffractometer equipped with an Oxford Instruments low-temprature attachment. Data were collected at 150(2) K using graphite-monochromoated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct method using SHELXS-97 and refined by full matrix least squares with SHELXL-97, refining on F^2.[1]

The positions of all the atoms were obtained by direct method. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of water molecules were generated through Fourier peaks for **1**.2H_2O, **1**.2H_2O(Regenerated). The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factor, generally 1.2 x U_{eq} of their parent atoms. All the H-bonding interactions, mean plane analyses, and molecular drawings were obtained using the ORTEP program. The selective crystal and refinement data, bond distances and bond angles and hydrogen bond parameter are summarized in **Tables S1-S3**, **Table S4** and **Table S5**, respectively. In **1**.2H_2O (initial as well as regenerated) the asymmetric unit contains half of the complex molecule and two lattice water molecules thus the overall molecular formula is taken by considering z = 2 with centrosymmetric $P\bar{1}$ space group. The disordered methyl groups, C20/C20$^{/}$ in **4**, obtained either by heating or by vapour diffusion are having double occupancy ratios of 55:45% or 53:47%, respectively.

1 G. M. Sheldrick, *Acta Cryst.*, 2008, ***A64***, 112-122, *Program for Crystal Structure Solution and Refinement*, University of Goettingen, Germany, 1997.

Table S1 Selected crystallographic parameters for **1**.2H_2O, **1** and regenerated **1**.2H_2O.

	1.2H_2O **(150K)**	**1 (150K)**	**1**.2H_2O **Regenerated(150K)**
Empirical formula	$C_9 H_{15} N_1 O_5 Cu_1$	$C_{18} H_{22} N_2 O_6 Cu_2$	$C_9 H_{15} N_1 O_5 Cu_1$
Formula weight	280.77	489.46	280.77
Crystal symmetry	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	7.842(2)	7.702(3)	7.900(3)
b /Å	8.568(2)	7.894(3)	8.684(3)
c /Å	9.994(3)	8.698(4)	10.058(4)
$\alpha/^\circ$	71.58(2)	100.46(4)	71.77(3)
$\beta/^\circ$	78.30(3)	106.16(4)	78.27(3)
$\gamma/^\circ$	69.45(3)	93.14(4)	69.51(3)
Volume/$Å^3$	593.4(3)	496.3(4)	610.5(4)
Z	2	1	2
μ/mm^{-1}	1.845	2.179	1.794
$D_{calcd.}$/ mg m^{-3}	1.571	1.638	1.527
F (000)	290	250	290
Crystal size mm^3	0.38 x 0.34 x 0.32	0.38 x 0.34 x 0.32	0.33 x 0.26 x 0.21
θ range(deg)	3.19 to 25.00	3.14 to 25.00	3.16 to 25.00
Reflections collected / unique	6111 / 2079 [R(int) = 0.0180]	4327 / 1748 [R(int) = 0.0291]	5298 / 2145 [R(int) = 0.1173]
Data / restraints / parameters	2079 / 0/ 162	1748 / 0 / 128	2145 / 24 / 162
R1, wR2 [$I > 2\sigma(I)$]	0.0242, 0.0681	0.0308, 0.0724	0.0715, 0.1986
R1, wR2(all data)	0.0271, 0.0692	0.0389, 0.0749	0.1070, 0.2349
GOF	1.090	1.001	1.008
Largest diff. peak/hole, (e $Å^{-3}$)	0.712 and -0.253	0.348 and -0.237	0.897 and -0.987
CCDC No.	**652141**	**737391**	

Table S2 Selected crystallographic parameters for **2**.2H_2O, **2** and regenerated **2**.2H_2O.

	2.2H_2O **(150K)**	**2 (150K)**	**2**.2H_2O **Regenerated(150K)**
Empirical formula	$C_{19} H_{28} N_2 O_8 Cu_2$	$C_{19} H_{24} N_2 O_6 Cu_2$	$C_{19} H_{28} N_2 O_8 Cu_2$
Formula weight	539.51	503.48	539.51
Crystal symmetry	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a /Å	7.8669(2)	7.855(2)	7.8434(14)
b /Å	10.2403(5)	10.137(3)	10.2268(16)
c /Å	15.6326(8)	13.539(4)	15.6268(12)
$\alpha/^{\circ}$	70.964(5)	75.74(3)	70.921(10)
$\beta/^{\circ}$	76.802(3)	85.36(3)	76.83(3)
$\gamma/^{\circ}$	76.981(4)	77.02(3)	77.201(14)
Volume/Å^3	1143.37(9)	1017.8(5)	1138.6(3)
Z	2	2	2
μ/mm^{-1}	1.906	2.128	1.914
$D_{calcd.}$/ mg m^{-3}	1.567	1.643	1.574
F (000)	556	516	556
Crystal size mm^3	0.23 x 0.19 x 0.17	0.23 x 0.18 x 0.15	0.23 x 0.18 x 0.15
θ range(deg)	2.98 to 25.00	3.03 to 25.00	2.99 to 25.00
Reflections collected / unique	9588 / 3969 [R(int) = 0.0309]	6443 / 3366 [R(int) = 0.0565]	9885 / 3989 [R(int) = 0.0726]
Data / restraints / parameters	3969 / 0 / 298	3366 / 0 / 264	3989 / 0 / 282
R1, wR2 [$I > 2\sigma(I)$]	0.0429, 0.1126	0.0566, 0.1111	0.0674, 0.1613
R1, wR2(all data)	0.0648, 0.1183	0.1126, 0.1204	0.1028, 0.1773
GOF	1.119	0.894	1.072
Largest diff. peak/hole, (e Å^{-3})	1.168 and -0.343	0.853 and -0.451	1.212 and -0.866
CCDC No.	**737392**	**737393**	

Table S3 Selected crystallographic parameters for **3**.2H$_2$O and **4**.

	3.2H$_2$O **(150K)**	**4 by Heating(150K)**	**4 by Vapour diffusion (150K)**
Empirical formula	$C_{20} H_{30} N_2 O_8 Cu_2$	$C_{40} H_{52} N_4 O_{12} Cu_4$	$C_{40} H_{52} N_4 O_{12} Cu_4$
Formula weight	553.54	1035.02	1035.02
crystal symmetry	Triclinic	Monoclinic	Monoclinic
space group	P $\bar{1}$	P 2_1/c	P 2_1/c
a /Å	7.8291(10)	11.699(2)	11.698(3)
b /Å	10.3446(10)	9.5859(12)	9.561(2)
c /Å	15.5698(15)	18.9713(11)	18.893(5)
α/ °	72.822(9)	90	90
β/ °	77.479(10)	96.559(10)	96.56(2)
γ/ °	78.022(10)	90	90
Volume/Å^3	1162.1(3)	2113.6(5)	2099.2(9)
Z	2	2	2
μ/mm^{-1}	1.877	2.052	2.066
$D_{calcd.}$/ mg m^{-3}	1.582	1.626	1.637
F (000)	572	1064	1064
Crystal size mm^3	0.28 x 0.26 x 0.22	0.28 x 0.26 x 0.22	0.28 x 0.24 x 0.22
θ range(deg)	3.00 to 25.00	2.93 to 25.00	2.89 to 27.50
Reflections collected / unique	9216 / 4079 [R(int) = 0.0473]	14593 / 3701 [R(int) = 0.0563]	19269 / 4822 [R(int) = 0.1298]
Data / restraints / parameters	4079 / 0 / 291	3701 / 39 / 293	4822 / 28 / 293
R1, wR2 [$I > 2\sigma(I)$]	0.0516, 0.1572	0.0383, 0.0784	0.0420, 0.0552
R1, wR2(all data)	0.0626, 0.1741	0.0583, 0.0836	0.1069, 0.0622
GOF	1.192	1.015	0.712
Largest diff. peak/hole, (e Å^{-3})	1.235 and -1.445	0.655 and -0.369	0.466 and -0.484
CCDC No.	**737394**	**737395**	**737396**

Table S4 Selected bond distances (Å) and bond angles (^{o}).

Bond length (Å)/ Bond angle (^{o})	**1**.$2H_2O$	**1**	**1**.$2H_2O$ **(Regenerated)**	**2**.$2H_2O$	**2**	**2**.$2H_2O$ **(Regenerated)**	**3**.$2H_2O$	**4-Heating**	**4-Vapour diffusion**
Cu1-Cu1#1	3.0178(12)	3.0165(18)	2.998(2)	3.0292(7)	3.0325(15)	3.0226(12)	3.0245(9)	3.0428(7)	3.0342(10)
Cu1-O1	1.9045(16)	1.899(2)	1.899(6)	1.928(3)	1.917(5)	1.913(4)	1.917(3)	1.984(2)	1.976(3)
Cu1-O1#	1.9245(18)	1.927(2)	1.910(6)	--	--	--	--	--	--
Cu1-O2	1.9557(16)	1.953(2)	1.943(6)	1.947(3)	1.929(5)	1.955(5)	1.941(3)	1.967(2)	1.964(3)
Cu1-O3	2.570(19)	2.494(1)	2.557(2)	2.654(2)	2.663(4)	2.641(3)	2.627(4)	2.675(2)	2.665(3)
Cu1-O4				1.937(3)	1.931(4)	1.924(4)	1.919(3)	1.917(2)	1.910(2)
Cu1-O5								2.394(2)	2.391(2)
Cu1-N1	1.990(2)	2.001(2)	1.982(6)	1.984(4)	2.002(5)	1.977(5)	1.969(5)	1.979(3)	1.968(3)
Cu2-O1				1.928(3)	1.932(4)	1.921(4)	1.917(3)	2.017(2)	2.010(2)
Cu2-O1 #								2.427(2)	2.417(2)
Cu2-O4				1.907(3)	1.894(5)	1.902(5)	1.904(3)	1.902(2)	1.904(3)
Cu2-O5				1.951(3)	1.958(5)	1.957(5)	1.948(3)	1.951(2)	1.947(3)
Cu2-O6				2.574(3)	2.519(5)	2.576(3)	2.573(5)	--	--
Cu2-N2				1.994(4)	2.000(5)	1.991(6)	1.980(5)	2.062(3)	2.052(3)
Cu(1)-O(1)-Cu(1)#1	104.02(8)	104.07(10)	103.8(3)	103.54(14)	103.9(2)	104.1(2)	104.18(16)	--	--
Cu(1)-O(1)-Cu(2)								99.02(9)	99.15(10)
O(1)-Cu(1)-O(1)#1	75.98 (8)	75.93(10)	76.2(3)	75.83(12)	75.31(19)	75.94(18)	75.42(14)	--	--
O(1)-Cu(1)- N(1)	94.56(8)	94.28(10)	94.3(3)	94.20(14)	94.1(2)	93.9(2)	94.84(16)	92.66(10)	92.93(12)
O(1)#1-Cu(1)-N(1)	163.30(7)	162.13(9)	163.3(3)						
O(4)-Cu(1)-N(1)				164.01(14)	162.4(2)	164.0(2)	164.49(16)	169.91(11)	170.34(13)
O(1)-Cu(1)-O(2)	170.87(6)	170.72(8)	170.7(2)	170.58(13)	170.71(18)	170.44(18)	170.25(15)	172.62(10)	173.10(10)
O(4)-Cu(1)-O(2)								96.71(9)	96.62(11)
O(4)-Cu(1)-O(5)#1								92.39(9)	92.50(9)
O(2)-Cu(1)-O(5)#1								105.83(9)	105.21(10)
N(1)-Cu(1)-O(5)#1								89.33(10)	89.22(10)
O(1)-Cu(1)-O(5)#1								79.61(9)	79.60(9)
Cu(1)-O(4)-Cu(2)								105.65(10)	105.41(11)
O(4)-Cu(2)-O(5)								170.99(10)	171.14(10)
O(4)-Cu(2)-O(1)#1								99.16(9)	99.15(10)
O(4)-Cu(2)-O(1)								77.44(9)	77.39(10)
O(1)-Cu(2)-O(5)								93.55(9)	93.81(11)
O(4)-Cu(2)-N(2)								91.88(10)	91.89(13)

O(5)-Cu(2)-N(2)								97.05(10)	96.91(13)

Table S5 Hydrogen bonding parameters (Å, °).

D-H...A	*d*(D...H)	*d*(H...A)	*d*(D...A)	∠D-H...A
		1.2H_2O		
O(222)-H(444)...O(2)#2	0.86(4)	2.00(4)	2.857(3)	171(3)
C(4)-H(4)...O(3)#3	0.95	2.68	3.377(3)	131.1
O(111)-H(111)...O(3)#4	0.80(4)	2.00(4)	2.764(3)	160(4)
C(6)-H(6A)...O(222)#1	0.99	2.65	3.539(4)	149.3
O(111)-H(222)...O(222)#2	0.57(4)	2.26(4)	2.812(4)	163(5)
		1		
C(2)-H(2)...O(3)#2	0.95	2.51	3.400(4)	155.2
C(6)-H(6A)...O(3)#3	0.99	2.55	3.430(4)	147.5
C(3)-H(3)...O(3)#4	0.95	2.60	3.381(5)	140.3
		1.2H_2O **(Regenerated)**		
C(2)-H(2)...O(3)#2	0.95	2.48	3.388(12)	159.5
O(111)-H(111)...O(3)#1	0.59	2.31	2.804(2)	141.9
C(4)-H(4)...O(3)#3	0.95	2.68	3.663(1)	125.53
O(111)-H(222)...O(111)#1	0.94	1.80	2.721(2)	168.8
O(222)-H(333)...O(2)#4	0.94	1.98	2.893(3)	164.6
		2.2H_2O		
C(2)-H(2)...O(3)#2	0.95	2.41	3.328(6)	163.1
C(4)-H(4)...O(3)#3	0.95	2.66	3.341(6)	129.0
C(11)-H(11)...O(1)#1	0.95	2.68	3.318(5)	125.4
C(12)-H(12)...O(6)#4	0.95	2.60	3.398(6)	141.2
		2		
C(2)-H(2)...O(4)#1	0.95	2.90	3.485(9)	120.6
		2.2H_2O **(Regenerated)**		
C(2)-H(2)...O(3)#1	0.95	2.42	3.337(9)	162.3
C(4)-H(4)...O(3)#2	0.95	2.67	3.346(9)	128.1
		3.2H_2O		
C(2)-H(2)...O(3)#1	0.95	2.40	3.323(6)	163.1
C(4)-H(4)...O(3)#2	0.95	2.60	3.238(7)	124.9
		4-Heating		
C(13)-H(13)...O(3)#2	0.95	2.36	3.121(5)	137.3
C(14)-H(14)...O(6)#2	0.95	2.43	3.316(4)	154.4
C(4)-H(4)...O(6)#3	0.95	2.68	3.357(5)	129.0
		4-Vapour diffusion		
C(13)-H(13)...O(3)#2	0.95	2.36	3.122(5)	137.1
C(14)-H(14)...O(6)#2	0.95	2.42	3.308(6)	155.0
C(4)-H(4)...O(6)#3	0.95	2.66	3.345(5)	129.3
C(6)-H(6A)...O(6)#3	0.99	2.54	3.366(5)	140.4

Symmetry transformations used to generate equivalent atoms:
For **1:** #1 -x+1,-y+1,-z #2 -x+1,-y,-z+1 #3 -x,-y+2,-z #4 -x+1,-y+1,-z+1
For **1-2H_2O:** #2 -x+1,-y+1,-z #3 x,+y+1,+z #4 -x+1,-y+1,-z+1
For **1 (Regenerated):** #1 x,y,z, #2 x-1,y,z, #3 –x, -y+1, -z, #4 x,y+1,z,
For **2:** #1 x-1,y,z #2 x+1,y,z #3 -x+2,-y+2,-z+1 #4 -x,-y+2,-z+2 #5 -x+1,-y+1,-z+1
For **2-2H_2O:** #1 x-1,y,z
For **2 (Regenerated):** #1 x-1,y,z #2 -x,-y+1,-z+1 #3 -x+1,-y+1,-z+1
For **3:** #1 x-1,y,z #2 -x,-y+1,-z+1 #3 x,y-1,z #4 -x+1,-y,-z+1
For **4-Heating:** #1 -x+2,-y,-z #2 -x+2,y-1/2,-z+1/2 #3 -x+2,-y+1,-z
For **4-Vapour diffusion:** #1 -x+1,-y,-z+1 #2 -x+1,y-1/2,-z+1/2 #3 -x+1,-y+1,-z+1

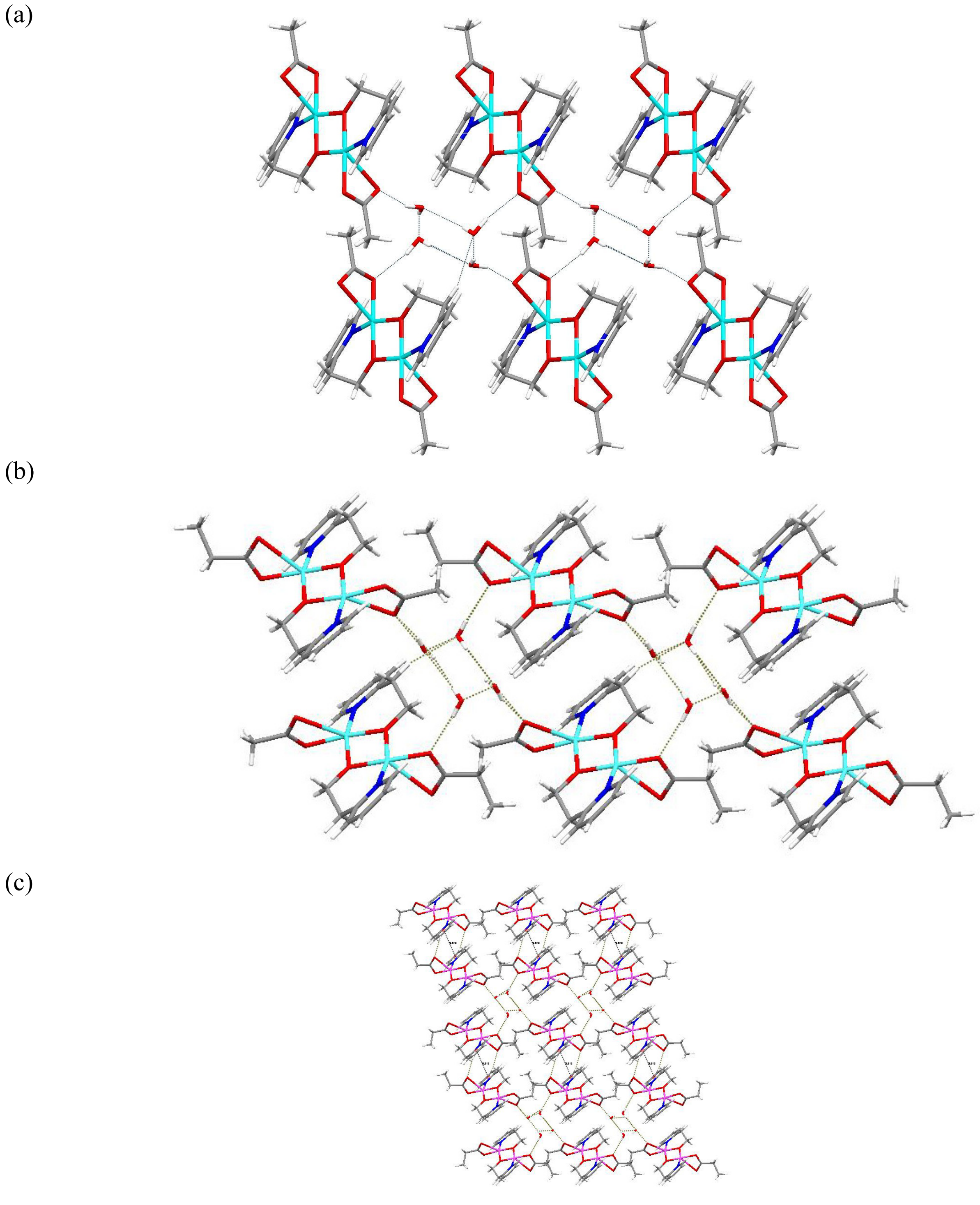


Fig. S1 Showing water tetramers along the *a*-axis: (a) for **1**.2H_2O (b) for **2**.2H_2O and (c) for **3**.2H_2O.

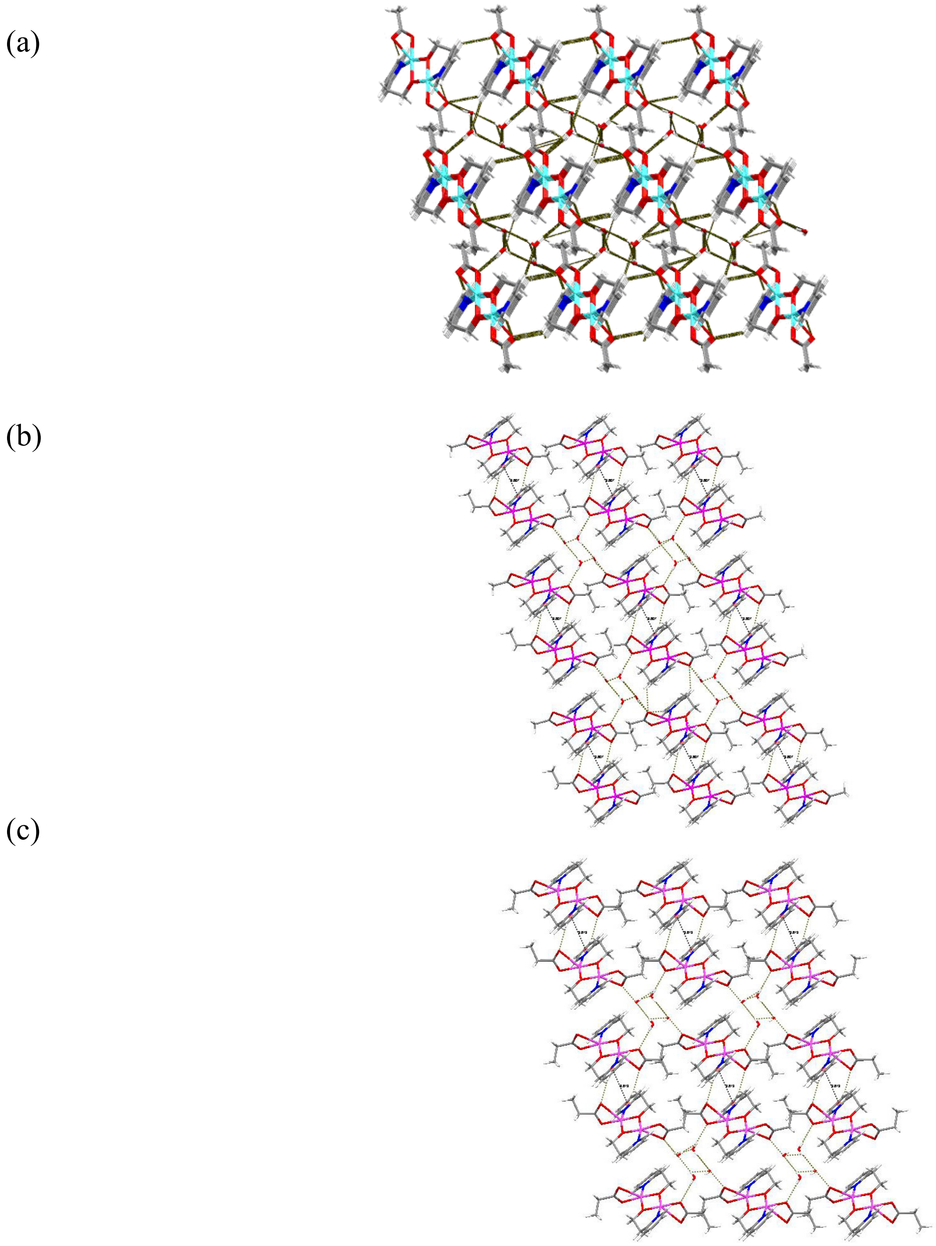


Fig. S2 Hydrogen bonded 2D polymeric chain along the *a*-axis: (a) for **1**.$2H_2O$ (b) for **2**.$2H_2O$ and (c) for **3**.$2H_2O$.

Packing diagrams of **1**.$2H_2O$-**3**.$2H_2O$ also reveal the presence of two types of hydrogen bonding: (i) one of the hydrogen atoms of each water molecule in the water tetramer is linked with one of the oxygen atoms of the bidentate OR or OR$^{/}$ group through O-H· · ·O hydrogen bonding and (ii) C-H· · ·O interaction between the pyridine C-H of hep^{-} and the oxygen atom of the bidentate OR or OR$^{/}$ group leading to the formation of a hydrogen bonded 2D polymeric chain. Moreover, **2**.$2H_2O$ and **3**.$2H_2O$ also exhibit strong π· · ·π stacking interactions between the two pyridine rings of two bridging hep^{-} ligands associated with the two adjacent dimeric units, with centroid to centroid distances of 3.377 and 3.358 Å, respectively, thus, further stabilizing the 2D polymeric chains

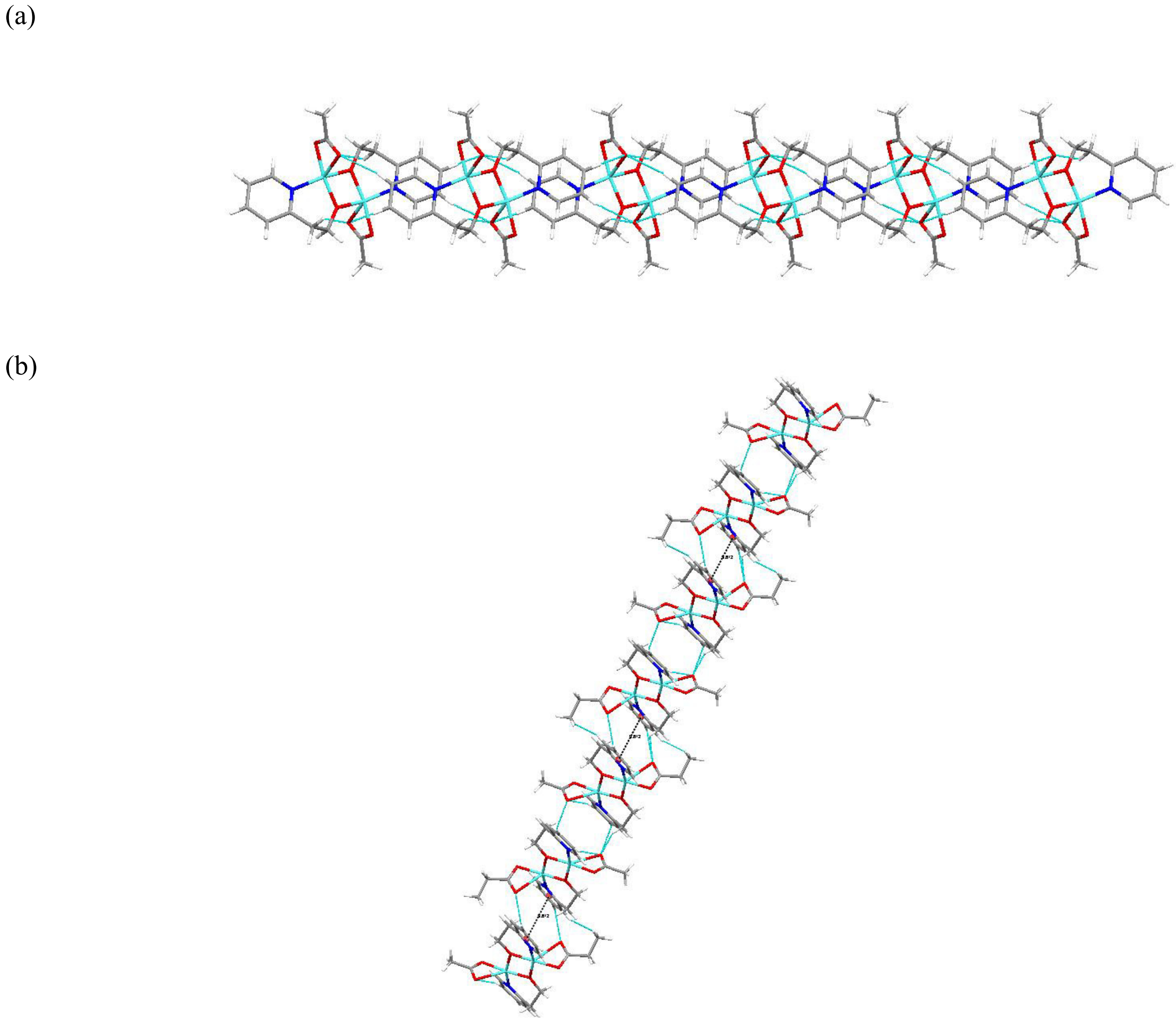


Fig. S3 Hydrogen bonded 1D polymeric chain along the *a*-axis: (a) **1** and (b) **2**.

The packing diagrams of **1** and **2** establish the presence of C-H· · ·O hydrogen bonding between the pyridine C-H of hep$^-$ and the axial oxygen atoms O3 from two different dimeric molecules. Moreover, in **2** the π· · ·π stacking inteactions between the pyridine rings of hep$^-$ of two neigboring dimeric units, with centroid to centroid distance of 3.612 Å, yields a 1D polymeric chain. If the weak interactions are ignored then **1**.2H_2O →**1** and **2**.2H_2O →**2** can be considered as 1D to 0D transformations.

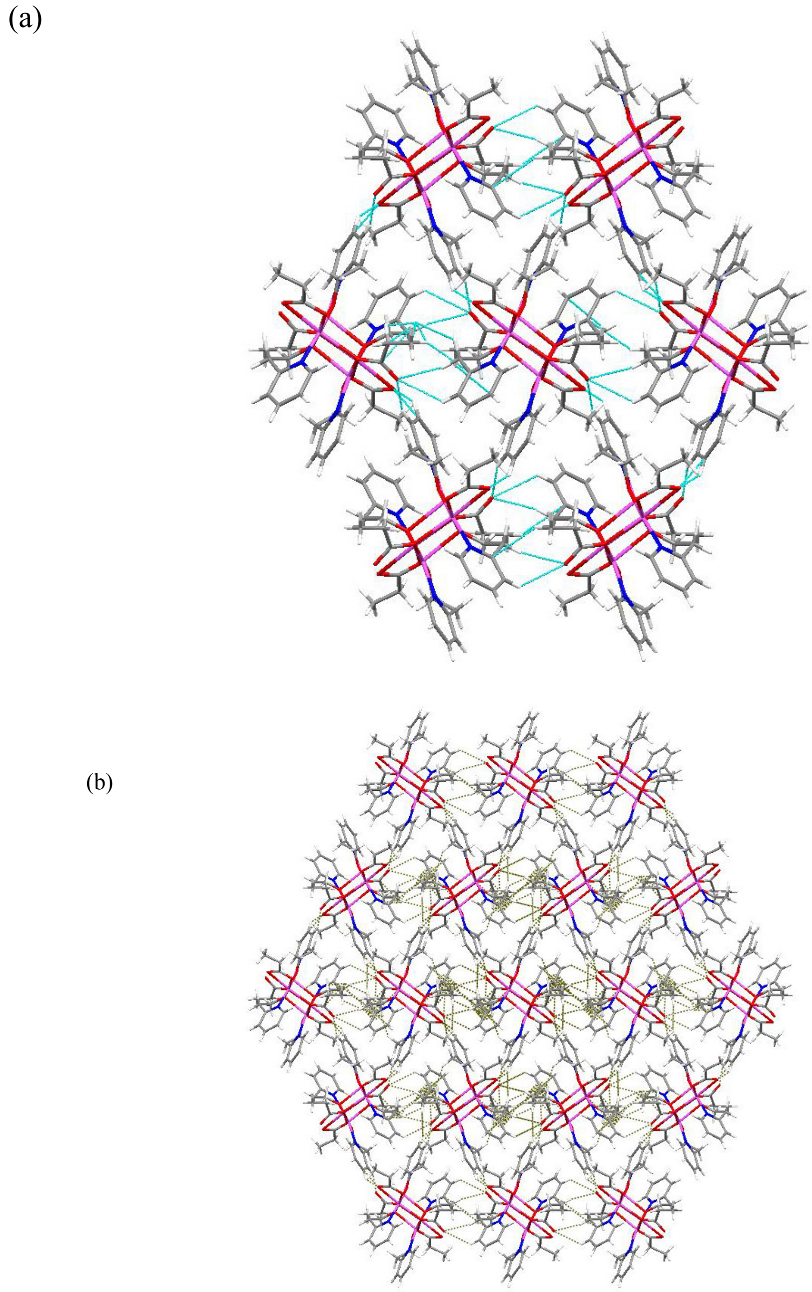


Fig. S4 (a) In **4** each tetramer is hydrogen bonded with six surrounding tetramers and **(**b) Hydrogen bonded 3D polymeric chain of **4** along the *a*-axis.

The packing diagram of **4** reveals the presence of intermolecular C-H· · ·O hydrogen bonding between the hydrogen atoms H(4), H(13), H(14) of the pyridine ring of hep^{-} ligand and the apical oxygen atom O(3) of the chelated O^{n}Pr^{-} ligand/pendant oxygen atom O(6) of μ-O^{n}Pr^{-}. Thus, each tetramer is surrounded by six neigboring tetramers yielding a 3D polymeric chain.

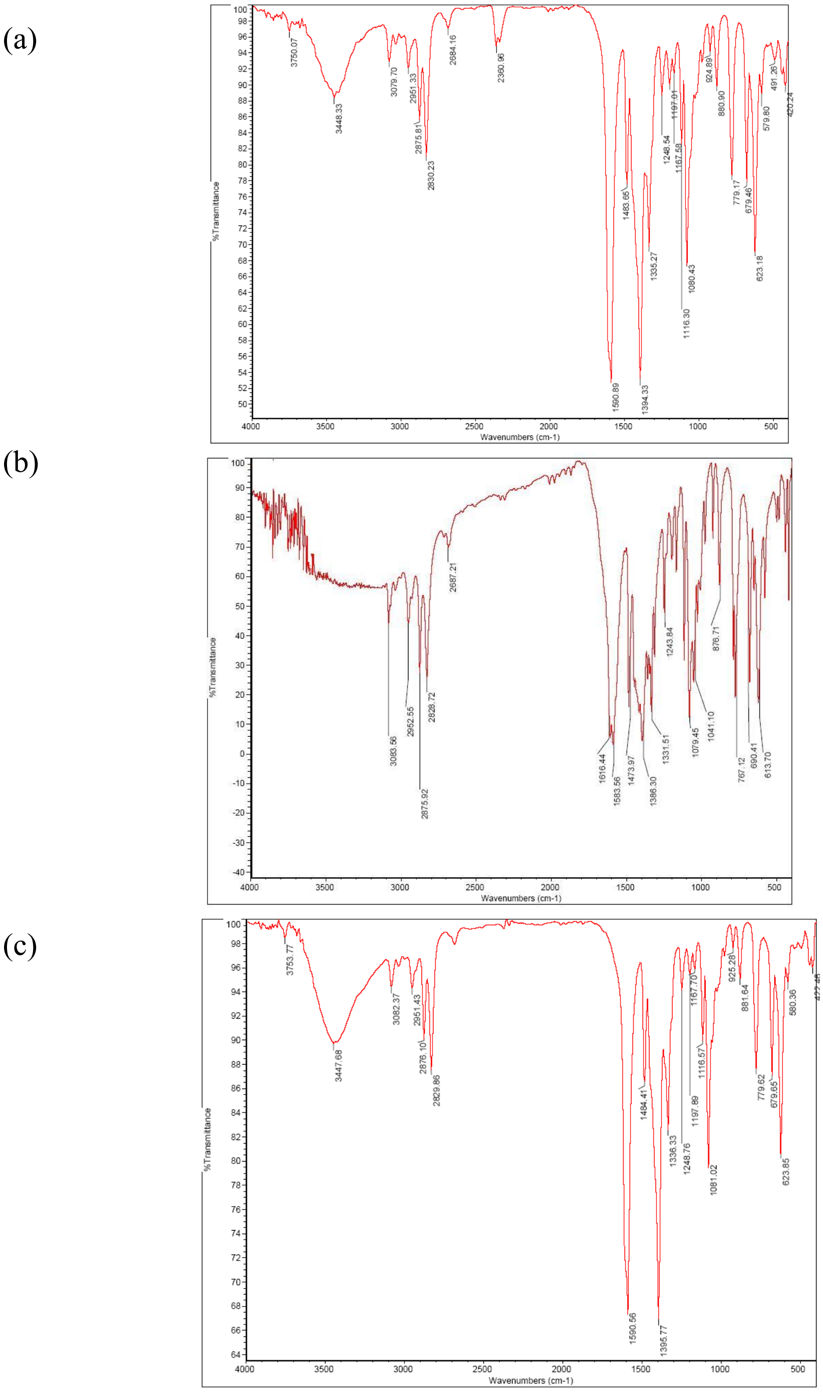


Fig. S5 IR spectra of (a) **1**.2H_2O (Blue crystal), (b) **1** (Blue crystal) and (c) **1**.2H_2O - Regenerated (Blue crystal) in KBr disk.

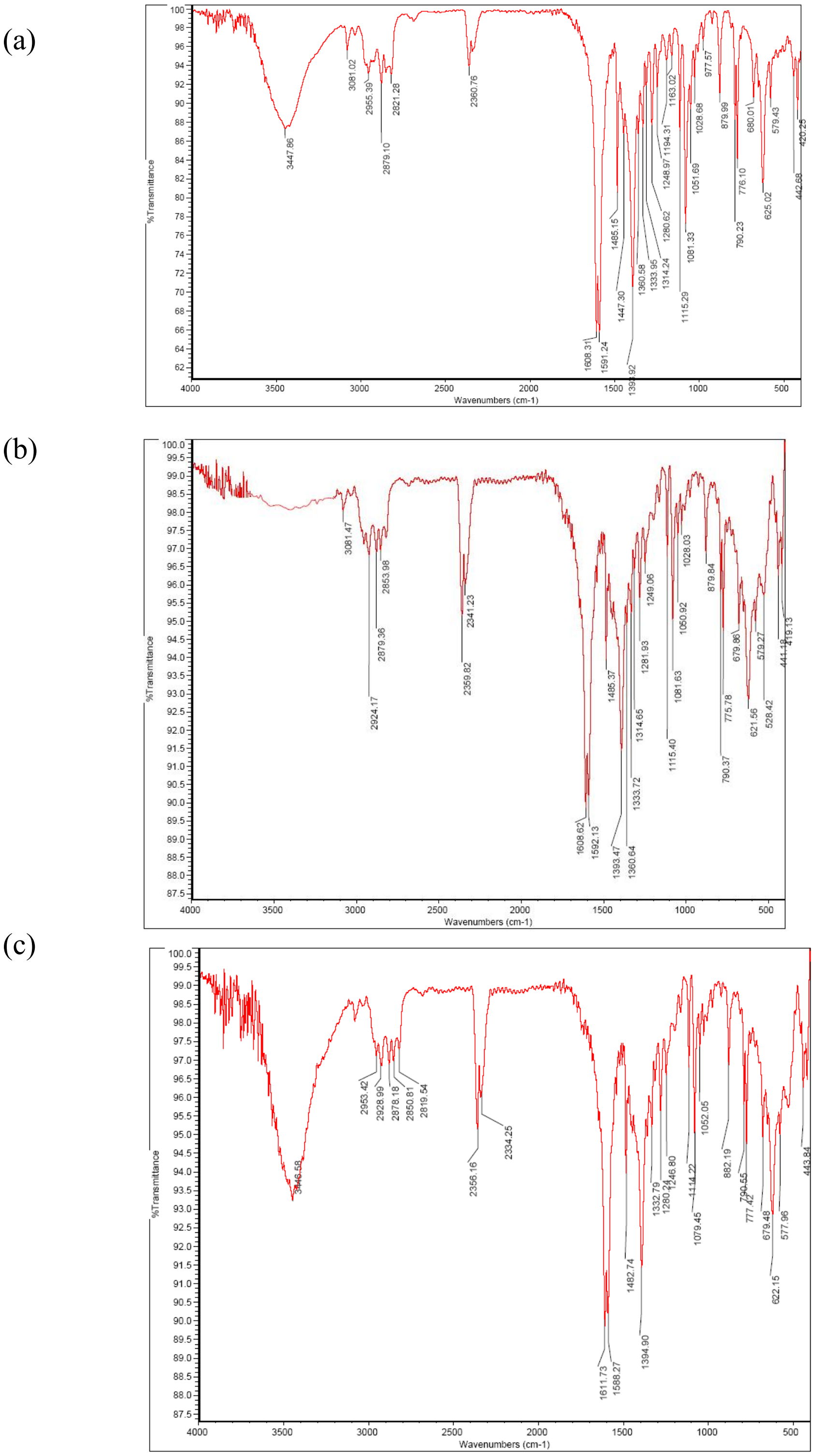


Fig. S6 IR spectra of (a) **2**.2H_2O (Blue crystal), (b) **2** (Blue crystal) and (c) **2**.2H_2O - Regenerated (Blue crystal) in KBr disk.

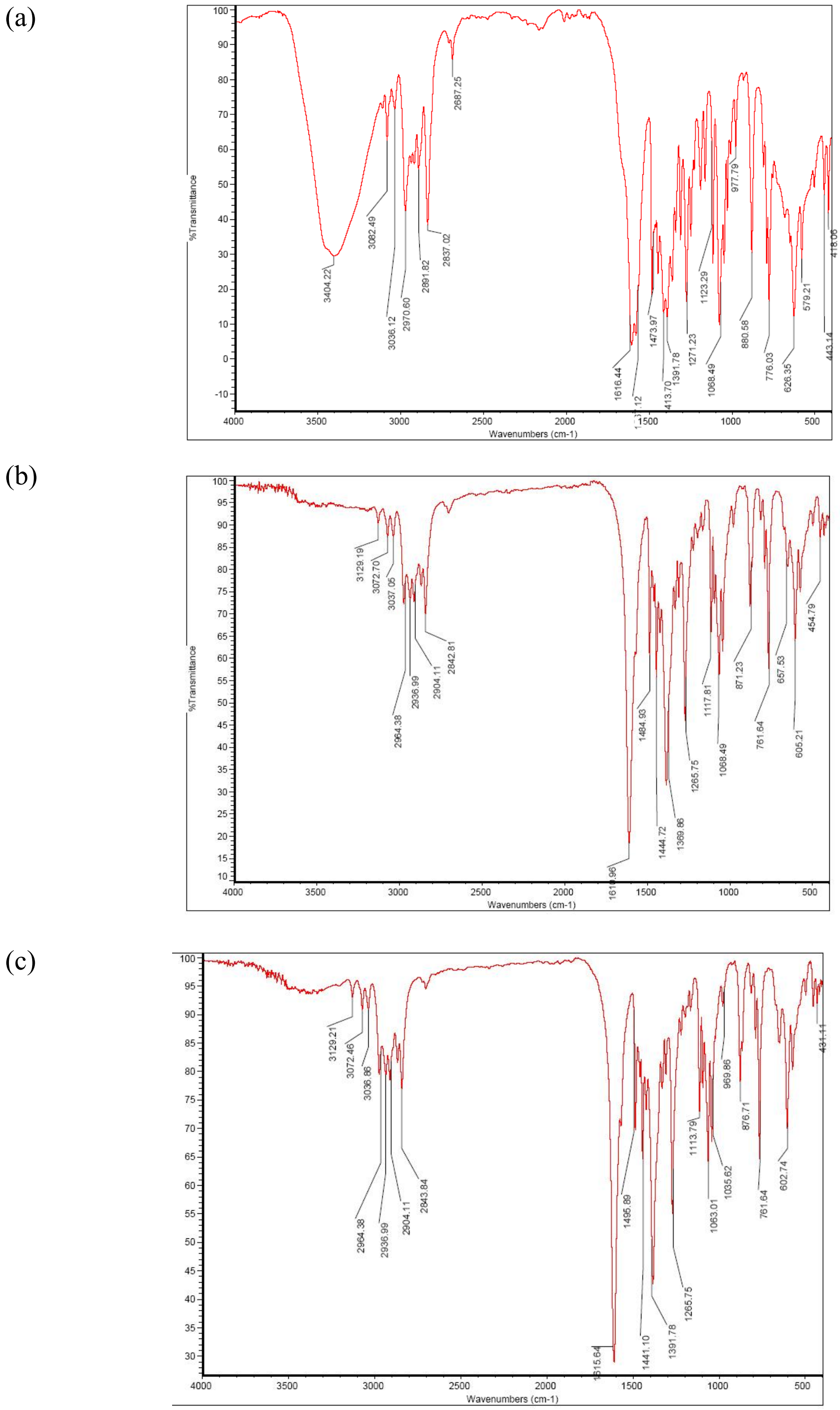
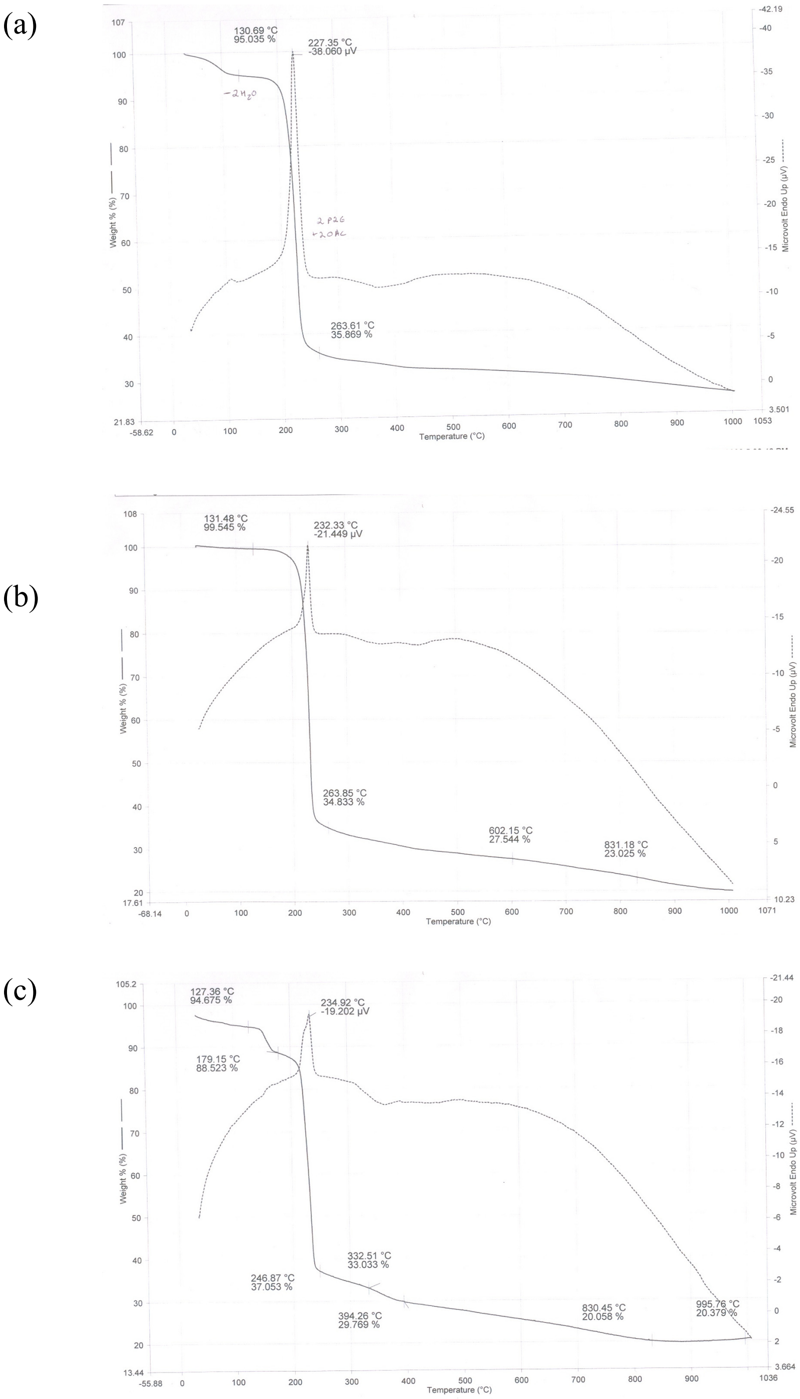
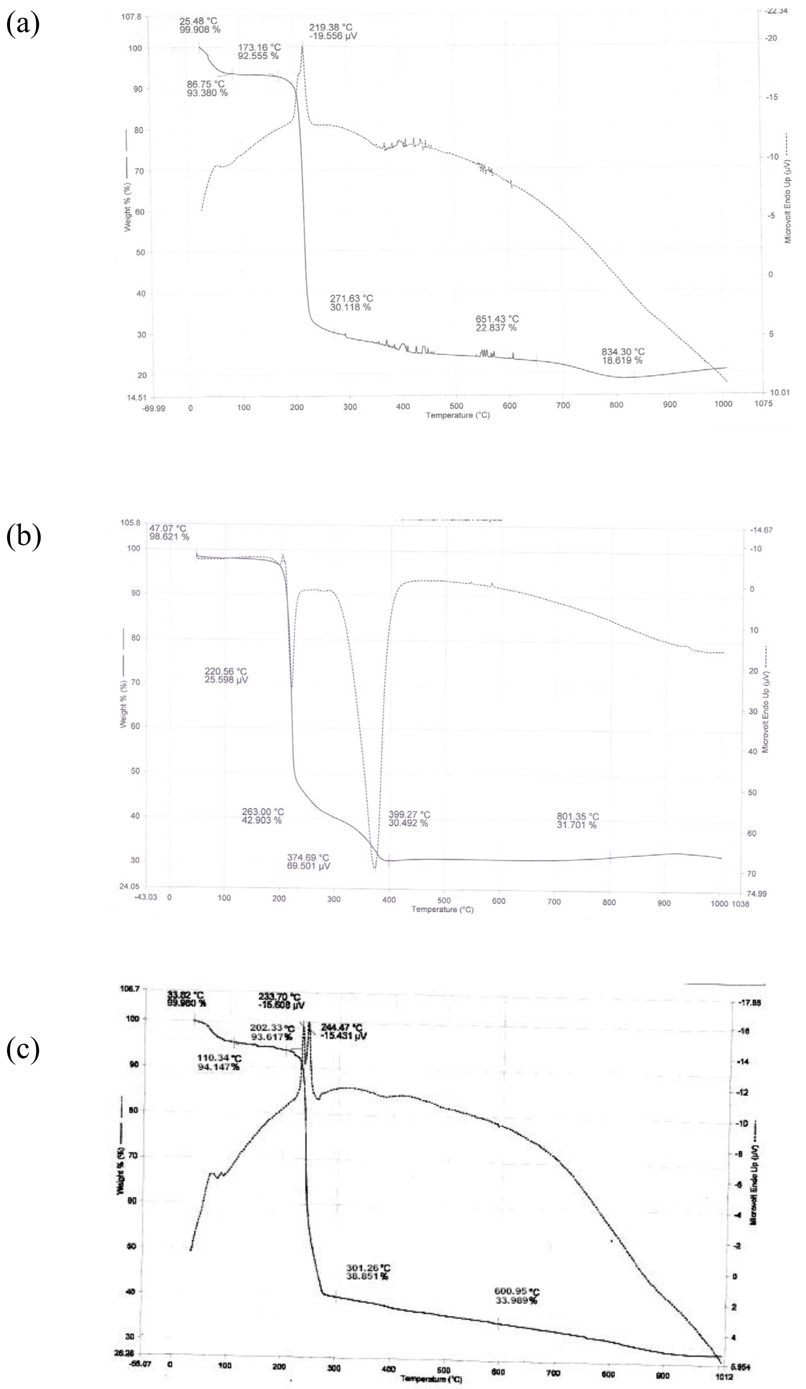


Fig. S7 IR spectra of (a) **3**.2H_2O (Blue crystal), (b) **4**-Heating (Green crystal) and (c) **4**- Vapour (Green crystal) in KBr disk.



Sr. No.	Compound No.	Temperature (°C) Range	Weight %
(a)	**1**.2H_2O	**130.69**	**95.03**
(b)	**1**	**Upto 180**	**No weight Loss**
(c)	**1**.2H_2O(Regenerated)	**127.36**	**94.675**

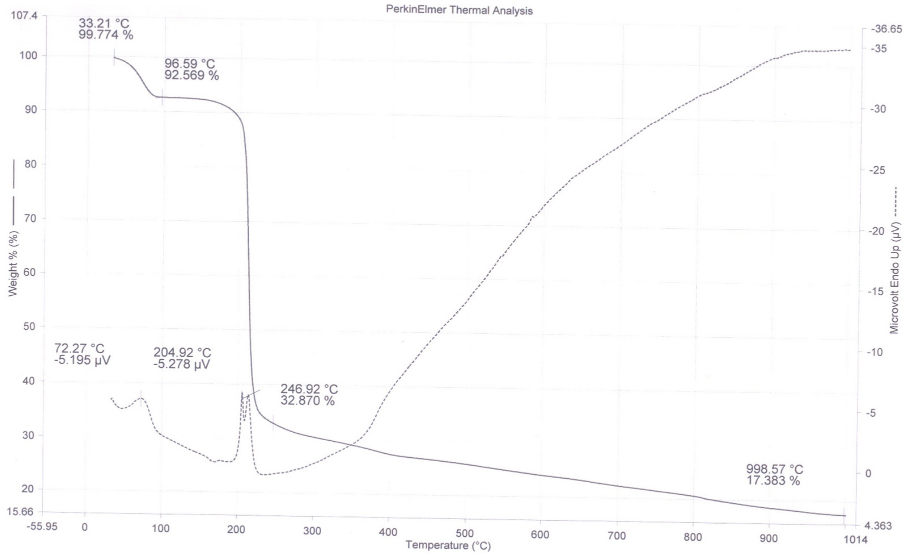
Fig. S8 TGA of (a) **1**.2H_2O (Blue crystal), (b) **1** (Blue crystal) and (c) **1**.2H_2O-Regenerated (Blue crystal).



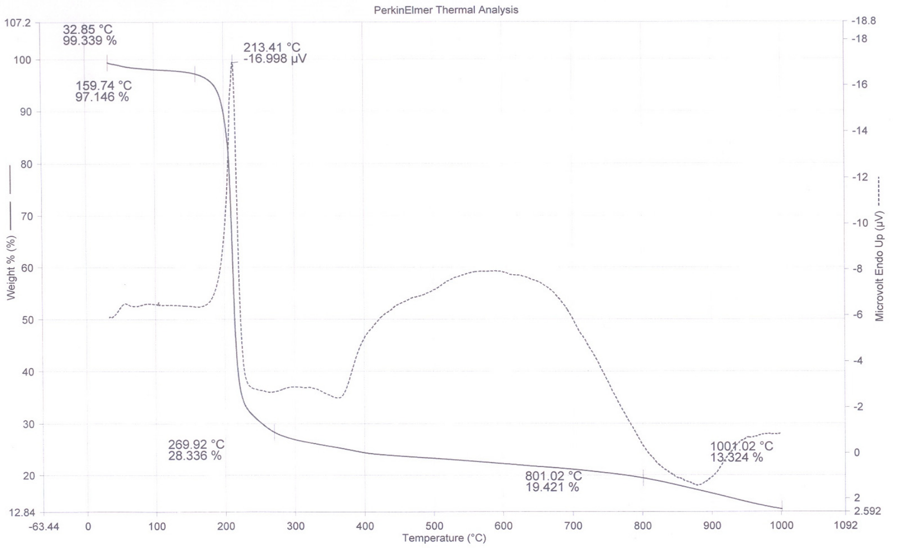
Sr. No.	Compound No.	Temperature (°C) Range	Weight %
(a)	**2**.2H_2O	**86.75**	**93.380**
(b)	**2**	**Upto 200**	**No weight Loss**
(c)	**1**.2H_2O(Regenerated)	**110.34**	**94.147**

Fig. S9 TGA of (a) **2**.2H_2O (Blue crystal), (b) **2** (Blue crystal) and (c) **2**.2H_2O-Regenerated (Blue crystal).

(a)



(b)



Sr. No.	Compound No.	Temperature (^{o}C) Range	Weight %
(a)	**3**.2H_2O	**96.59**	**92.569**
(b)	**4**	**Upto 180**	**No weight Loss**

Fig. S10 TGA of (a) **3**.2H_2O (Blue crystal) and (b) **4** (Green crystal).

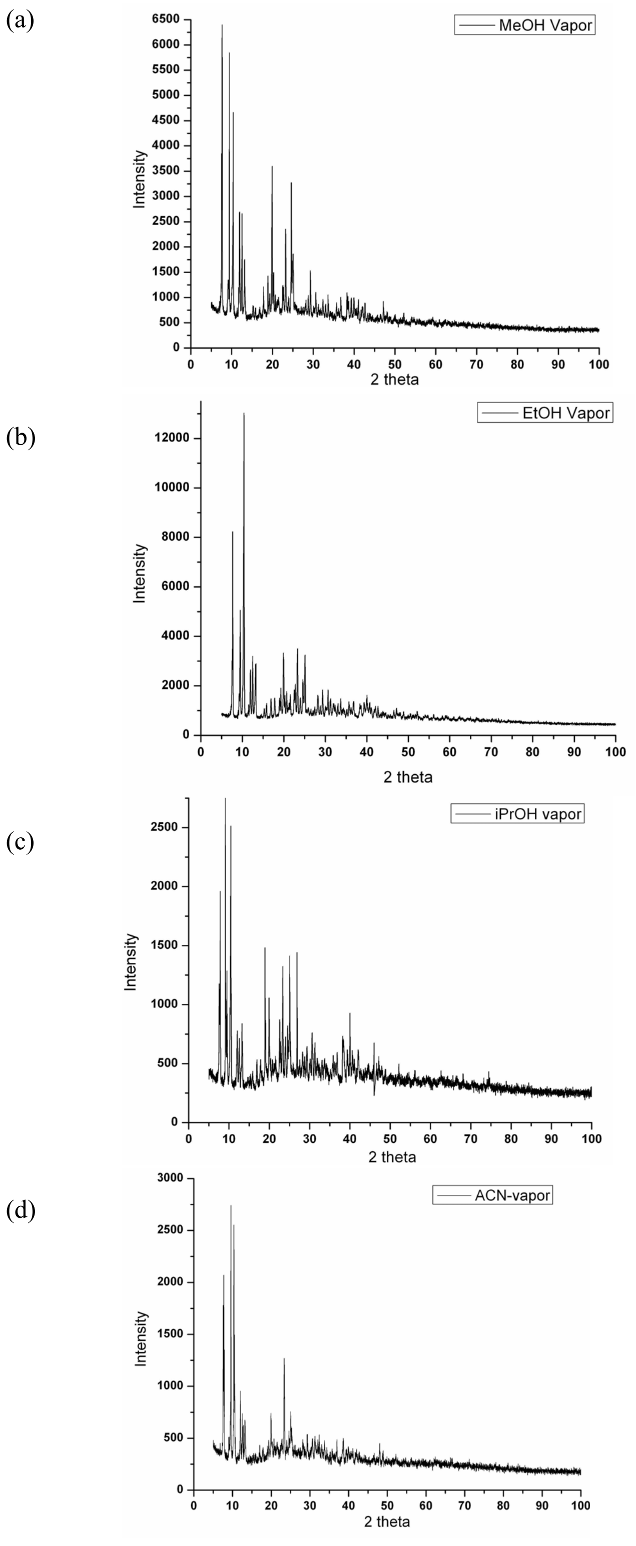


Fig. S11 Powder XRD patterns for **4** by vapor diffusion in different solvent vapor a) MeOH b) EtOH c) ^{i}PrOH and d) ACN.