Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Selective gelation of N-(4-pyridyl)nicotinamide by copper(II) salts

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1. ^{1}H-NMR ($CDCl_3$): 4-pyridyl nicotinamide (**4PNA**)

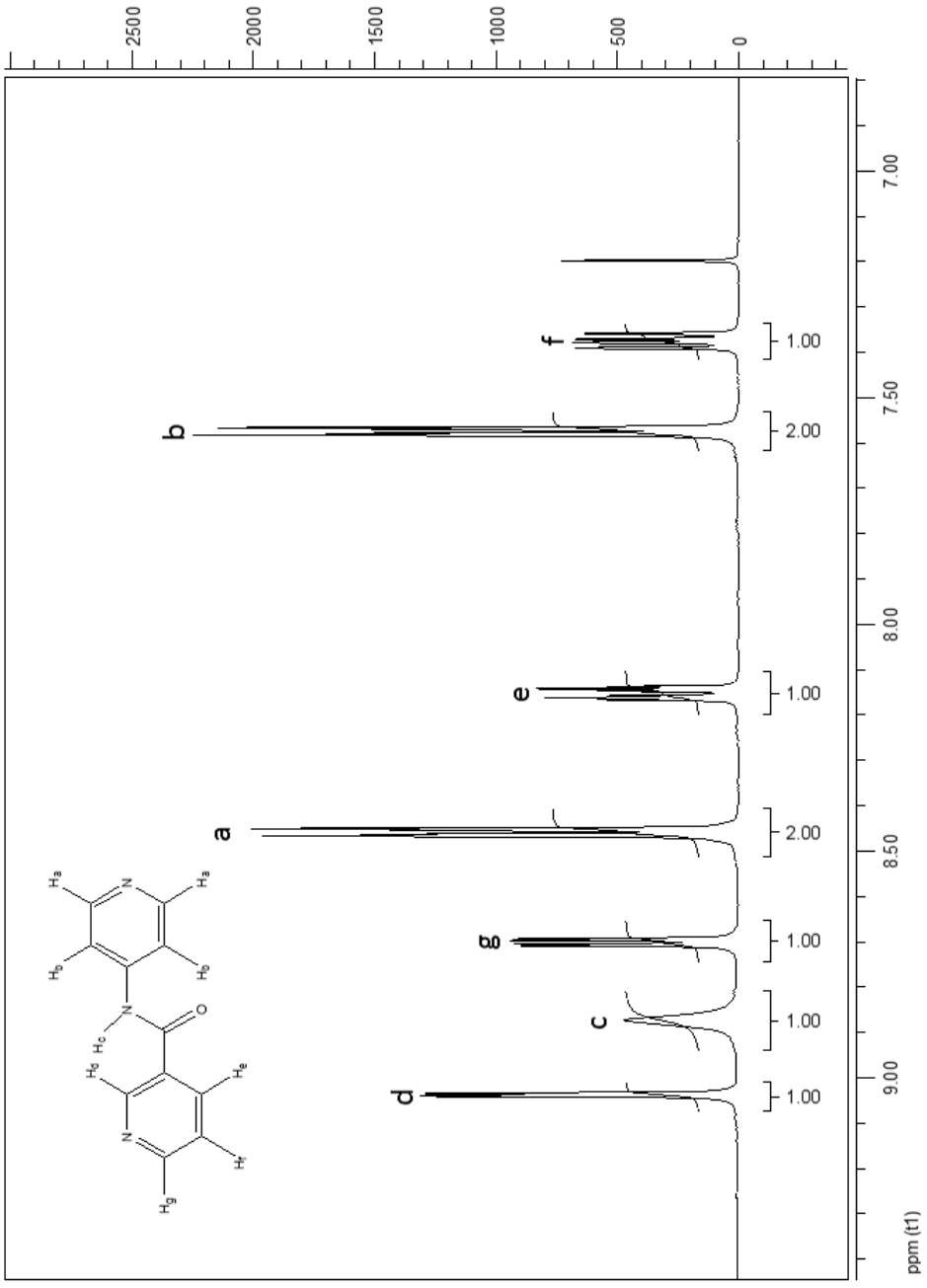

Figure S1: ^{1}H-NMR spectrum of 4-pyridyl nicotinamide (**4PNA**) in $CDCl_3$

2. ^{13}C-NMR (CD_3OD): *4-pyridyl nicotinamide (**4PNA**)*

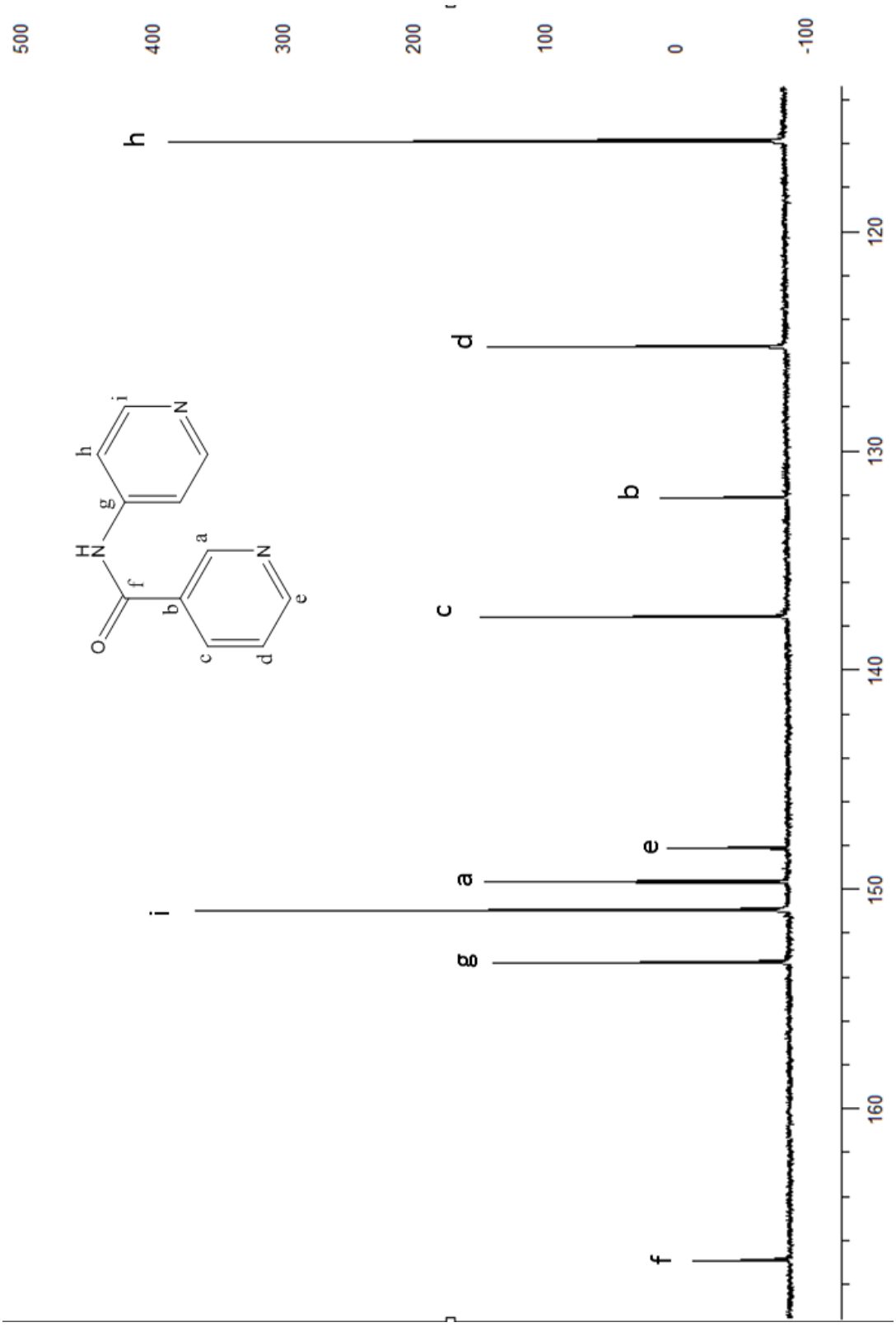

Figure S2: ^{13}C-NMR spectrum of **4PNA** in CD_3OD

3. Synthesis of metal complexes of 4PNA in a 1:2 metal:ligand ratio

Table S1: Preparation of complexes					
Entry	**Metal Salts**	**Metal Salts (mmol)**	**Ligand**	**Crystallising Medium**	**Outcome**
1	$Cu(OAc)_2.2H_2O$	0.1	0.2	Water-EtOH	Crystals
2	$Cd(OAc)_2.2H_2O$	0.1	0.2	Water-EtOH	Crystals
3	$Zn(NO_3)_2.6H_2O$	0.1	0.2	Water-EtOH	Crystals
4	$Cd(NO_3)_2.4H_2O$	0.1	0.2	Water-EtOH	Crystals
5	$Cu(NO_3)_2.3H_2O$	0.062	0.125	DMF	Crystals
6	$Zn(OAc)_2.2H_2O$	0.1	0.2	Water-EtOH	Powder

Synthesis of Copper(II) nitrate complex of **4PNA***:* A solution of **4PNA** (25 mg, 0.125 mmol) in 0.5 mL DMF was mixed with a solution of $Cu(NO_3)_2.3H_2O$ (15.2 mg, 0.062 mmol) in DMF (0.5 mL). Blue crystals of copper(II) nitrate complex of ***4PNA*** were obtained overnight (18 mg).

4. FT-IR (cm^{-1}) of metal complexes.

Entry 1*:* 3255m, 3171m, 3075m, 3002m, 1687vs, 1601vs, 1507vs, 1429vs, 1332s, 1298s, 1240w, 1209w, 1117s, 1065w, 1026s, 895m, 839s, 728s, 679m, 622m, 601m, 542s.

Entry 2*:* 3247w, 3170w, 3069w, 1686s, 1597vs, 1523vs, 1421vs, 1333s, 1301s, 1212s, 1117s, 1065w, 1045m, 1015s, 936w, 896m, 834s, 730s, 711s, 672m, 622m, 591m, 538s.

Entry 3*:* 3430b, 2516w, 2427w, 2356m, 1858w, 1678vs, 1620s, 1568s, 1492vs, 1426m, 1384vs, 1341m, 1315m, 1292s, 1108m, 1063s, 1023s, 920m, 900s, 873w, 842w, 828m, 811m, 756m, 700vs, 651s, 602m, 528m, 420m.

Entry 4*:* 3668w, 3391b, 3306b, 2446w, 2361s, 1929b, 1769w, 1681vs, 1596vs, 1523vs, 1418m, 1384vs, 1333vs, 1297vs, 1208s, 1115s, 1065m, 1047m, 1021vs, 930m, 897s, 822vs, 729m, 699vs, 596m, 530s, 418m.

Entry 5*:* 3432b, 3077w, 1693s, 1655m, 1600vs, 1518vs, 1429s, 1384vs, 1335vs, 1302vs, 1213s, 1118m, 1059w, 1029m, 898w, 837m, 738m, 699m, 601w, 540m.

Entry 6*:* 3262b, 3081m, 3013w, 1683vs, 1594vs, 1516vs, 1478m, 1397vs, 1331s, 1293s, 1243w, 1210s, 1114s, 1064m, 1024s, 928w, 897m, 838s, 738m, 707s, 678s, 619m, 595m, 540s, 429w.

5. Gelation Experiments:

5.1 Gelation test for Ligand (4PNA)

The gelation ability of the ligand **4PNA** was studied at various concentration in different solvents and also in solvent mixtures. The ligand **4PNA** was dissolved in 1 mL of corresponding solvent by heating followed by sonication until a clear solution is obtained. The solution was left undisturbed overnight and checked for gel formation.

Table S2: Gelation studies of 4PNA in different solvents with different concentrations

Ligand conc.	Water	Ethanol	Methanol	DMF	DMSO	DMF-water (1:1)	DMSO-water (1:1)
1 wt%	Solution	Solution	Solution	Solution	Solution	Solution	Solution
2 wt%	Partial gel	Solution	Solution	Solution	Solution	Solution	Solution
4 wt%	Gel	Solution	Solution	Solution	Solution	Solution	Solution
6 wt%	Gel	Solution	Solution	Solution	Solution	Solution	Precipitate
8 wt%	Gel	Solution	Solution	Solution	Solution	Precipitate	Precipitate

5.2 Gelation test for metal salt with 4PNA

Gelation experiment of **4PNA** was studied with Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) salts. The required amount of metal salt was dissolved in 0.5 mL of water, and mixed with corresponding amount (1:2 ratio) of **4PNA** in 0.5 mL of DMF. It was sonicated for 1-4 minutes and kept without disturbing. Only copper(II) salt formed gel and was confirmed by tube inversion test.

5.3 Gelation test for copper(II) acetate with 4PNA at various concentrations

(a) 1:2 metal:ligand ratio: Gelation experiments were performed with $Cu(OAc)_2.2H_2O$ and **4PNA** in 1:2 metal:ligand ratio at different concentrations in 50 % DMF/water mixture (v/v) (Table S3). The minimum gelator concentration (MGC) was found to be 2 wt% in 50 % DMF/water mixture (v/v) and 1.5 wt% in pure water.

Table S3: Gelation test for copper(II) acetate complex (1:2 metal:ligand ratio)

Total conc. (metal salt+ligand) wt%	**Observation**
1.5%	Partial gel
2%	Gel
3%	Gel + Crystal
6%	Gel + Crystal
9%	Gel + Precipitate

(b) 1:1 metal:ligand ratio: Gelation experiments were performed with different concentration of $Cu(OAc)_2.2H_2O$ and **4PNA** in 1:1 metal:ligand ratio in 50 % DMF/water mixture (v/v) (Table S4). The minimum gelator concentration (MGC) was found to be 4 wt% in 50 % DMF/water mixture (v/v).

Table S4: Gelation test for copper(II) acetate complex (1:1 metal:ligand ratio)	
Total conc. (metal salt+ligand) wt%	Observation
2 %	Clear solution
4%	Gel
6%	Gel
8%	Gel + Precipitate

(c) Varying solvent composition: To evaluate the effect of DMF/water ratio in gelation, we fixed the gelator concentration as 4 wt% (1:2 metal-ligand ratio) and experiments were performed with varying solvent composition (Table S5).

Table S5: Gelation test for copper(II) acetate complex in various solvent composition	
DMF/H_2O	**Observations**
20% DMF	Solution + Crystals
30% DMF	Solution + Crystals
40% DMF	Gel
50% DMF	Gel
60% DMF	Gel
70% DMF	Clear solution
80% DMF	Clear solution

5.4 Gelation test for copper(II) chloride with 4PNA at various concentrations

(a) 1:2 metal:ligand ratio: A solution of $CuCl_2$ in 0.5 mL of water was mixed with of **4PNA** in 0.5 mL of DMF and was sonicated for one minute resulting in opaque greenish blue solution, which was allowed to stand overnight to yield green gel 2.6 - 10 wt% concentration (Table S6).

Table S6: Gelation test for copper(II) chloride complex (1:2 metal:ligand ratio)	
Total conc. (metal salt+ligand) wt%	**Observation**
1.5 wt%	Partial gel
2 wt%	Partial gel
2.6 wt%	Opaque greenish blue gel
3 wt%	Opaque greenish blue gel
6 wt%	Opaque greenish blue gel
8 wt%	Opaque greenish blue gel
10 wt%	Opaque greenish blue gel

(b) 1:1 metal:ligand ratio: Gelation experiments were performed with $CuCl_2$ and **4PNA** in 1:1 metal:ligand ratio at 3.3 wt% concentration in 1:1 and 3:1 DMF/water mixture (v/v) yielded greenish blue gels.

(c) Varying solvent composition: The total concentration (metal salt+ligand) was fixed at 3 wt% (1:2 metal-ligand ratio) and gelation was observed at various DMF/water mixture (Table S7).

Table S7: Gelation test for copper(II) chloride complex in various solvent composition	
DMF/H_2O	**Observations**
Pure water	Gel
10 % DMF	Partial gel
20 % DMF	Partial gel
30 % DMF	Partial gel
40 % DMF	Gel
50 % DMF	Gel
60 % DMF	Gel
70 % DMF	Gel
80 % DMF	Gel
90 % DMF	Gel
Pure DMF	Partial gel

5.5 Gelation test for copper(II) nitrate with 4PNA at various concentrations

(a) 1:2 metal:ligand ratio: A solution of $Cu(NO_3)_2.3H_2O$ in 0.5 mL of water was mixed with of **4PNA** in 0.5 mL of DMF and it was kept without disturbing. Sonication was avoided due to immediate precipitation and an opaque deep blue gel was observed in 3-6 wt% concentration (Table S8). The gel was deformed upon shaking, indicating lower gel strength compared to copper acetate gel.

Table S8: Gelation test for copper(II) nitrate complex (1:2 metal:ligand ratio)	
Total conc. (metal salt+ligand) wt%	Observation
2%	Partial gel
2.5%	Partial gel
3%	Opaque blue gel
4.5%	Opaque blue gel
6.4%	Opaque blue gel

(b) 1:1 metal:ligand ratio: Gelation experiments were performed with $Cu(NO_3)_2.3H_2O$ and **4PNA** in 1:1 metal:ligand ratio at different concentrations in 50 % DMF/water mixture (v/v) (Table S9).

Table S9: Gelation test for copper(II) nitrate complex (1:1 metal:ligand ratio)	
Total conc. (metal salt+ligand) wt%	Observation
3%	Clear solution
5%	Clear solution
7%	Precipitate
9%	Precipitate

(c) Varying solvent composition: The total concentration (metal salt+ligand) was fixed at 6 wt% (1:2 metal-ligand ratio) and gelation was observed only at 1:1 DMF/water (Table S10).

Table S10: Gelation test for copper(II) nitrate complex in various solvent composition	
DMF/H_2O	**Observations**
20% DMF	Precipitate
30% DMF	Precipitate
40% DMF	Precipitate
50% DMF	Gel
60% DMF	Clear solution
70% DMF	Clear solution
80% DMF	Clear solution

5.6 Gelation test for copper(II) perchlorate with 4PNA at various concentrations

(a) Varying solvent composition: Gelation was observed above 4 wt% (1:2 metal:ligand ratio) at higher DMF concentration (9:1 DMF/water, v/v) and pure DMF. This was achieved by mixing an aqueous solution of $Cu(ClO_4)_2.6H_2O$ (0.1 mL water or DMF) with corresponding amount (1:2 metal:ligand ratio) of 4PNA in DMF (0.9 mL). The resulting solution was sonicated for one minute and allowed to stand overnight to yield greenish-blue gel (Table S11).

Table S11: Gelation test for copper(II) perchlorate complex in various solvent composition	
DMF/H_2O	**Observations**
Pure water	Complete precipitate
20% DMF	Complete precipitate
40% DMF	Little precipitate with a blue solution
60% DMF	Little precipitate with a blue solution
80% DMF	Blue solution
90% DMF	Gel
Pure DMF	Gel
Pure water	Complete precipitate

(b) 1:2 metal:ligand ratio: Gelation experiments were performed at various gelator concertation in 9:1 DMF/water and pure DMF . (Table S12).

Table S12: Gelation test for copper(II) perchlorate complex in various concentration		
wt %	**DMF**	**90% DMF**
8 wt%	Gel	Gel
6 wt%	Gel	Gel
4 wt%	Gel	Gel
3 wt%	Partial gel	Partial gel

5.7 Gelation test for copper(II) sulphate with 4PNA at various concentrations

(a) Varying solvent composition: Copper(II) sulphate complexes of 4PNA displayed similar properties as copper(II) perchlorate salts. In this case, the required amount of $Cu(SO_4).5H_2O$ in water (0.2 mL) and mixing with the corresponding amount (1:2 metal:ligand ratio) of 4PNA in DMF (0.8 mL), the mixture was sonicated for one minute and allowed to stand overnight to yield greenish-blue gel (Table S13).

Table S13: Gelation test for copper(II) sulphate complex in various conditions				
wt%	**40% DMF**	**60% DMF**	**70% DMF**	**80% DMF**
4.5	Blue ppt	Blue ppt	Broken gel	Gel with slight ppt
6	Blue ppt	Partial gel	Broken gel	Gel with more ppt
7.5	Blue ppt	Partial gel	Partial gel	Gel with more ppt

5.8. SEM: Xerogel of copper(II) complexes of **4PNA** (1:2 metal:ligand ratio) were prepared for SEM analaysis. The morphologies of the xerogels were similar to that of copper(II) acetate xerogels (Figure S3)

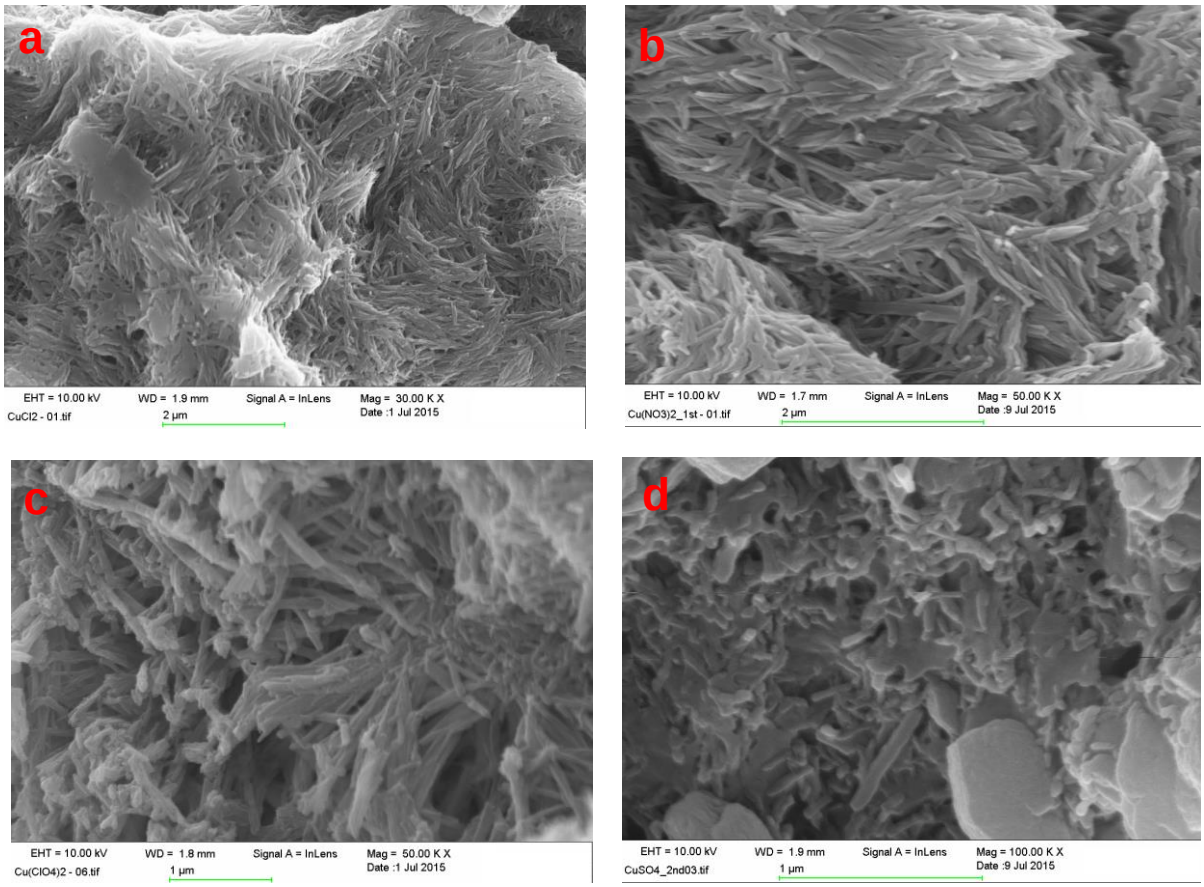

Figure S3: SEM images of (a) copper chloride gels of 4PNA at 3 wt% in 1:1 DMF/water (v/v); (b) copper nitrate gels of 4PNA at 4 wt% in 1:1 DMF/water (v/v); (c) copper perchlorate gels of 4PNA at 4 wt% in 9:1 DMF/water (v/v; (d) copper sulfate gels of 4PNA at 6 wt% in 8:2 DMF/water (v/v).

5.9 T_{gel} Experiment: $Cu(OAc)_2.2H_2O$ (6.7 mg, 0.033 mmol) in 0.5 mL water was mixed with a solution of (13.3 mg 0.066 mmol) **4PNA** in 0.5 mL DMF in a standard 7 mL vial and was sonicated for 4 minutes. A blue gel of copper(II) acetate complex of **4PNA** was obtained overnight. A small spherical glass ball (360 mg) was placed on the top of the gel and was heated in an oil bath. The temperature at which the ball touched the bottom of the vial was recorded (58 ^{0}C for 2 wt% and 61 ^{0}C for 4 wt%) as T_{gel}. The gel was reformed on keeping overnight at room temperature. Although, the gels were thermoreversible, heating at elevated temperature (<90 ^{0}C) resulted in a brown mass.

T_{gel} of copper nitrate gel (6.4 wt%) was prepared in similar fashion. Gel was synthesized by mixing a solution of $Cu(NO_3)_2.3H_2O$ (24.1 mg 0.1 mmol) in 0.5 mL of water with a solution of **4PNA** (40 mg 0.2 mmol) in 0.5 mL of DMF. T_{gel} was found to be 53 ^{0}C. However, the solution didn't form gel after cooling back to room temperature, indicating that the gels are thermoirreversible.

Copper chloride gel (3 wt%) was synthesized by mixing a solution of $CuCl_2$ (7.5 mg 0.05 mmol) in 0.5 mL of water with a solution of **4PNA** (22.5 mg, 0.11 mmol) in 0.5 mL of DMF. T_{gel} was found to be 64^{0}C. The gel was reformed on keeping overnight at room temperature.

Copper perchlorate gel (4 wt%) was synthesized by mixing a solution of $Cu(ClO_4)_2.6H_2O$ (19.2 mg 0.05 mmol) in 0.1 mL of water with a solution of **4PNA** (20.8 mg, 0.10 mmol) in 0.9 mL of DMF. T_{gel} was found to be 55^{0}C. However, the solution didn't form gel after cooling back to room temperature, indicating that the gels are thermoirreversible.

Copper sulphate gel (5 wt%) was synthesized by mixing a solution of $CuSO_4.5H_2O$ (19.3 mg 0.077 mmol) in 0.2 mL of water with a solution of **4PNA** (30.7 mg, 0.154 mmol) in 0.8 mL of DMF. T_{gel} was found to be 65^{0}C. The gel was reformed on keeping overnight at room temperature.

6. Characterisation

6.1 Cambridge Structural database search: A search motif was introduced with two chlorides and two pyridyl moieties (with hydrogen atoms at 2 and 6 position only) resulted in 98 hits. Adding one water molecule to the above search resulted in only 9 hits.

6.1 Crystal data

	Table S14: Crystal data for Complex 1, 2, 3 & 4			
Crystal data	**1**	**2**	**3**	**4**
Empirical formula	$C_{26}H_{24}CuN_6O_6$	$C_{26}H_{26}CdN_6O_7.2H_2O$	$C_{22}H_{22}N_8O_{10}Zn$	$C_{22}H_{22}CdN_8O_{10}$
Colour	Clear dark violet	Colourless	Colourless	Colourless
Formula weight	580.05	682.96	623.85	670.88
Crystal size (mm)	0.40 x 0.22 x 0.09	0.15 x 0.08 x 0.05	0.14 x 0.12 x 0.015	0.25 x 0.16 x 0.04
Crystal system	triclinic	Monoclinic	triclinic	triclinic
Space group	Pī	$P2_1/c$	Pī	Pī
a (Å)	8.0578(6)	16.3055(3)	7.4378(4)	7.3668(5)
b (Å)	8.3568(6)	22.8004(4)	8.9941(4)	9.1365(6)
c (Å)	10.1944(6)	15.2496(3)	9.8914(5)	9.9565(6)
α (^{0})	79.288(5)		75.2719(17)	76.1428(18)
β (^{0})	69.725(6)	97.353(2)	72.7974(17)	73.5323(18)
γ (^{0})	82.953(6)		82.7345(17)	83.610(2)
Volume (Å^3)	631.44(7)	5622.75(18)	610.39(5)	623.27(7)
Z	1	8	1	1
$D_{calc.}$(g/cm^3)	1.525	1.614	1.697	1.787
F(000)	299	2784	320	338
μ MoKα (mm^{-1})	0.920	0.841	1.083	0.951
Temperature (K)	120.0(2)	120.0(2)	120.0(2)	120.0(2)
Reflections collected/ unique/observed [I>2σ(I)]	7769/3689/3339	112852/14250/10961	13125/3403/2891	19999/3310/3264
Data/restraints/parameters	3689/0/226	14250/1/789	3403/0/199	3310/1/157
Goodness of fit on F^2	1.080	1.023	1.040	1.008
Final R indices [I>2σ(I)]	R_1 = 0.0348 wR_2 = 0.0768	R_1 = 0.0329 wR_2 = 0.0608	R_1 = 0.0343 wR_2 = 0.0736	R_1 = 0.0592 wR_2 = 0.1492
R indices (all data)	R_1 = 0.0403 wR_2 = 0.0810	R_1 = 0.0570 wR_2 = 0.0675	R_1 = 0.0463 wR_2 = 0.0777	R_1 = 0.0595 wR_2 = 0.1497

6.3 Illustration of the Crystalline structure of $[Cd(4PNA)_2(NO_3)_2(H_2O)_2]$

The nitrogen atom of the amide moiety is hydrogen bonded to the oxygen atom of the nitrate anion (N–H…O) to form a 1-D hydrogen bonded network similar to **3**. These 1-D chains are further hydrogen bonded to adjacent 1-D chains via hydrogen bonding oxygen atom of amide moiety and nitrate anions with the metal coordinated water molecule. These hydrogen bonding interactions result in a 2-D hydrogen bonded network (Figure S4).

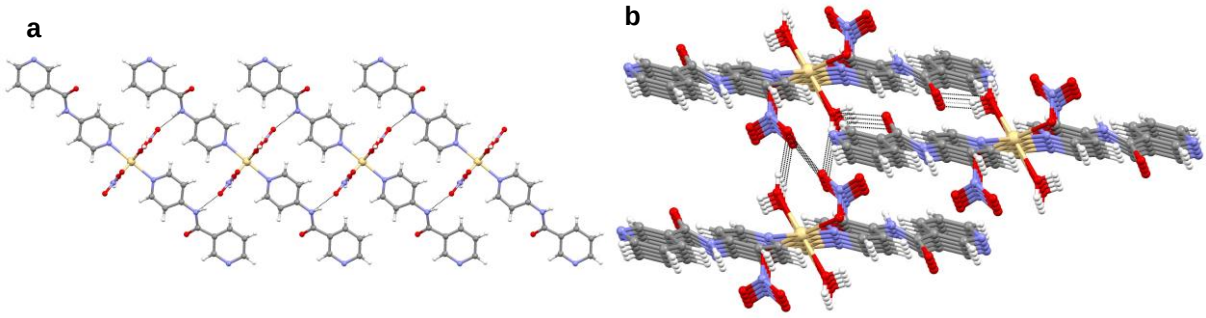

Figure S4: (a) I-D hydrogen bonded network in **4** and (b) the formation of a 2-D hydrogen bonded network from 1-D hydrogen bonded chains.

Hydrogen Bonding Parameters

Table S15: Hydrogen bonding parameters for Complex 1, 2, 3 & 4					
D–H•••A	**D–H (Å)**	**H•••A (Å)**	**D•••A (Å)**	**D–H•••A (^{0})**	**Symmetry operation for A**
Complex 1					
N(2)–H(2)•••O(3)	0.85(2)	1.99(2)	2.8188(19)	164.0(17)	1+x, y, z
C(2)–H(2A)•••O(3)	0.95(2)	2.52(3)	3.174(2)	126.2(15)	1+x, y, z
C(5)–H(5)•••O(1)	0.95(2)	2.37(2)	3.300(2)	166.5(17)	-x, -y, 2-z
C(8)–H(8)•••O(3)	0.95(2)	2.36(2)	3.270(2)	161(2)	1+x, y, z
Complex 2					
O(1W)–H(1WA)•••O(15)	0.85	1.85	2.682(2)	163	x, y, z
N(2)–H(2)•••O(13)	0.89(3)	1.99(3)	2.856(2)	166(3)	x, 1/2-y, -1/2+z
O(1W)–H(1WB)•••O(3W)	0.94	1.80	2.710(2)	163	x, y, z
N(2A)–H(2A)•••O(12)	0.84(3)	2.12(3)	2.950(2)	172(2)	x, 1/2-y, 1/2+z
N(2B)–H(2B)•••N(3B)	0.78(3)	2.41(3)	3.149(3)	158(3)	1-x, 1-y, -z
N(2C)–H(2C)•••O(18)	0.87(3)	2.10(3)	2.947(3)	165(2)	x, 3/2-y, 1/2+z
O(2W)–H(2WA)•••O(1B)	0.79	1.98	2.720(2)	155	x, 3/2-y, 1/2+z
O(2W)–H(2WB)•••O(6W)	0.85	1.86	2.706(2)	175	1-x, 1-y, 1-z
O(3W)–H(3WA)•••O(4W)	0.88	1.98	2.792(3)	154	-x, 1-y, 1-z
O(3W)–H(3WB)•••O(17)	0.88	1.86	2.710(2)	162	x, y, z
O(4W)–H(4WA)•••O(3W)	0.89	1.92	2.794(2)	167	x, y, z
O(4W)–H(4WB)•••O(11)	0.96	1.83	2.748(2)	157	x, y, z
O(5W)–H(5WA)•••O(14)	0.88	2.11	2.946(2)	158	x, y, z
O(5W)–H(5WB)•••O(16)	0.95	1.76	2.691(2)	167	1-x, 1-y, 1-z
O(6W)–H(6WA)•••N(3)	0.82	2.08	2.895(3)	173	x, 1/2-y, 1/2+z
O(6W)–H(6WB)•••O(5W)	0.83	1.98	2.776(3)	161	x, y, z
C(3A–H(3A)•••O(12)	0.95	2.37	3.203(3)	146	x, 1/2-y, 1/2+z
C(3C)–H(3C)•••O(18)	0.95	2.52	3.450(3)	166	x, 3/2-y, 1/2+z
C(4A)–H(4A)•••O(11)	0.95	2.53	3.444(3)	162	x, y, 1+z
C(4C)–H(4C)•••O(17)	0.95	2.59	3.465(3)	153	x, y, 1+z
C(5B)–H(5B)•••O(6W)	0.95	2.48	3.426(3)	173	1-x, 1-y, -z
C(6)–H(6)•••O(1C)	0.95	2.28	3.232(3)	175	x, y, -1+z
C(6A)–H(6A)•••O(1A)	0.95	2.39	3.123(3)	133	-x, 1-y, 2-z
C(10A) –H(10A)•••N(3A)	0.95	2.62	3.211(3)	121	x, 1/2-y, -1/2+z
C(11A)–H(11A)•••O(12)	0.95	2.57	3.349(3)	139	x, 1/2-y, 1/2+z
C(11C)–H(11C)•••O(18)	0.95	2.50	3.271(3)	138	x, 3/2-y, 1/2+z
C(4S)–H(4SA)•••O(2W)	0.98	2.56	3.468(3)	155	1-x, 1-y, 1-z
C(6S)–H(6SC)•••O(14)	0.98	2.41	3.385(3)	176	x, y, z
Complex 3					
N(2)–H(2)•••O(3)	0.83(3)	2.12(2)	2.920(2)	161(2)	x, 1+y, z
O(5)–H(5A)•••O(4)	0.81(3)	2.08(3)	2.852(2)	160(3)	1+x, y, z
O(5)–H(5B)•••O(1)	0.82(3)	1.90(3)	2.7114(19)	176(3)	1-x, -y, 1-z
C(3)–H(3)•••O(3)	0.95	2.51	3.282(2)	138	x, 1+y, z
C(5)–H(5)•••O(4)	0.95	2.43	3.364(3)	166	-x, 1-y, 1-z
Complex 4					
N(2)–H(2)•••O(4)	0.88	2.10	2.959(4)	164	x, 1+y, z
O(5)–H(5A)•••O(1)	0.88	1.92	2.726(4)	152	x, y, -1+z
O(5)–H(5B)•••O(3)	0.80	2.08	2.861(4)	169	-x, 1-y, 1-z
C(9A)–H(9A)•••O(3)	0.95	2.54	3.287(6)	136	x, 1+y, 1+z
C(9A)–H(9A)•••O(3)	0.95	2.45	3.341(6)	156	-x, 2-y, 2-z
C(10B)–H(10B)•••O(3)	0.95	2.37	3.296(7)	165	-x, 2-y, 2-z
C(11A)–H(11A)•••O(4)	0.95	2.55	3.367(7)	145	x, 1+y, z
C(11B)–H(11B)•••O(2)	0.95	2.46	3.410(5)	175	x, 1+y, z
C(11B)–H(11B)•••O(4)	0.95	2.58	3.307(7)	133	x, 1+y, z

6.4. Powder X-Ray: XRPD experiments were carried out in order to establish their crystalline phase purity. The simulated pattern obtained from the crystal structures were matched with the bulk solid (as synthesised).

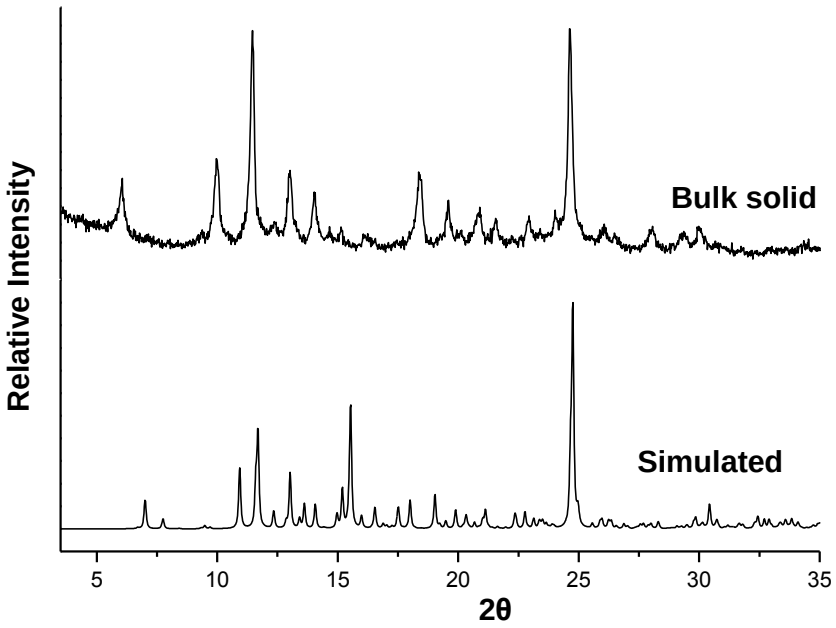

Figure S5: Comparison of PXRD pattern of complex **2** (as synthesised) with the crystal structure. The XRPD pattern do not correlate with the all the peaks of simulated pattern presumably due to the loss of the uncoordinated water molecule in **2.**

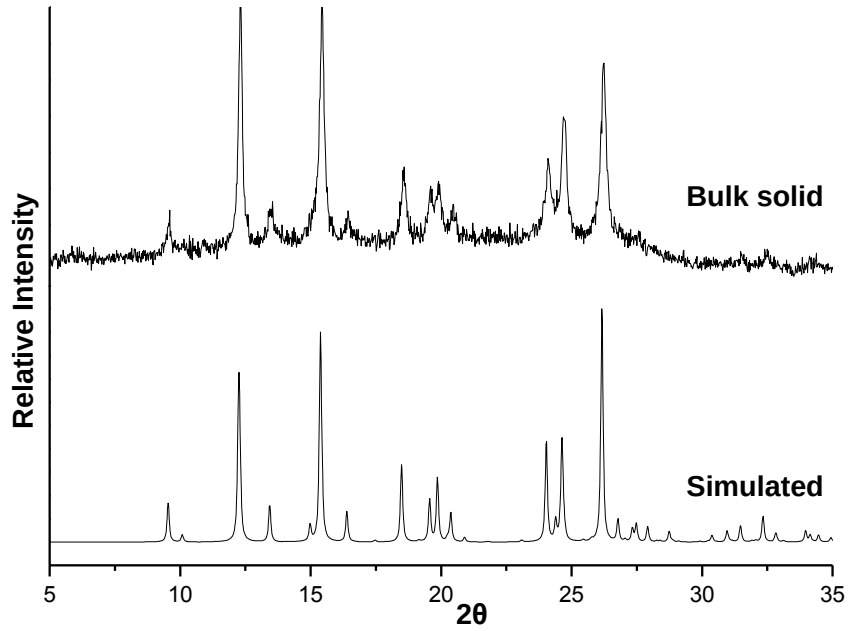

Figure S6: Comparison of PXRD pattern of complex **3** (as synthesised) with the crystal structure.

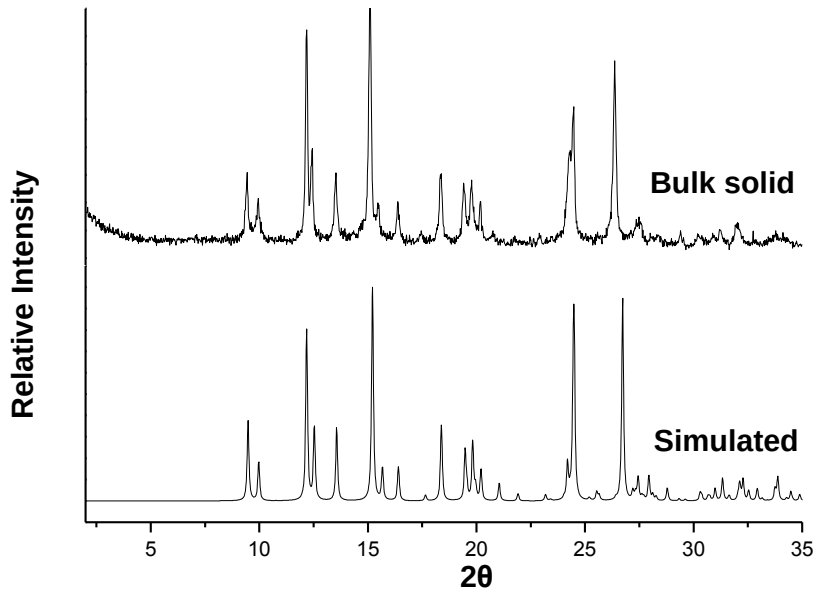

Figure S7: Comparison of PXRD pattern of complex **4** (as synthesised) with the crystal structure.

6.5. of FT-IR (cm^{-1}) of metal complexes: Comparison of complex and xerogels

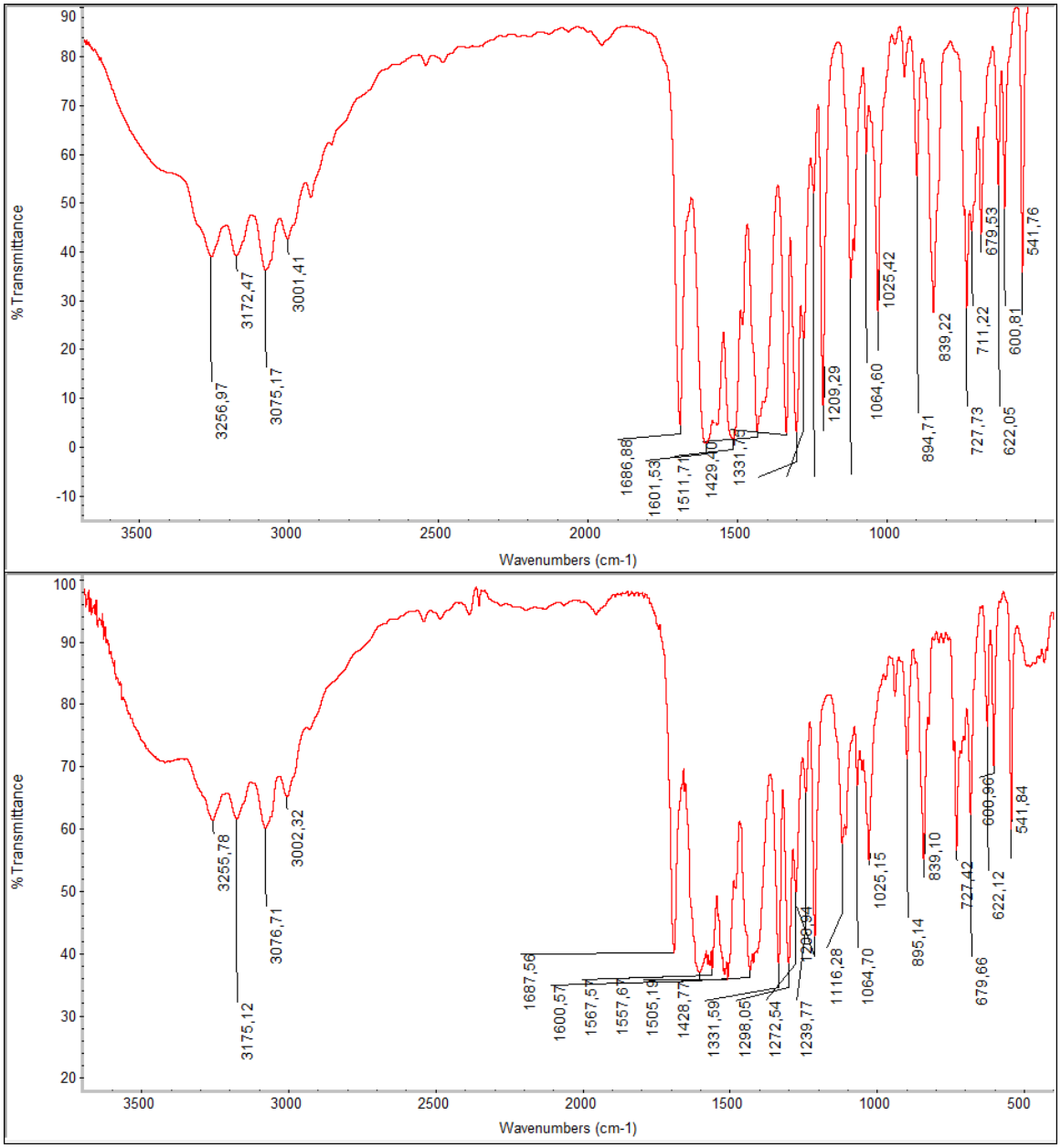

Figure S8: IR spectra comparison of the complexes (top) and xerogels (bottom) of copper(II) acetate and **4PNA.**

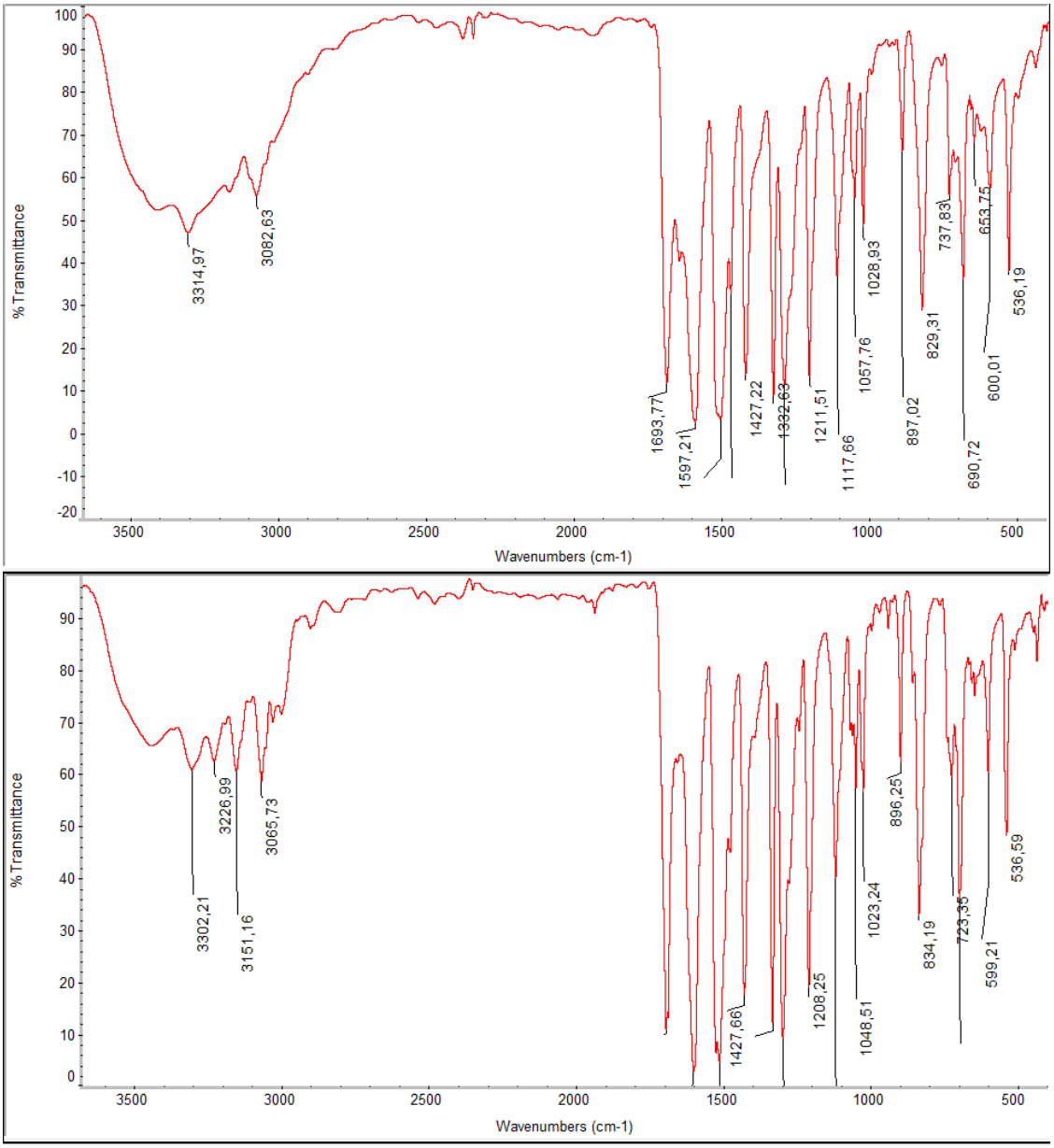

Figure S9: IR spectra comparison of the complexes (top) and xerogels (bottom) of copper(II) chloride and **4PNA.**

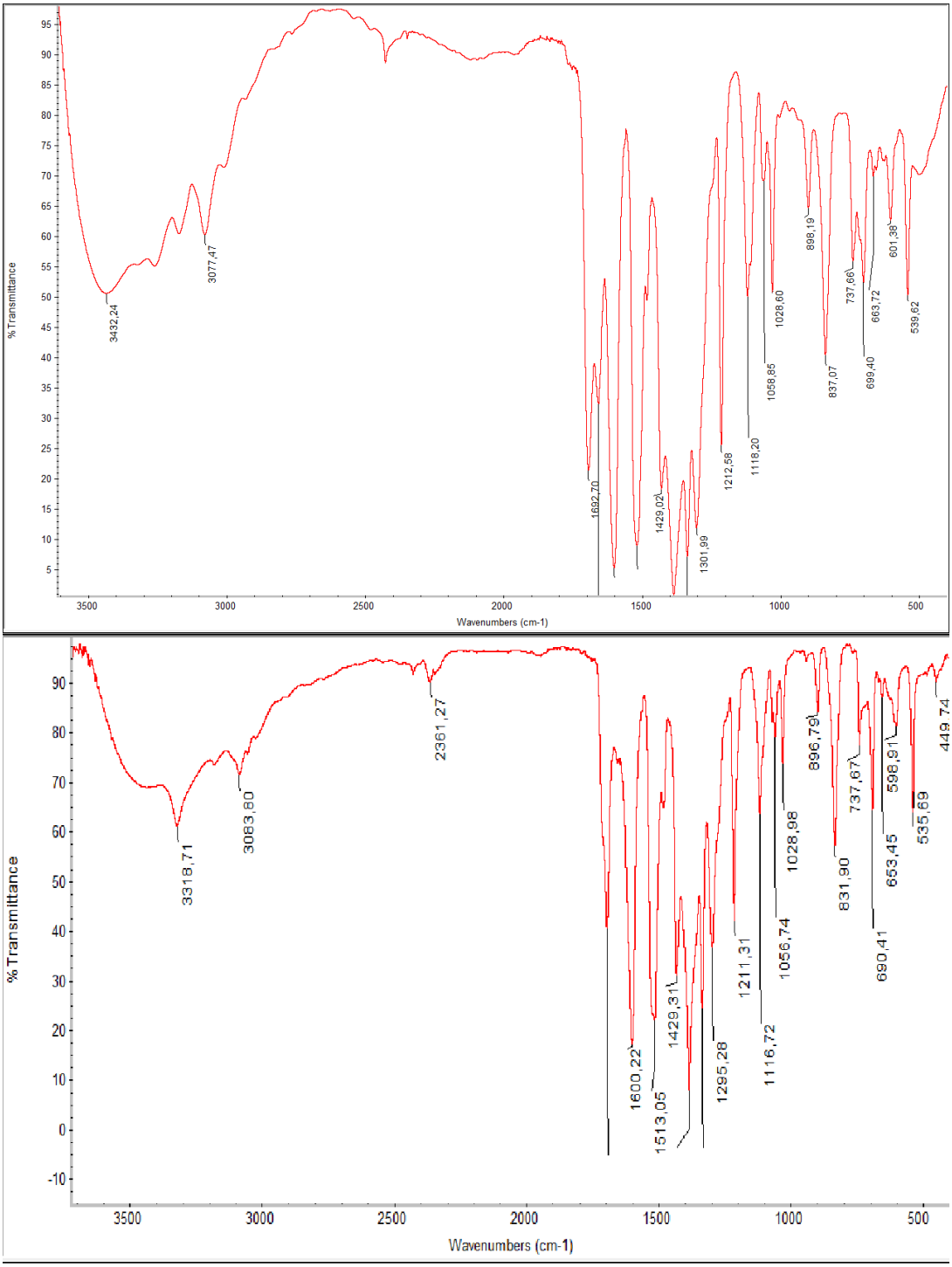

Figure S10: IR spectra comparison of the complexes (top) and xerogels (bottom) of copper(II) nitrate and **4PNA.**

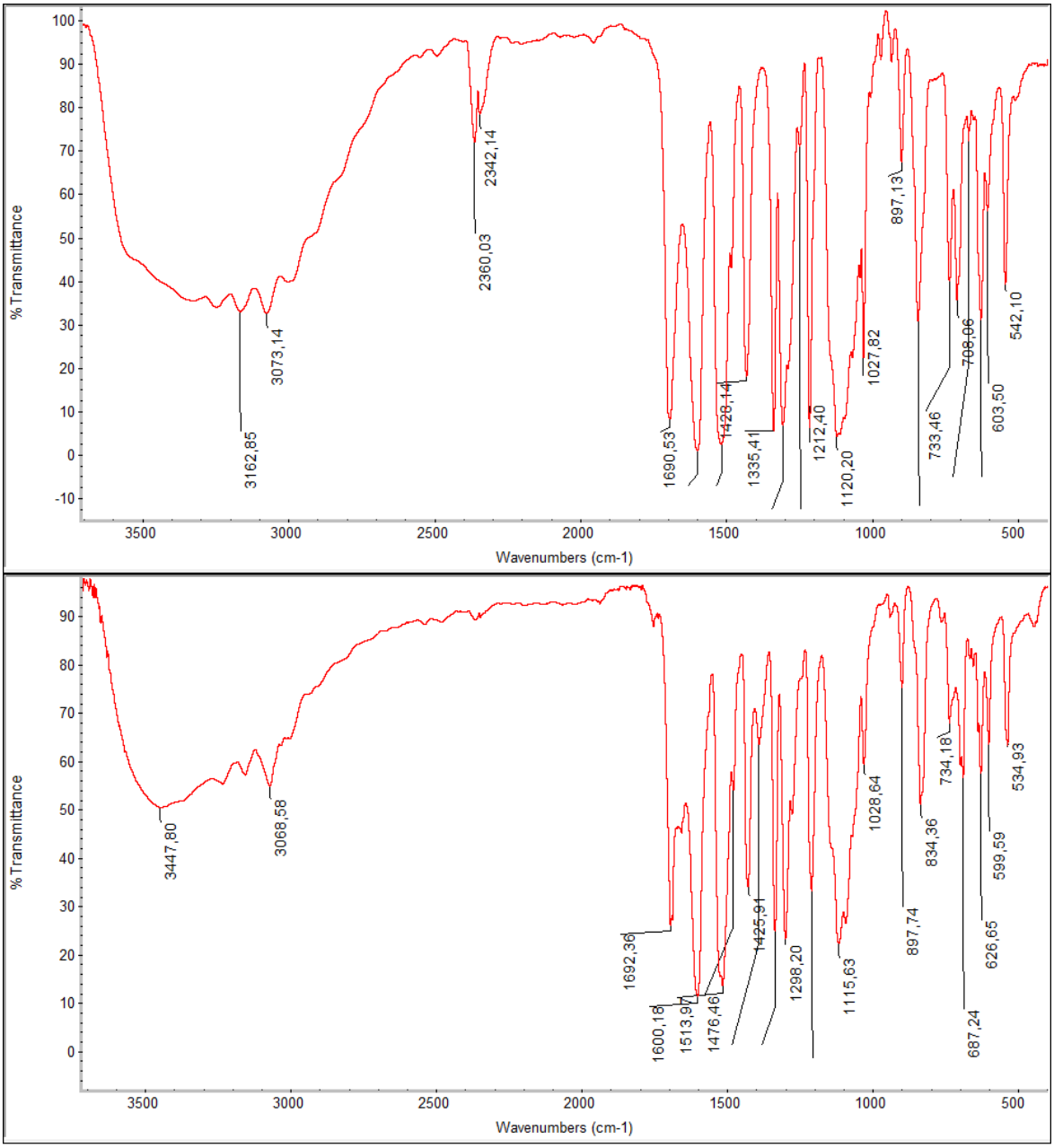

Figure S11: IR spectra comparison of the complexes (top) and xerogels (bottom) of copper(II) perchlorate and **4PNA.**

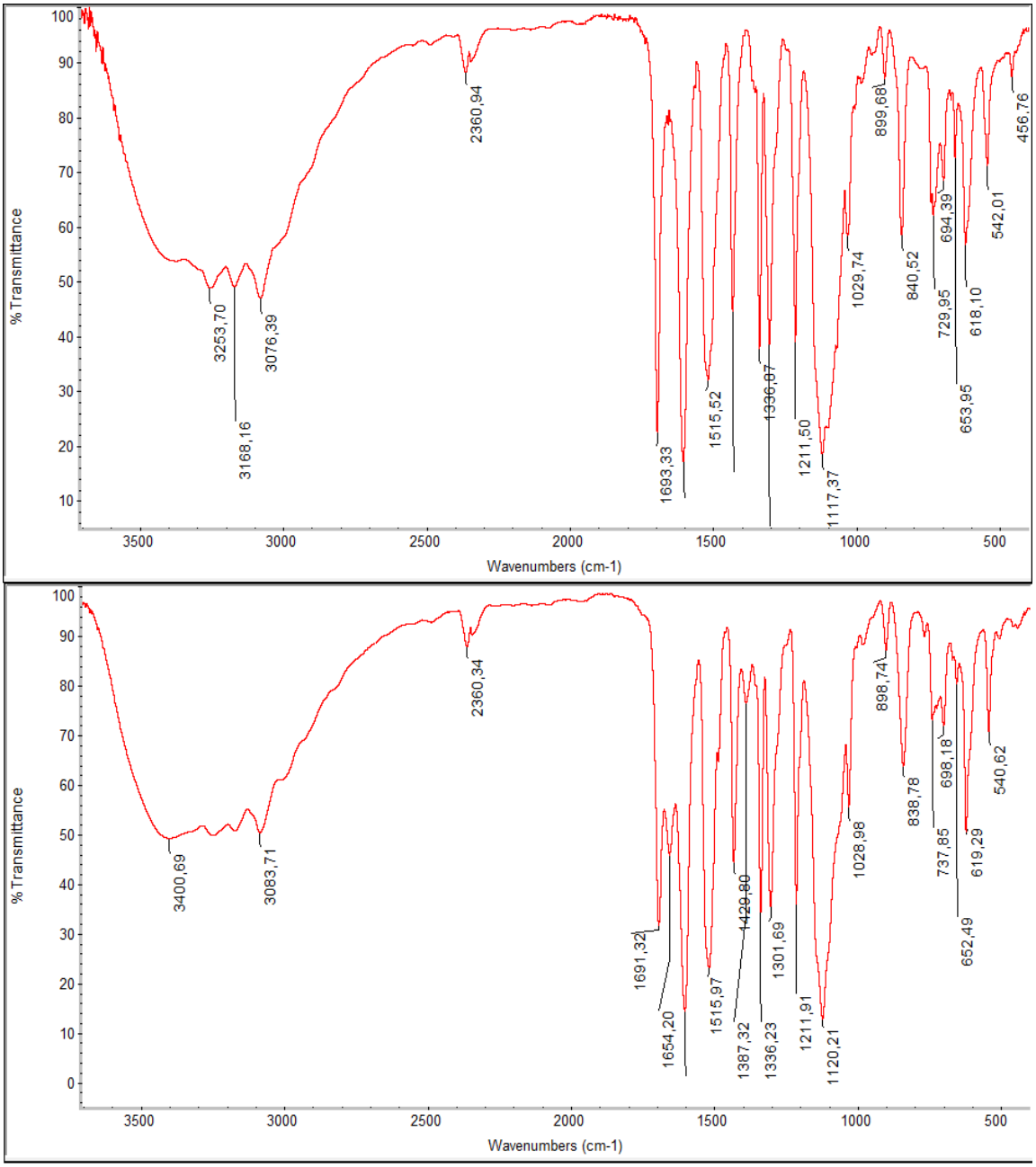

Figure S12: IR spectra comparison of the complexes (top) and xerogels (bottom) of copper(II) sulphate and **4PNA.**