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# Introduction

Organic fluoro compounds are an important class of compounds that are beneficial to chemistry in general and materials science in particular. This class of compounds possesses low polarity and high thermal stability because of the remarkable C-F bond strength. The molecular self-assembly of fluoro compounds are mainly governed by the weak interactions such as  $\pi-\pi_F$ , C-H···F, C-F··· $\pi_F$ , F···F, C-F···C=O, C-F··· $M^+$ , anion··· $\pi_F$  *etc.*<sup>1</sup> Such properties have been exploited in catalysis,<sup>2*a*</sup> liquid crystals,<sup>2*b*</sup> solid-state photoreactions,<sup>2*c*</sup> inclusion materials,<sup>2*d*</sup> chirality,<sup>2*e*</sup> molecular recognition and sensing,<sup>2*f*</sup> organic electronics,<sup>2*g*</sup> alternative energy,<sup>2*h*</sup> and biomedical applications.<sup>2*i*</sup> Among the various organic fluoro compounds, perfluoro aromatic units play an important role in designing intriguing supramolecular assemblies. Research in this area received thrust with the early discovery of phenyl-perfluorophenyl stacking interactions in benzenehexaflurobenzene complex,<sup>3a</sup> later a crystal structure of the benzene-d<sub>6</sub>-hexaflurobenzene complex has also been reported.<sup>3b</sup> Since then a lot of effort has been made to exploit these weak interactions in crystal engineering.4-6 Phenylperfluorophenyl stacking interaction has been exploited in carrying out topochemical [2+2] photodimerization and photopolymerization of olefinic compounds.<sup>7</sup> Gdaniec et al. have shown that phenyl-perfluorophenyl interaction plays an important role in self-assembling hydrogen bonded carboxylic acid dimers.<sup>8</sup> Weak interaction (20-50 kJ mol<sup>-1</sup>) involving anion and electron deficient aromatics (anion- $\pi$ ) is one of the non-covalent interactions currently being studied with vigor in supramolecular chemistry.9 Various studies indicate that such weak interaction offers a new avenue for the design of neutral anion receptors.<sup>10</sup> Anion- $\pi$  interaction has been successfully implemented in developing synthetic ionchannel that displays remarkable anion selectivity.<sup>11</sup> Anion- $\pi$ interaction is also shown to display strong synergistic effect along with cation- $\pi$  and  $\pi$ - $\pi$  interactions.<sup>12</sup>

As a part of our ongoing research endeavour to develop intriguing coordination compounds<sup>13</sup> displaying remarkable

# Studying fluorous interactions in a series of coordination compounds derived from mono-pyridyl ligands equipped with hydrogen bonding functionality: exploiting anion $\cdots \pi_F$ interaction in separating $ClO_4^$ anion from a competing mixture of anions<sup>†</sup>

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A series of coordination compounds (both coordination complexes (CCs) and coordination polymers (CPs)) *viz*. [Cu(L1)<sub>4</sub>·(SO<sub>4</sub>)·(DMSO)]CC1, [(H<sub>2</sub>O)<sub>2</sub>(DMSO)Cd(L1)<sub>2</sub>( $\mu_2$ SO<sub>4</sub>)(Cd(L1)<sub>2</sub>·(SO<sub>4</sub>)·(DMSO)·(H<sub>2</sub>O)] CC2, [Cu(L2)<sub>2</sub>(H<sub>2</sub>O)·(Cl)<sub>2</sub>] CC3, [Cu(L2)<sub>2</sub>( $\mu$ -SO<sub>4</sub>)(H<sub>2</sub>O)]<sub>∞</sub> CP1, [(Cu(L2)<sub>4</sub>( $\mu$ -SiF<sub>6</sub>)·3H<sub>2</sub>O]<sub>∞</sub> CP2, [(Cu(L3)<sub>4</sub>(ClO<sub>4</sub>))·ClO<sub>4</sub>·H<sub>2</sub>O]·CC4, [(Cu(L3)<sub>4</sub>(H<sub>2</sub>O))·H<sub>2</sub>O·2BF<sub>4</sub>] CC5, [((Cl)Cu(L3)<sub>4</sub>( $\mu$ -Cl)Cu(L3)<sub>4</sub>)·Cl·H<sub>2</sub>O] CC6, [(Cu<sub>2</sub>(L3)<sub>4</sub>( $\mu$ -Cl)<sub>2</sub>·(Cl)<sub>2</sub>)·H<sub>2</sub>O] CC7, [Cu(L3)<sub>2</sub>(Cl)<sub>2</sub>] CC8, and [(Cu(L4)<sub>4</sub>·(H<sub>2</sub>O)<sub>2</sub>)·SO<sub>4</sub>·5H<sub>2</sub>O] CC9 derived from ligands equipped with pyridyl and pentafluorophenyl/phenyl moieties along with hydrogen bonding backbone (amide/urea) with Cu<sup>II</sup>/Cd<sup>II</sup> metal centers have been synthesized and characterized by single crystal X-ray diffraction (SXRD). Their various fluorous interactions along with hydrogen bonding have been investigated. The results show that almost all the coordination compounds except CC9 studied herein display various fluorous interactions; in one such example *i.e.* in CC4, anion– $\pi_F$ along with other supramolecular interactions (F···F, C–H···F) shapes the supramolecular assembly, which is exploited to separate environmentally relevant perchlorate anion from a competing mixture of anions *viz*. SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, Cl<sup>-</sup> by following *in situ* synthesis of the corresponding coordination compound.

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<sup>†</sup> Electronic supplementary information (ESI) available: ORTEP diagram, hydrogen bonding parameter, PXRD patterns and TGA Plots of the compounds. CCDC 926124–926134. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce40359a

structure and properties (anion separation, metallogelation etc.), we have been investigating pyridyl based ligands equipped with hydrogen bonding backbone. To study the effect of both anion- $\pi$  and hydrogen bonding on the resultant supramolecular structures of coordination compounds, we synthesized three new ligands, namely N-(3-pyridyl), N'-(pentafluorophenyl) urea (L1),<sup>14a</sup> N-(3-picolyl)pentafluorobenzamide (L2) and N-(4-pyridyl)-pentafluorobenzamide (L3), equipped with both perfluorophenyl moiety and hydrogen bonding backbone; we also synthesized the nonfluorous analogue of L1 i.e. N-(3-pyridinyl)-N'-phenyl-urea (L4) in order to compare the corresponding structure of the coordination compound with that obtained from L1. These ligands were reacted with various transition metal (Cu<sup>II</sup>, Cd<sup>II</sup>) salts to produce as many as 11 new coordination compounds namely, [Cu(L1)4·(SO4)·(DMSO)]CC1, [(H2O)2(DMSO)Cd  $(L1)_2(\mu_2SO_4)(Cd(L1)_2(SO_4)(DMSO)(H_2O)]$  CC2,  $[Cu(L2)_2(H_2O)(Cl)_2]$ CC3,  $[Cu(L2)_2(\mu-SO_4)(H_2O)]_{\infty}$  CP1,  $[{Cu(L2)_4(\mu-SiF_6)}-3H_2O]_{\infty}$  CP2,  $[{Cu(L3)_4(ClO_4)} - ClO_4 + H_2O] CC4, [{Cu(L3)_4(H_2O)} - H_2O.2BF_4] CC5,$ 

$$\label{eq:cl} \begin{split} & [\{(Cl)Cu(L3)_4(\mu\text{-}Cl)Cu(L3)_4\}\text{-}Cl\text{-}H_2O]\ CC6, [\{Cu_2(L3)_4(\mu\text{-}Cl)_2\text{-}(Cl)_2\}\text{-}H_2O] \\ & CC7, [Cu(L3)_2(Cl)_2]\ CC8, [\{Cu(L4)_4\text{-}(H_2O)_2\}\text{-}SO_4\text{-}5H_2O]\ CC9. \end{split}$$

Single crystal structures of these coordination compounds were studied in detail in order to understand various weak noncovalent interactions involving perfluorophenyl ring, hydrogen bonding functionality and various anions. It may be important to mention that CSD searches with perfluorophenyl moiety, any transition metal and amide/ urea functionality as search fragments resulted in 33 and 11 hits, respectively.<sup>14b</sup> It was demonstrated that L3 was capable of separating  $ClO_4^-$  from a complex mixture of anions ( $Cl^-$ ,  $SO_4^{2-}$ ,  $BF_4^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ) in the form of a crystalline  $Cu^{II}$  coordination complex.

## **Results and discussions**

Thus, we reacted L1, L2, L3, L4 (Scheme 1) with various  $Cu^{II}$  and  $Cd^{II}$  salts in 1:0.5 (ligand:metal salt) molar ratio in





Table 1 Crystallograph.	ic parameters for	CC1-CC9, CP1, CI	P2								
Crystal parameters	CC1	CC2	CC3	CP1	CP2	CC4	CC5	CC6	CC7	CC8	CC9
CCDC number	926124	926125	926126	926133	926134	926127	926128	926129	926130	926131	926132
Empirical formula	$C_{50}H_{30}Cu$	$C_{52}H_{42}Cd_2$	$\mathbf{C}_{26}\mathbf{H}_{16}\mathbf{Cl}_2$	$C_{26}H_{16}Cu$	$C_{52}H_{34}Cu$	$C_{48}H_{22}Cl_2$	$\mathrm{C}_{48}\mathrm{H}_{24}\mathrm{B}_2$	$\mathrm{C}_{96}\mathrm{H}_{48}\mathrm{Cl}_4$	$C_{48}H_{22}Cl_4$	$\mathrm{C}_{24}\mathrm{H}_{10}\mathrm{Cl}_2$	$C_{48}H_{45}$
	$F_{20}N_{12}O_9S_2$	$F_{20} N_{12} O_{17} S_4$	$Cu F_{10}N_4O_3$	$\mathrm{F_{10}N_4O_7S}$	$F_{26}N_8O_7Si$	$CuF_{20}N_8O_{13}$	CuF <sub>28</sub> N <sub>8</sub> O <sub>6</sub>	$Cu_2F_{40}N_{16}O_{12}$	$Cu_2F_{20}N_8O_5$	$CuF_{10}N_4O_2$	CuN <sub>12</sub> O <sub>15</sub> S
Formula weight	1450.52	1840.02	756.87	782.03	1468.52	1433.18	1425.91	2646.32	1437.60	710.80	1137.56
Crystal size/mm	$0.28 \times$	$0.39 \times$	$0.78 \times$	$0.22 \times$	$0.28 \times$	$0.26 \times$	$0.32 \times$	$0.34 \times$	$0.28 \times$	$0.22 \times$	$0.30 \times$
	$0.17 \times 0.12$	$0.33 \times 0.20$	$0.06 \times 0.04$	0.10  imes 0.04	$0.17 \times 0.09$	$0.16 \times 0.08$	$0.26 \times 0.18$	$0.27 \times 0.18$	$0.24 \times 0.18$	0.14  imes 0.09	0.24  imes 0.15
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Tetragonal	Monoclinic	Tetragonal	Monoclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$	$Par{I}$	C2/c	$P2_1/m$	C2/c	P4/ncc	$P2_1/c$	P4/n	$P2_1/c$	$P2_1/c$	P4/n
ajằ	17.7530(15)	14.0690(15)	42.976(14)	4.8692(8)	42.460(15)	16.0850(7)	15.859(2)	22.2079(12)	20.7225(11)	12.1671(9)	17.8802(14)
$b/ m \AA$	17.8428(15)	16.4751(18)	7.960(3)	47.735(8)	8.054(3)	16.0850(7)	20.759(3)	22.2079(12)	10.7393(6)	14.9959(12)	17.8802(14)
$c/ m \AA$	19.7082(17)	17.8873(19)	8.547(3)	6.2805(10)	18.087(6)	20.6375(12)	16.412(2)	11.9119(13)	23.8872(13)	7.1861(5)	8.4406(9)
$\alpha^{ m o}$	102.910(2)	70.271(2)	06	06	90	06	06	06	06	06	06
Blo	102.857(2)	81.333(2)	96.420(5)	91.129(4)	98.341(6)	06	90.950(3)	06	101.5360(10)	100.349(2)	06
y/o	90.683(2)	67.876(2)	) 06	) ) 06	) 06	06	) ) 06	06	) 06	) 06	06
Volume/Å <sup>3</sup>	5920.0(9)	3614.0(7)	2905.5(18)	1459.5(4)	6120(4)	5339.5(5)	5402.4(13)	5874.8(8)	5208.6(5)	1289.82(17)	2698.5(4)
Z	4	2	4	2	4	4	4	2	4	2	2
F(000)	2908	1816	1500	782	2948	2852	2828	2620	2840	702	1164
$\mu$ Mo K $\alpha$ /mm <sup>-1</sup>	0.567	0.826	1.037	0.938	0.512	0.653	0.559	0.578	1.151	1.159	0.520
Temperature/K	100(2)	100(2)	298(2)	298(2)	298(2)	298(2)	100(2)	100(2)	298(2)	298(2)	298(2)
$R_{ m int}$	0.0778	0.0524	0.0592	0.055	0.0565	0.0588	0.0884	0.0814	0.0649	0.0592	0.0659
Range of $h, k, l$	-18/17,	-16/16,	-46/44,	-5/5,	-48/48,	-16/16,	-14/14,	-27/26,	-22/22,	-11/11,	-20/20,
	-18/18,	-18/18,	-8/7,	-20/54,	-9/8,	-16/16,	-18/18,	-27/27,	-11/11,	-14/14,	-20/20,
	-20/20	-20/19	6/6-	-6/7	-20/19	-21/21	-15/14	-14/14	-26/26	-6/6	6/6-
$\theta \min/\max/\circ$	1.09/21.32	1.21/24.11	1.91/22.50	1.71/24.00	0.97/23.99	1.79/21.57	1.28/19.00	1.30/25.80	1.74/23.13	1.70/19.57	1.61/24.19
Reflections collected/	32538/11	30827/11	5471/1909	5684/2286	$12\ 591/4655$	33 626/1556	26493/4317	55 537/5650	40938/7352	7004/1135	27596/2172
unique/observed	135/5040	435/8097	/1740	/1945	/2760	/1281	/2890	/4823	/5427	/939	/1943
$[I > 2\sigma(I)]$											
Data/restraints/	11 135/0/1666	11435/0/968	1909/0/209	2286/0/229	4655/0/435	1556/20/210	4317/0/838	5650/0/391	7352/0/784	1135/0/196	2172/0/190
parameters											
Goodness of fit on $F^2$	0.941	1.049	1.309	1.261	0.995	1.028	1.031	1.005	0.975	0.984	1.160
Final R indices	$R_1 = 0.0829$	$R_1 = 0.0688$	$R_1 = 0.1141$	$R_1 = 0.0949$	$R_1 = 0.0916$	$R_1 = 0.0678$	$R_1 = 0.0729$	$R_1 = 0.0982$	$R_1 = 0.0441$	$R_1 = 0.0399$	$R_1 = 0.0784$
$[I > 2\sigma(I)]$	$WR_2 = 0.2092$	$wR_2 = 0.1769$	$WR_2 = 0.2674$	$WR_2 = 0.2200$	$WR_2 = 0.2497$	$WR_2 = 0.2069$	$WR_2 = 0.1891$	$WR_2 = 0.2629$	$WR_2 = 0.1285$	$WR_2 = 0.1169$	$WR_2 = 0.2371$
R indices (all data)	$R_1 = 0.1518$	$R_1 = 0.0997$	$R_1 = 0.1244$	$R_1 = 0.1148$	$R_1 = 0.1386$	$R_1 = 0.0791$	$R_1 = 0.1097$	$R_1 = 0.1122$	$R_1 = 0.0663$	$R_1 = 0.0512$	$R_1 = 0.0847$
	$WR_2 = 0.2412$	$WR_2 = 0.1966$	$WR_2 = 0.2736$	$WR_2 = 0.2359$	$WR_2 = 0.2937$	$WR_2 = 0.2269$	$WR_2 = 0.2206$	$WR_2 = 0.2771$	$WR_2 = 0.1452$	$WR_2 = 0.1283$	$WR_2 = 0.2412$

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Fig. 1 a) Two crystallographically independent molecular complex in the asymmetric unit and b) 2D hydrogen bonded network in CC1.

separate trials. These resulted in a series of coordination polymers (CPs) and coordination complexes (CCs) depending on counteranion used. Suitably grown single crystals of the CPs and CCs were then subjected to SXRD experiments (see Table 1). It may be mentioned here that all the crystals were of relatively poor X-ray quality and our continuous efforts to grow better X-ray quality crystals proved unsuccessful.

#### Crystal structure of $[Cu(L1)_4 \cdot (SO_4) \cdot (DMSO)]$ (CC1)

Reaction of L1 with  $CuSO_4$  in aqueous DMSO/acetonitrile mixture resulted in X-ray quality crystals (blue, block shaped) of CC1. SXRD data revealed that the compound crystallized in the centrosymmetric triclinic space group  $P\overline{1}$ . The asymmetric unit contained two coordination complex molecules of CC1 – each having a Cu<sup>II</sup> metal center displaying slightly distorted octahedral geometry wherein the equatorial positions were coordinated by the four ligand molecules and the apical centers were occupied by sulfate anion and DMSO (both disordered) molecules. The crystallographically independent molecules in the asymmetric unit were held together by  $\pi_{\rm F} - \pi_{\rm F}$  (~4.089 Å) and C-F $\cdots \pi_{\rm F}$  (~3.070 Å) interactions. The ligand molecules display highly non-planer conformation (dihedral angles: central urea moiety-terminal pyridyl units = 8.6-14.3°, central urea moiety-pentafluoro rings = 64.0-70.8°, pentafluoro rings-terminal pyridyl rings =  $74.2-81.5^{\circ}$ ). The urea moiety was found to be involved in hydrogen bonding interactions with the disordered sulfate anion of the adjacent coordination complex  $[N \cdots O = 2.784(17) - 3.34(3) \text{ Å}; \angle N - H \cdots O =$ 137.0-177.5°] resulting in a two dimensional hydrogen bonded network. Intermolecular F···F (2.723(13)-2.997(12) Å) and C-F··· $\pi$  (~3.063 Å) interactions were also observed within the crystal lattice (Fig. 1).

# $\label{eq:crystal} \begin{array}{l} Crystal \ structure \ of \ [(H_2O)_2(DMSO)Cd(L1)_2 \\ (\mu_2\text{-}SO_4)(Cd(L1)_2\cdot(SO_4)\cdot(DMSO)\cdot(H_2O)](CC2) \end{array}$

Reaction of L1 with CdSO<sub>4</sub> in aqueous DMSO/acetonitrile mixture resulted in X-ray quality crystals (colourless, block shaped) of CC2. SXRD data revealed that the compound crystallized in the centrosymmetric triclinic space group  $P\bar{1}$ . The asymmetric unit contained a bi-metallic Cd<sup>II</sup> coordination complex which was formed by sulfate bridging; each metal center displayed slightly distorted octahedral geometry. The equatorial positions of the metal centers were coordinated the O atoms of sulfate, DMSO and water molecules whereas the axial positions were occupied by the pyridyl N atoms. Some disordered solvent molecules which could not be identified from difference Fourier map were removed by applying SQUEEZE.<sup>14c</sup> The ligands displayed highly non-planar conformation (dihedral angles: central urea moiety-terminal pyridyl units = 4.07-11.90°, central urea moiety-pentafluoro rings = 56.0-59.86°, pentafluoro rings-terminal pyridyl rings = 55.5-66.4°). The bi-metallic coordination complex molecules were further assembled into a 2D hydrogen bonded network sustained by intermolecular urea-sulfate hydrogen bonding 2D networks were further packed in parallel fashion sustained



Fig. 2 a) Discrete molecular complex and b) interdigited packing of the 2D network in CC2.



**Fig. 3** a) Unidirectional propagation of molecular complex *via* H bonding and b) overall 2D propagation of 1D hydrogen bonded network sustained F…F interactions in **CC3**.

by inter-layer F…F (2.915(8)–2.937(9) Å) and  $\pi_F - \pi_F$  (3.838 Å) interactions (Fig. 2).

### Crystal structure of [Cu(L2)<sub>2</sub>(H<sub>2</sub>O)·(Cl)<sub>2</sub>] CC3

Reaction of L2 with  $CuCl_2$  in aqueous ethanol/methanol mixture resulted in X-ray quality crystals (blue, needle shaped) of CC3. The compound CC3 crystallized in the centrosymmetric monoclinic space group C2/c. The crystal was thin and poorly diffracting, which resulted a low quality data set which was reflected in its high *R* factor (11.41%). The asymmetric unit was comprised of half occupied  $Cu^{II}$  and a water molecule (coordinated to the metal center) – both sitting on a 2-fold axis, one fully occupied ligand and one chloride ion – both coordinated to the metal center, which displayed a highly distorted square pyramidal geometry wherein the equatorial positions were occupied by N and Cl and the axial position was coordinated by the water molecule. The ligand displayed a highly nonplanar conformation (dihedral angles: central amide moiety-terminal pyridyl units = 85.9°, central amide moietypentafluoro rings = 55.2°, pentafluoro rings-terminal pyridyl rings = 37.1°). The coordination complex self-assembled into 1D hydrogen bonded network sustained by N-H···O interactions [N···O = 2.9 (13) Å;  $\angle$ N-H···O = 146.7°] involving the amide functionality. The 1D networks were further self-assembled into a 2D network *via* O-H···Cl interactions [O···Cl = 3.072(6) Å]. F···F short contacts (2.675(19)-2.960(18) Å) were also observed between the adjacent 2D networks (Fig. 3).

#### Crystal structure of $[Cu(L2)_2(\mu$ -SO<sub>4</sub>)(H<sub>2</sub>O)]<sub>x</sub> (CP1)

Reaction of L2 with CuSO<sub>4</sub> in aqueous ethanol/methanol mixture resulted in X-ray quality crystals (blue, plate shaped) of CP1. The compound CP1 crystallized in the centrosymmetric monoclinic space group  $P2_1/m$ . The asymmetric unit was comprised of a fully occupied metal bound ligand, a half occupied Cu<sup>II</sup>, a half occupied water molecule and half a molecule of counteranion sulfate - all the partially occupied species were residing on a mirror plane. The ligand displayed non-planar conformation (dihedral angles: central amide moiety-terminal pyridyl units = 62.2°, central amide moiety-pentafluoro rings = 55.0°, pentafluoro rings-terminal pyridyl rings =  $41.3^{\circ}$ ). The metal center displayed distorted square pyramidal geometry wherein the equatorial sites were occupied by N and O atoms of the pyridyl ligand, a counteranion sulfate and a water molecule, and the axial position was coordinated by the O atoms of a bridging sulfate. Classical amide-amide intra-polymeric hydrogen bonding was observed  $[N \cdots O = 2.874 (9) Å;$  $\angle N-H\cdots O = 178.2^{\circ}$ ]. The 1D chains were further packed in parallel fashion into 2D sheet sustained by O-H···O [O···O = 2.735-2.838 Å] interactions involving metal bound water and sulfate O atoms of the adjacent chains. Short contact interactions like C=O··· $\pi_{\rm F}$  (3.191 Å) were observed in this structure (Fig. 4).

#### Crystal structure of $[{Cu(L2)_4(\mu-SiF_6)}\cdot 3H_2O]_{\infty}$ (CP2)

Reaction of L2 with  $Cu(BF_4)_2$  in aqueous ethanol/methanol mixture resulted in X-ray quality crystals (blue, plate shaped) of CP2. SXRD analysis established the existence of  $SiF_6^{2-}$  instead of  $BF_4^{-}$  as counteranion; it was known in the literature



Fig. 4 a) 1D coordination polymer displaying classical amide…amide hydrogen bonding and b) parallel packing of the 1D coordination polymeric chains sustained via O-H…O interactions in CP1.



Fig. 5 Parallel packing of 1D coordination polymeric chains sustained via F···F interactions in CP2.

that such occurrence happened due to the reaction of BF<sub>4</sub> anion with SiO<sub>2</sub> component of a reaction glass vessel.<sup>14d</sup> The compound CP2 crystallized in the centrosymmetric monoclinic space group C2/c. The asymmetric unit was comprised of one  $Cu^{II}$  metal center, one metal coordinated  $SiF_6^{2-}$  – both residing on a 2-fold axis, two fully occupied ligands coordinated to the metal center and three lattice occluded water molecules. Unidentified solvent molecules that could not be identifed from difference Fourier map were removed by applying SQUEEZE.<sup>14c</sup> The ligand displayed highly non-planar conformation (dihedral angles: central amide moiety-terminal pyridyl units = 87.6-76.7°, central amide moiety-pentafluoro rings = 57.4-48.4°, pentafluoro rings-terminal pyridyl rings = 72.9-30.9°). The metal center displayed slightly octahedral geometry wherein the equatorial positions were occupied by pyridyl N atoms and the apical positions were coordinated by F atoms coming from the bridging  $SiF_6^{2-}$  resulting in a 1D coordination polymer. The 1D chains were packed in parallel fashion and the lattice occluded water molecules were tightly held in the crystal structure via O-H···O [O···O = 2.818(14)-2.886(12) Å] and N-H…O [N…O = 2.768(13)-2.852(12) Å; ∠N- $H \cdots O = 158.2 - 165.4^{\circ}$  interactions involving the amide moiety.

Inter-chain F…F (2.891 Å), C–F… $\pi_F$  (3.116 Å) interactions were also observed (Fig. 5).

#### $[{Cu(L3)_4(ClO_4)} \cdot ClO_4 \cdot H_2O] CC4$

Reaction of L3 with  $Cu(ClO_4)_2$  in aqueous ethanol/methanol mixture resulted in X-ray quality crystals (blue, plate shaped) of CC4. The compound CC4 crystallized in the tetragonal space group P4/ncc. In the asymmetric unit the metal center  $Cu^{II}$  (residing on a 4-fold symmetry) was coordinated by a fully occupied ligand and a ClO<sub>4</sub><sup>-</sup> counteranion disordered over a 4-fold axis; a non-coordinated highly disordered counteranion ClO<sub>4</sub><sup>-</sup> and a water molecule - both located on a 4-fold axis - were also present. The metal center displayed distorted square pyramidal geometry. The ligand displayed a highly non-planar conformation (dihedral angles: central amide moiety-terminal pyridyl units = 17.71°, central amide moiety-pentafluoro rings = 78.62°, pentafluoro rings-terminal pyridyl rings = 84.35°). However, the coordinated counteranion  $ClO_4^-$  was found to display anion- $\pi$  interactions with pentafluorophenyl ring ( $d_{ClO_4}$  oxygen-pentafluoro ring centroid ~ 3.490 Å,  $\angle O_{pentafluoro ring centroid}$ - $C_{pentafluoro ring} \sim 96.14^{\circ}$ ). In the



Fig. 6 a) anion- $\pi$  interaction between anion and pentafluoro ring and b) overall packing diagram viewed along c axis in CC4



Fig. 7 a) Anion- $\pi$  interaction between BF<sub>4</sub><sup>-</sup> and pentafluoro ring and b) lattice occluded water mediated hydrogen bonded dimers in CC5.

complex, appreciable F…F contact (2.806 Å) and C–H…F interactions (C…F = 3.243 Å,  $\angle$ C–H…F = 137°) were also observed (Fig. 6).

## $\left[\left\{Cu(L3)_4(H_2O)\right\}\cdot H_2O\cdot 2BF_4\right](CC5)$

Reaction of L3 with  $Cu(BF_4)_2$  in aqueous ethanol/methanol mixture resulted in X-ray quality crystals (blue, block shaped) of CC5. The compound CC5 crystallized in the monoclinic space group  $P2_1/c$ . The asymmetric unit contained four ligands, one metal center ( $Cu^{II}$ ), two  $BF_4^-$  anion and one water molecule. The ligand displayed a highly non-planar conformation (dihedral angle: pentafluoro–phenyl ring = 62.40–85.17°, the dihedral angle between amide plane–phenyl ring = 76.72–87.60°, the corresponding angle with amide plane–pentafluoro ring = 57.40–74.1°). Interestingly, the amide functionality did not display any classical amide…amide hydrogen bonding with the lattice occluded solvent molecules, which in turn were interacting with the metal bound water resulting in solvate mediated hydrogen bonded dimer of the coordination

complex (O···O = 2.689(11)–2.858(12) Å). Fluorine atoms of BF<sub>4</sub><sup>-</sup> anion were involved in various hydrogen bonding [N···F = 2.751(14)–2.887(14) Å;  $\angle$ N–H···F = 151.1–172.2°] with the amide moiety. The counteranion BF<sub>4</sub><sup>-</sup> were found to display anion– $\pi$  interactions with the adjacent pentafluorophenyl rings ( $d_{\text{tetrafluoroborate fluorine-pentafluoro ring centroid} \sim 2.963–3.426$  Å,  $\angle$ F<sub>tetrafluoroborate fluorine-pentafluoro ring centroid</sub> ~ 2.963–3.426 Å,  $\angle$ F<sub>tetrafluoroborate-pentafluoro ring centroid</sub> ~ 98.13–99.03°). Various other fluorous short contacts such as F···F [~2.883(19), 2.901(14) Å], C–F··· $\pi$ .(~3.166 Å), C–F··· $\pi$ F (~3.097 Å) were observed within the crystal lattice (Fig. 7).

Interestingly when L3 was reacted with CuCl<sub>2</sub> in aqueous ethanol/methanol mixture, it gave three different coordination compounds namely [{(Cl)Cu(L3)<sub>4</sub>( $\mu$ -Cl)Cu(L3)<sub>4</sub>}·Cl·H<sub>2</sub>O] CC6, [{Cu<sub>2</sub>(L3)<sub>4</sub>( $\mu$ -Cl)<sub>2</sub>·(Cl)<sub>2</sub>}·H<sub>2</sub>O] CC7 and [Cu(L3)<sub>2</sub>(Cl)<sub>2</sub>] (CC8) under different temperatures; while CC6 was formed in a crystallization room equipped with air conditioning that maintained a constant temperature of 22 °C round the clock, CC7 and CC8 were grown concomitantly during summer when the room temperature was ~30–40 °C with occasional formation of CC7 alone in a few batches (Scheme 2).



Scheme 2



Fig. 8 a) Discrete molecular complex and b) 2D propagation of the supramolecular assembly along the a-b plane sustained by N–H···O and N–H···Cl interactions.

#### $[\{(Cl)Cu(L3)_4(\mu\text{-}Cl)Cu(L3)_4\}\text{-}Cl\text{-}H2O] CC6$

The block shaped blue crystals of CC6 crystallized in the tetragonal space group P4/n. The asymmetric unit contained two metal centers, two coordinated chloride - all resided on a 4-fold axis, two ligands both coordinated to each metal center, one uncoordinated chloride seated on a glide plane and a solvate water molecule. The complex CC6 can be best described as a bimetallic coordination complex wherein the metal centers were bridged by chloride; while one of the Cu<sup>II</sup> centers displayed perfect octahedral geometry, the other one showed slightly distorted square pyramidal geometry. Some disordered solvent molecules which could not be identified from difference Fourier map were removed by applying SQUEEZE.<sup>14c</sup> The equatorial positions in both metal centers were occupied by pyridyl N atoms and the apical positions were coordinated by chloride on both the metal centers. The ligand displayed highly non-planar conformation (the dihedral angles: pentafluoro-phenyl ring = 73.03-73.19°, amide plane-phenyl ring = 46.21°-57.80°, amide plane-pentafluoro ring =  $28.43-28.11^{\circ}$ ). The complex was found to propagate through the *a*-*b* plane *via* hydrogen bonding involving amide N-H moiety and a solvate water molecule as well as a noncoordinated chloride anion  $[N \cdots O = 2.745(8), \angle N - H \cdots O =$ 166.5°; N…Cl = 3.050(7) Å, ∠N-H…Cl = 165.3°]. Supramolecular assembly was governed by various fluorous interactions viz. F…F short contact (2.939(7)-2.955(7) Å), weak C-H…F interaction (C…F = 3.184 Å,  $\angle$ C–H…F = 135°) and  $\pi_{\rm F}$ – $\pi_{\rm F}$ stacking interaction (~4.00 Å). Interestingly, orthogonal C- $F \cdots C = O$  interaction (2.904 Å) was observed in this complex, which is not so common in the literature (Fig. 8).<sup>1</sup>

#### $[{Cu_2(L3)_4(\mu-Cl)_2\cdot(Cl)_2}\cdot H_2O] CC7$

The sky-blue plate shaped crystals of CC7 crystallized in the monoclinic space group  $P2_1/c$ . The crystal was thin and poorly diffracting, which resulted low quality data. The asymmetric unit contained four fully occupied ligands, two metal atoms, one solvate water molecule and four coordinated chlorides. It is a bimetallic complex wherein two crystallographically independent chlorides acted as bridges to coordinate the adjacent metal centers. Both the metal centers displayed slightly distorted square pyramidal geometry wherein the equatorial positions on each metal center were occupied by



**Fig. 9** 1D propagation of the supramolecular assembly *via* O–H···O and N–H···CI hydrogen bonding in **CC7**.

the pyridyl N and chloride whereas the apical positions in each metal center were coordinated by chloride. The ligand displayed a highly non-planar conformation (dihedral angles: central amide moiety–terminal pyridyl units = 11.89°–22.54°, central amide moiety–pentafluoro rings = 58.79°–76.61°, pentafluoro rings–terminal pyridyl rings = 39.43°–58.67°). The amide moiety did not display classical amide…amide hydrogen bonding; instead, it was involved in hydrogen bonding interactions with both the metal bound chloride and solvate water molecule resulting into 1D network [N···Cl = 3.174(4)– 3.272(4) Å ;  $\angle$ N–H···Cl = 159.6–168.8°, N···O = 2.913 (5) Å ;  $\angle$ N–H···O = 172.9°, O···O = 2.844(6)]; in this complex various fluorous contacts *viz*. F···F short contact (~2.822 Å), a rarely observed<sup>1</sup> C–F···C=O interaction (2.911 Å), and C–F··· $\pi$  interactions (~3.054 Å) were observed (Fig. 9).

#### $[Cu(L3)_2(Cl)_2](CC8)$

The deep blue needle shaped crystals of CC8 crystallized in the monoclinic centrosymmetric space group  $P2_1/c$ . The asymmetric unit contained one half occupied Cu<sup>II</sup> metal center located on a center of symmetry, a ligand and a chloride both coordinated to the metal center. It is a slightly distorted square planar complex wherein the metal center was coordinated by two ligands and two chloride ions in a trans fashion. The ligand displayed highly non-planar conformation (dihedral angles: central amide moiety-terminal pyridyl units = 9.47°, central amide moiety-pentafluoro rings = 56.04°, pentafluoro rings-terminal pyridyl rings = 49.29°). In the crystal structure, the molecules were held together by N-H···Cl interactions [N···Cl = 3.287 (4) Å;  $\angle$ N-H···Cl = 152.4°] leading to the formation of a 2D network. Several fluorous short contacts such as F…F (2.710(8)-2.873(7) Å), C-F··· $\pi$  (3.137 Å), C-H···F (C···F = 3.227(7), ∠C-H···F = 138° were also observed (Fig. 10).

#### $[{Cu(L4)_4 \cdot (H_2O)_2} \cdot SO_4 \cdot 5H_2O] (CC9)$

Reaction of L4 with  $CuSO_4$  in aqueous ethanol/methanol mixture resulted in X-ray quality crystals (blue, block shaped) of CC9. The compound CC9 crystallized in the tetragonal space group P4/n. The asymmetric unit was comprised of one Cu<sup>II</sup>



Fig. 10 a) Discrete molecular complex and b) its propagation in 2D sustained by N–H…Cl hydrogen bonding in CC8.

metal center, two coordinated water molecules - all located on a 4-fold axis, one fully occupied ligand coordinated to the metal center, one solvate water molecule located a glide plane and disordered around a center of symmetry, an uncoordinated counteranion sulfate seating on a 4-fold rotation-inversion axis and a solvate water molecule disordered over two positions. It is a coordination complex wherein the metal center displayed a perfect octahedral geometry; the equatorial positions were occupied by the pyridyl N atoms whereas the apical positions were coordinated by the water molecules. The ligand displayed a non-planar conformation (dihedral angles: central urea moiety-terminal pyridyl units = 30.08°, 15.43°; terminal pyridyl rings =  $20.43^\circ$ ). The uncoordinated sulfate counteranion was found to be involved in extensive hydrogen bonding with the urea functionalities of the neighbouring metal complexes; all four O atoms of the sulfate was found to be involving in N-H...O interactions with the urea moieties  $[N \cdots O = 2.836(7) - 2.981$  (6) Å;  $\angle N - H \cdots O =$ 152.4-167.9°]. Further hydrogen bonding interactions involving the metal bound water, lattice occluded water and urea carbonyl O atom lead to the formation of an overall 3D network. Weak interactions such as C-H··· $\pi$  (3.66 Å) were also present. However,  $\pi$ - $\pi$  interactions, as observed in its fluorous analogue (CC1), were not observed in this structure (Fig. 11).

#### Anion separation

Anion separation and anion binding is important in the context of environmental cleanup.<sup>15</sup> Perchlorate ( $ClO_4^-$ ) anion is an important environmental contaminant that causes various health hazards. It can halt the production of thyroid hormone.<sup>16</sup> Therefore selective removal of  $ClO_4^-$  is important. From the crystal structures of CC4 and CC5 (*vide supra*), it is evident that the counteranion in both the structures display



Fig. 11 a) Discrete molecular complex and b) its propagation in 3D sustained by O–H…O and N–H…O hydrogen bonding interactions in CC9.

anion- $\pi$  interaction with the pentafluoro ring; one of the counteranions (ClO<sub>4</sub><sup>-</sup>) in CC4 is also coordinated to the metal center. We have taken cue from this observation and tried to exploit it in selective separation of ClO<sub>4</sub><sup>-</sup> via in situ crystallization. It may be noted that the hydration energies of ClO<sub>4</sub> and BF<sub>4</sub><sup>-</sup> are significantly different ( $\Delta_{hyd}G^*$ , -430 kJ mol<sup>-1</sup>;  $\Delta_{\text{hvd}}G^*$ , -190 kJ mol<sup>-1</sup>)<sup>17</sup> and it would normally be difficult to get selectivity towards ClO4 over BF4 as it would have to overcome Hofmeister bias.18 Considering significant differences in the supramolecular environment of the respective anions  $(ClO_4^- \text{ and } BF_4^-)$  in CC4 and CC5 as discussed above, we tried to separate ClO<sub>4</sub><sup>-</sup> from a complex mixture of aqueous solution containing competing anions namely  $SO_4^{2-}$ ,  $NO_3^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $Cl^-$ . For this purpose, we have carried out two sets of experiments under two different conditions (condition I and II). In condition I, L3 was reacted with a mixture of CuSO<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, Cu(ClO<sub>4</sub>)<sub>2</sub>, Cu(BF<sub>4</sub>)<sub>2</sub>, and CuCl<sub>2</sub> in aqueous ethanol/methanol (metal:ligand = 1:2). In condition II, all the metal salts except  $Cu(ClO_4)_2$  were taken in twice the amount used in condition I. FT-IR, PXRD, elemental analysis and EDX data (Fig. 12 and 13) clearly indicated that the anion ClO<sub>4</sub><sup>-</sup> was separated out exclusively as crystalline CC4 in each case. Thus it is apparent that the synergistic effect of both anion-metal coordination and anion- $\pi$  interactions in the crystal structure of CC4 play a crucial role in selective separation of  $ClO_4^-$  (Scheme 3).

### Conclusion

In this present work a series of coordination compounds *viz.* **CC1–CC8**, **CP1** and **CP2** derived from monopyridyl ligands equipped with hydrogen bonding functionality (urea/amide) and perfluoro moiety have been synthesized and the corresponding single crystal structures were determined in order to study the various fluorous interactions such as  $\pi-\pi_F$ ,  $\pi_F-\pi_F$ , C–F···H, C–F··· $\pi_F$ , F···F, C–F···C=O, C–F··· $M^+$ , anion··· $\pi_F$  present in the crystal structures. Except C–F··· $M^+$ , all the other fluorous interactions were present in these structures. In CC1 intermolecular F···F and C–F··· $\pi$  interactions were evident; in CC3 only F···F short contacts were present; in CP1, C=O··· $\pi_F$  could be seen; in CP2 inter-chain F···F and C–F··· $\pi_F$  were the main fluorous interactions. In CC4

# ANION SEPARATION TABLE FOR CC4



## **ELEMENTAL ANALYSIS TABLE**

As synthesized CC4	Cond. I	Cond. II
Calc. for $C_{48}H_{22}Cl_2F_{20}N_8O_{13}Cu$	Calc. for	Calc. for
(%) C,40.23;H,1.55;N,7.82; FoundC,40.66; H,1.82; N,7.36	$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	C <sub>48</sub> H <sub>22</sub> Cl <sub>2</sub> F <sub>20</sub> N <sub>8</sub> O <sub>13</sub> Cu (%) C,40.23;H,1.55;N,7.82; foundC,41.07;H,1.40;N,6.98

Fig. 12 PXRD patterns, FT-IR spectra, and elemental analysis data in various conditions of CIO<sub>4</sub><sup>-</sup> separation for CC4.



Fig. 13 EDX data for condition I (a) and condition II (b) showing presence of chlorine in both conditions.



anion– $\pi_{\rm F}$  interactions along with pentafluorophenyl ring F…F contacts and C–H…F interactions were prominent. In CC5 along with anion– $\pi_{\rm F}$  and F…F short contacts, C–F… $\pi$  and C–F… $\pi_{\rm F}$  were noticed; CC6 contained F…F short contacts, weak C–H…F interactions,  $\pi_{\rm F}$ – $\pi_{\rm F}$  stacking interactions, rarely observed C–F…C=O interaction. In CC7, F…F short contacts, C–F…C=O interactions and C–F… $\pi$  interactions, and lastly in CC8 short contacts like F…F, C–F… $\pi$  and C–H…F were present. It is interesting to note that in the nonfluorous analogue of CC1 *i.e.* CC9, no  $\pi$ – $\pi$  interactions were observed whereas in CC1,  $\pi_{\rm F}$ – $\pi_{\rm F}$  interaction has been exploited to separate perchlorate (ClO<sub>4</sub><sup>2–</sup>) from a competing mixture of anions *viz.* SO<sub>4</sub><sup>2–</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>.

## **Experimental section**

## Materials and method

All chemicals were commercially available and used without further purification. The elemental analysis was carried out using a Perkin-Elmer 2400 Series-II CHN analyzer. FT-IR spectra were recorded using Perkin-Elmer Spectrum GX, and TGA analyses were performed on a SDT Q Series 600 Universal VA.2E TA instrument. Powder X-ray patterns were recorded on a Bruker AXS D8 Advance Powder (Cu K $\alpha_1$  radiation,  $\lambda =$ 1.5406 Å) Diffractometer. The mass spectrum was recorded on QTOF Micro YA263. NMR spectra were recorded using 300 MHz Bruker Avance DPX300 spectrometer.

## Synthesis of L1 (N-(3-pyridyl), N -(pentafluorophenyl) urea)

Synthetic procedure: the synthesis of ligand includes two steps a) and b).

a) This step includes synthesis of nicotinoyl azide which is done according to ref. 19.

b) In the next step nicotinoyl azide (1.00 g, 6.75 mmol) was dissolved in dry toluene (50 mL) and stirred at reflux for 2 h when no more  $N_2$  was evolved. The solution was cooled to room temperature, then 2,3,4,5,6-pentafluoroaniline (1.1 g, 6.01 mmol) in toluene (10 ml) was added dropwise through an addition funnel and a colorless precipitation was obtained. The suspension was stirred for 15 min at room temperature. The entire mass was evaporated, the white mass was purified through column chromatography, 60–120 mesh silica and 4% methanol/chloroform as eluent.

Analytical data: (yield: 450 mg, 24.7%) m.p.: 196 °C. Elemental analysis calcd for  $C_{12}H_6 F_5 N_3O$  (%): C 47.54, H 1.99, N 13.86. Found: C 48.04, H 2.01, N 13.54. <sup>1</sup>H NMR (500 MHz, [D6] DMSO):  $\delta$  = 9.286 (s, 1H, N–H), 8.67 (s, 1H, N–H), 8.613–8.616 (d, J = 1.5 Hz 1H, Py–H), 8.220–8.211 (d, J = 4.5 Hz, 1H, Py–H), 7.922–7.906 (d, J = 8 Hz, 1H, Py–H), 7.334–7.308 (dd, J = 4.5, 1 Hz, 1H, Py–H), IR (KBr pellet): 3294 (s, N–H stretch), 3259 (m, aromatic C–H stretch), 3134w, 3101w, 2899m, 2827w, 1680 (s, urea C=O stretch), 1653s, 1600s, 1548 (s, amide N–H bend), 1525s, 1489s, 1410w, 1329s, 1288s, 1226s, 1193m, 1062s, 1041s, 1003s, 979s, 802s, 705s cm<sup>-1</sup>. HRMS ESI (CH<sub>3</sub>OH): m/z (%): 304 [(PyNHCONHC<sub>6</sub>F<sub>5</sub>)]<sup>+</sup>, 121, 301.

## Synthesis of L2 (N-(3-picolyl)-pentafluorobenzamide)

Synthetic procedure: 2,3,4,5,6-pentafluorobenzoyl chloride (1.00 g, 4.34 mmol) was taken in a 250 ml RB flask in 80 ml DCM, 3-picolylamine (0.47 g, 4.34 mmol) in 30 ml DCM was dropwise added to this solution at 0  $^{\circ}$ C and the mixture was then allowed to stir for 12 hours at room temperature. Then the resulting solution was evaporated, a white mass was obtained and recrystallized in methanol-water mixture. Yield: 65% (0.85 g, 2.8 mmol).

Analytical data: m.p.: 118 °C. Elemental analysis calcd for  $C_{13}H_7F_5N_2O$  (%): C 51.67, H 2.33, N 9.27. Found: C 51. 4, H 2.13, N 9.08. <sup>1</sup>H NMR (500 MHz, [D6] DMSO):  $\delta$  = 9.522 (s, 1H, N–H), 8.552 (s, 1H, Py–H), 8.502–8.494 (d, 1H, *J* = 4 Hz, Py–H), 7.728–7.712 (d, 1H, *J* = 8 Hz, Py–H), 7.420–7.395 (dd, *J* = 8, 4.7 Hz, 1H, Py–H), 4.662 (s, 2H,–CH<sub>2</sub>–), IR (KBr pellet): 3180 (s, N–H stretch), 2985s, 2970m, 2819s, 1677 (s, urea C=O stretch), 1656w, 1627w, 1571 (s, amide N–H bend), 1525s, 1449s, 1429w, 1413m, 1365s, 1326s, 1269m, 1118s, 1053s, 1037s, 983s, 881m, 802s, 742m, 709s, 682m, 646m, 632m cm<sup>-1</sup>. HRMS ESI (CH<sub>3</sub>OH): *m/z* (%): 302 [(PyCH<sub>2</sub>NHCOC<sub>6</sub>F<sub>5</sub>]]<sup>+</sup>, 121, 301.

#### Synthesis of L3 (N-(4-pyridyl)-pentafluorobenzamide)

Synthetic procedure: 4-aminopyridine (0.42 g, 4.34 mmol) was taken in a 250 ml RB flask in 40 mL THF. 2,3,4,5,6-Pentafluorobenzoyl chloride (0.41 g, 4.34 mmol) in 30 ml DCM was added to this solution at 0 °C and the mixture was stirred for 30 minutes. Then the resulting solution was stirred for 6 days at room temperature. The product was separated as white colored precipitate, the precipitate was filtered and used without further purification. Yield: 70% (0.88 g, 3.05 mmol).

Analytical data: m.p.: 159 °C. Elemental analysis calcd for  $C_{12}H_5F_5N_2O$  (%): C 50.01, H 1.75, N 9.72. Found: C 49.45, H 1.96, N 9.42.<sup>1</sup>H NMR (300 MHz, [D6] DMSO):  $\delta$  = 11.407 (s, amide N–H), 8.551–8.541 (d, J = 5 Hz, 2H, Py–H), 7.641–7.632 (d, J = 4.5, 2H, Py–H), IR (KBr pellet): 3169 (s, N–H stretch), 3051 (m, aromatic C–H stretch), 2968s, 2883m, 2804w, 1708 (s, urea C=O stretch), 1651s, 1626s, 1595 (s, amide N–H bend), 1537s, 1514s, 1492s, 1421m, 1338s, 1301s, 1219s, 995s, 947s, 864s, 773m, 682w, 669m, 565s, 538s cm<sup>-1</sup>. HRMS ESI (CH<sub>3</sub>OH): m/z (%): 289 [(PyNHCOC<sub>6</sub>F<sub>5</sub>)]<sup>+</sup>, 96.

#### Synthesis of L4 (N-(3-pyridinyl)-N' -phenyl-urea)

Ligand is synthesized according to the literature procedure<sup>20</sup>

#### Synthesis of CCs and CPs

[Cu(L1)<sub>4</sub>·(SO<sub>4</sub>)·(DMSO)] CC1. Coordination complexes CC1 was synthesized by layering an aqueous ethanolic solution of CuSO<sub>4</sub> (12 mg, 0.049 mmol) over a methanolic solution of L1 (30 mg, 0.097 mmol). After two weeks blue plate shaped X-ray quality crystals were obtained. Yield: 15.51% (45 mg, 0.027 mmol). Elemental analysis calcd for C<sub>50</sub>H<sub>30</sub>CuF<sub>20</sub>N<sub>12</sub>O<sub>9</sub>S<sub>2</sub> (%): C 41.40, H, 2.08, N 11.59. Found: C, 40.79; H, 2.12; N, 11.69. FT-IR (KBr pellet): 3267s, 3220m, 3078w, 3031w, 2989, 1733s (s, urea C=O stretch), 1720s (s, urea C=O stretch), 1652m, 1622s, 1593 (s, urea N−H bend), 1525s, 1504m, 1483m, 1463w, 1433m, 1328m, 1298m, 1251w, 1217s, 1135 (s, asymmetric S–O stretching), 1086m, 1049s, 1010m, 981s, 950m, 883m, 800m, 694s, 648w, 611m, 555s cm<sup>−1</sup>.

 $[(H_2O)_2(DMSO)Cd(L1)_2(\mu_2SO_4)(Cd(L1)_2\cdot(SO_4)\cdot(DMSO)\cdot(H_2O)]$ CC2. Coordination complex of L1 was synthesized by layering an aqueous ethanolic solution of CdSO<sub>4</sub> (38 mg, 0.049 mmol) over a methanolic solution of L1 (30 mg, 0.097 mmol). After two weeks colourless plate shaped X-ray quality crystals were obtained. Yield: 46.9% (43 mg, 0.0234 mmol). Elemental analysis calcd for  $C_{52}H_{36}Cd_2F_{20}N_{12}O_{17}S_4$  (%): C 44.06, H, 1.98, N 9.16. Found: C, 33.95; H, 2.51; N, 9.41. FT-IR (KBr pellet): 3342s, 3304m, 3080w, 2294m, 1722s (s, urea C=O stretch), 1595 (s, urea N-H bend), 1570s, 1546s, 1525s, 1496s, 1479s, 1427s, 1334s, 1280s, 1205 (s, bridge sulfate asymmetric S-O stretching), 1190m, 1066s, 1020 (s, unidentate asymmetric S-O stretching), 970s, 923w, 864s, 808m, 748m, 707s, 630m, 574w, 547s 513s cm<sup>-1</sup>.

 $[Cu(L2)_2(H_2O)\cdot(Cl)_2]$  CC3. Coordination complex CC3 was synthesized by layering a methanolic toluene solution of CuCl<sub>2</sub> (13.5 mg, 0.049 mmol) over a methanolic solution of L2 (30 mg, 0.097 mmol). After two weeks sky blue needle shape X-ray quality crystals were obtained. Yield: 58% (22 mg, 0.029 mmol). Elemental analysis calcd for C<sub>26</sub>H<sub>14</sub>Cl<sub>2</sub>CuF<sub>10</sub>N<sub>4</sub>O<sub>3</sub> (%): C 41.37, H, 1.87, N 7.42. Found: C, 36.77; H, 2.41; N, 6.36. FT-IR (KBr pellet): 3263s, 3099w, 1658 (s, amide C=O stretch), 1558 (s, amide N-H bend), 1521s, 1500s, 1427s, 1338s, 1352s, 1257s, 1122s, 1062s, 991s, 757s, 696m cm<sup>-1</sup>.

[Cu(L2)<sub>2</sub>( $\mu$ -SO<sub>4</sub>)(H<sub>2</sub>O)]<sub>∞</sub> CP1. Coordination polymer CP1 was synthesized by layering an aqueous methanolic solution of CuSO<sub>4</sub> (12 mg, 0.049 mmol) over a methanolic solution of L2 (30 mg, 0.097 mmol). After two weeks blue block shape X-ray quality crystals were obtained. Yield: 53.7% (38 mg, 0.027 mmol). Elemental analysis calcd for C<sub>26</sub>H<sub>16</sub>CuF<sub>10</sub>N<sub>4</sub>O<sub>7</sub>S (%): C 39.93, H, 1.81, N 7.81. Found: C, 37.87; H, 1.62; N, 6.40. FT-IR (KBr pellet): 3282s (asymmetric O–H stretching), 3090, 3018, 2831, 1658 (s, amide C=O stretch), 1564m, 1523 (s, amide N–H bend), 1492s, 1444m, 1417w, 1348m, 1323m, 1273m, 1203m, 1122 (s, asymmetric S–O stretching), 1104m, 1064s, 1018s, 1010m, 987s, 950m, 810s, 765s, 704s, 686, 650w, 603s cm<sup>-1</sup>.

[{Cu(L2)<sub>4</sub>(µ-SiF<sub>6</sub>)}·2H<sub>2</sub>O]<sub>∞</sub> CP2. Coordination polymer CP2 was synthesized by layering a toluene methanolic solution of Cu(BF<sub>4</sub>)<sub>2</sub> (13.5 mg, 0.049 mmol) over a methanolic solution of L2 (30 mg, 0.097 mmol). After two weeks blue block shape X-ray quality crystals were obtained. FT-IR (KBr pellet): 3496, 3258, 3051, 1676 (s, amide C=O stretch), 1520 (s, amide N-H bend), 1501s, 1439w, 1663w, 1333s, 1270m, 1194m, 1118s, 1056w, 991s, 890s, 799s, 744s, 686w, 659s, 482m cm<sup>-1</sup>. Yield: 42% (35 mg, 0.021 mmol). Elemental analysis calcd for C<sub>52</sub>H<sub>34</sub>CuF<sub>26</sub>N<sub>8</sub>O<sub>7</sub>Si (%): C 42.52, H, 2.33, N 7.63. Found: C, 40.62; H, 2.27; N, 7.20. FT-I.R (KBr pellet): 603s cm<sup>-1</sup>.

[{Cu(L3)<sub>4</sub>(ClO<sub>4</sub>)}·ClO<sub>4</sub>·H<sub>2</sub>O] CC4. Coordination complex CC4 was synthesized by layering an aqueous ethanolic solution of Cu(ClO<sub>4</sub>)<sub>2</sub> (18.5 mg, 0.049 mmol) over a methanolic solution of L3 (28 mg, 0.097 mmol). After two weeks deep blue blocked shape X-ray quality crystals were obtained. Yield: 48.84% (35 mg, 0.024 mmol). Elemental analysis calcd for C<sub>48</sub>H<sub>22</sub>Cl<sub>2</sub>F<sub>20</sub>N<sub>8</sub>O<sub>13</sub>Cu (%): C 40.23, H, 1.55, N 7.82. Found: C, 40.66; H, 1.82; N, 7.36. FT-IR (KBr pellet): 3342 (s, aromatic C-H stretch), 3311w, 1720 (s, amide C=O stretch), 1658s, 1623s, 1596 (s, amide N-H bend), 1431s, 1338s, 1319s, 1319s, 1298s, 1211s, 1118 (s, asymmetric Cl-O stretching of free ClO4), 1097 (s, asymmetric Cl-O stretching of unidentate ClO4), 1058m, 1029s, 993s, 952s, 873m, 864m, 838s, 783s, 622s, 590s, 572s, 541s cm<sup>-1</sup>.

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[{Cu(L3)<sub>4</sub>(H<sub>2</sub>O)}·H<sub>2</sub>O·2BF<sub>4</sub>] CC5. Coordination complex CC5 was synthesized by layering an aqueous ethanolic solution of Cu(BF<sub>4</sub>)<sub>2</sub> (13.5 mg, 0.049 mmol) over a methanolic solution of L3 (28 mg, 0.097 mmol). After two weeks deep blue blocked shape X-ray quality crystals were obtained. Yield: 52% (38 mg, 0.026 mmol). Elemental analysis calcd for C<sub>48</sub>H<sub>24</sub>B<sub>2</sub>CuF<sub>28</sub>N<sub>8</sub>O<sub>6</sub> (%): C 40.95, H, 1.58, N 7.96. Found: C, 40.12; H, 1.62; N, 7.51. FT-IR (KBr pellet): 3338 (m, aromatic C-H stretch), 3309m, 3193w, 3103w, 1720 (s, amide C=O stretch), 1693s, 1656s, 1600 (s, amide N-H bend), 1514s, 1431s, 1336s, 1321s, 1299s, 1211s, 1097s, 1083s, 1027s, 995ms, 875s, 838s, 783s, 572m, 541s cm<sup>-1</sup>.

[{(Cl)Cu(L3)<sub>4</sub>( $\mu$ -Cl)Cu(L3)<sub>4</sub>}-Cl·H<sub>2</sub>O] CC6. Coordination complex CC6 was synthesized by layering an aqueous ethanolic solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (8.5 mg, 0.05 mmol) over a methanolic solution of L3 (28 mg, 0.097 mmol). After two weeks deep blue blocked shape X-ray quality crystals were obtained at 22 °C. Yield: 30.5% (40 mg, 0.015 mmol). Elemental analysis calcd for C<sub>96</sub>H<sub>48</sub>Cl<sub>4</sub>F<sub>40</sub>N<sub>16</sub>O<sub>23</sub>Cu<sub>2</sub> (SQUEEZE calculation included) (%): C 40.85, H, 1.71, N 7.88. Found: C, 39.57; H, 1.81; N, 7.33. FT-IR (KBr pellet): 3064 (s, aromatic C–H stretch), 2887, 1705 (s, amide C=O stretch), 1654 (s, amide C=O stretch), 1600 (s, amide N–H bend), 1518s, 1506s, 1429m, 1296m, 1213m, 1099, 1026s, 995m, 833m, 781, 572, 532 cm<sup>-1</sup>.

Thermogravimetric analysis (TG) revealed the weight loss of 9.5% in the first step which corresponds the solvated two water molecules (calc. weight loss = 19.6%). These results indicate solvent loss while loading the sample.

[{Cu<sub>2</sub>(L3)<sub>4</sub>( $\mu$ -Cl)<sub>2</sub>·(Cl)<sub>2</sub>}·H<sub>2</sub>O] CC7. Coordination complex CC7 was synthesized by layering an aqueous ethanolic solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (8.5 mg, 0.05 mmol) over a methanolic solution of L3 (28 mg, 0.097 mmol). After one week sky blue plate shape X-ray quality crystals were obtained at 38 °C. Yield: 51.5% (37 mg, 0.0257 mmol). Elemental analysis calcd for C<sub>48</sub>H<sub>22</sub>Cl<sub>4</sub>Cu<sub>2</sub>F<sub>20</sub>N<sub>8</sub>O<sub>5</sub> (%): C 40.05, H, 1.54, N 7.78. Found: C, 40.48; H, 1.53; N, 7.46. FT-IR (KBr pellet): 3344 (s, water O-H stretch), 3224 (m, aromatic C-H stretch), 3164w, 3078w, 3001w, 1716 (s, amide C=O stretch), 1710, 1652s, 1596 (s, amide N-H bend), 1504s, 1425s, 1336s, 1321w, 1292m, 1211s, 1099m, 1064m, 1027m, 995s, 952m, 873m, 829s, 781s, 669m, 572m, 536m cm<sup>-1</sup>.

 $[Cu(L3)_2(Cl)_2]$  CC8. Coordination complex CC8 was synthesized by layering an aqueous ethanolic solution of CuCl<sub>2</sub>·2H<sub>2</sub>O (8.5 mg, 0.05 mmol) over a methanolic solution of L3 (28 mg, 0.097 mmol). After one week deep blue needle shape X-ray quality crystals were obtained below ~38 °C and above 22 °C. Yield: 61.8% (22 mg, 0.0309 mmol). Elemental analysis calcd for C<sub>24</sub>H<sub>10</sub>Cl<sub>2</sub>F<sub>10</sub>N<sub>4</sub>O<sub>2</sub>Cu (%): C 40.55, H, 1.42, N 7.78. Found: C, 40.49; H, 1. 35; N, 7.73. FT-IR (KBr pellet): 3309, 3253 (s, aromatic C-H stretch), 3172 (w), 3085w, 3004w, 1720 (s, amide C=O stretch), 1685s, 1618s, 1595 (s, amide N-H bend), 1515s, 1504s, 1431s, 1415m, 1338s, 1321s, 1294m, 1211m, 1095m, 1066s, 1029m, 993s, 948s, 873s, 831s, 781m, 671, 590w, 570w, 532s cm<sup>-1</sup>.

 $[{Cu(L4)_4 \cdot (H_2O)_2} \cdot SO_4 \cdot 5H_2O]$  CC9. Coordination complexes CC9 was synthesized by layering an aqueous ethanolic

solution of CuSO<sub>4</sub> (12.1 mg, 0.049 mmol) over a methanolic solution of L4 (21.4 mg, 0.097 mmol). After two weeks green block shaped X-ray quality crystals were obtained. Yield: 46.22% (26 mg, 0.0231 mmol). Elemental analysis calcd for  $C_{48}H_{45}CuN_{12}O_{15}S$  (%): C 51.56, H, 5.04, N 15.00. Found: C, 51.64; H, 4.31; N, 15.42. FT-IR (KBr pellet): 3340w, 3274s, 3199m, 3136m, 3082s, 3029m, 1703s (s, urea C=O stretch), 1620 (s, urea N-H bend), 1589s, 1566s, 1550s, 1483s, 1444s, 1326s, 1290s, 1259s, 1240s, 1227s, 1112 (s, free sulfate asymmetric S-O stretching), 1097s, 1064w, 973s, 906m, 810m, 752s, 692s cm<sup>-1</sup>.

#### ClO<sub>4</sub><sup>-</sup> anion separation as CC4 by L3

Condition I (L3:Cu(ClO<sub>4</sub>)<sub>2</sub>:other copper salt = (2:1:1)). a) To a methanol and ethanol solution of L3 (28.8 mg, 0.1 mmol), an aqueous solution of a mixture of CuCl<sub>2</sub> (8 mg, 0.05 mmol), CuSO4·5H<sub>2</sub>O (12.1 mg, 0.05 mmol), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (12.2 mg, 0.05 mmol), Cu(ClO<sub>4</sub>)<sub>2</sub> (18.5 mg, 0.05 mmol), Cu(BF<sub>4</sub>)<sub>2</sub> (13.5 mg, 0.049 mmol) was kept undisturbed and the solution allowed to evaporate slowly. After one week good looking block shaped green crystals were obtained. The crystals were washed in distilled water and finally with methanol and characterized by elemental analysis, X-ray powder diffraction (XRPD) and FT-IR.

Condition II (L3:Cu(ClO<sub>4</sub>)<sub>2</sub>: other copper salts) = (2:1:2). b) To a methanol and ethanol solution of L3 (28.8 mg, 0.1 mmol), an aqueous solution of a mixture of CuCl<sub>2</sub>(16.2 mg, 0.05 mmol), CuSO4·5H<sub>2</sub>O (24.2 mg, 0.1 mmol), Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (24.2 mg, 0.1 mmol), Cu(ClO<sub>4</sub>)<sub>2</sub> (18.5 mg, 0.05 mmol), Cu(BF<sub>4</sub>)<sub>2</sub> (27.8 mg 0.1 mmol) was kept undisturbed and the solution allowed to evaporate slowly. After one week good looking block shaped green crystals were obtained. The crystals were washed in DMF, distilled water and finally with methanol and characterized by elemental analysis, X-ray powder diffraction (XRPD) and FT-IR.

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