Supplementary data for *Dalton Transactions*

Synthesis, Structure, Magnetism and Nuclease Activity of Tetranuclear Copper(II) Phosphonates Containing Ancillary 2,2'-Bipyridine or 1,10-Phenanthroline Ligands

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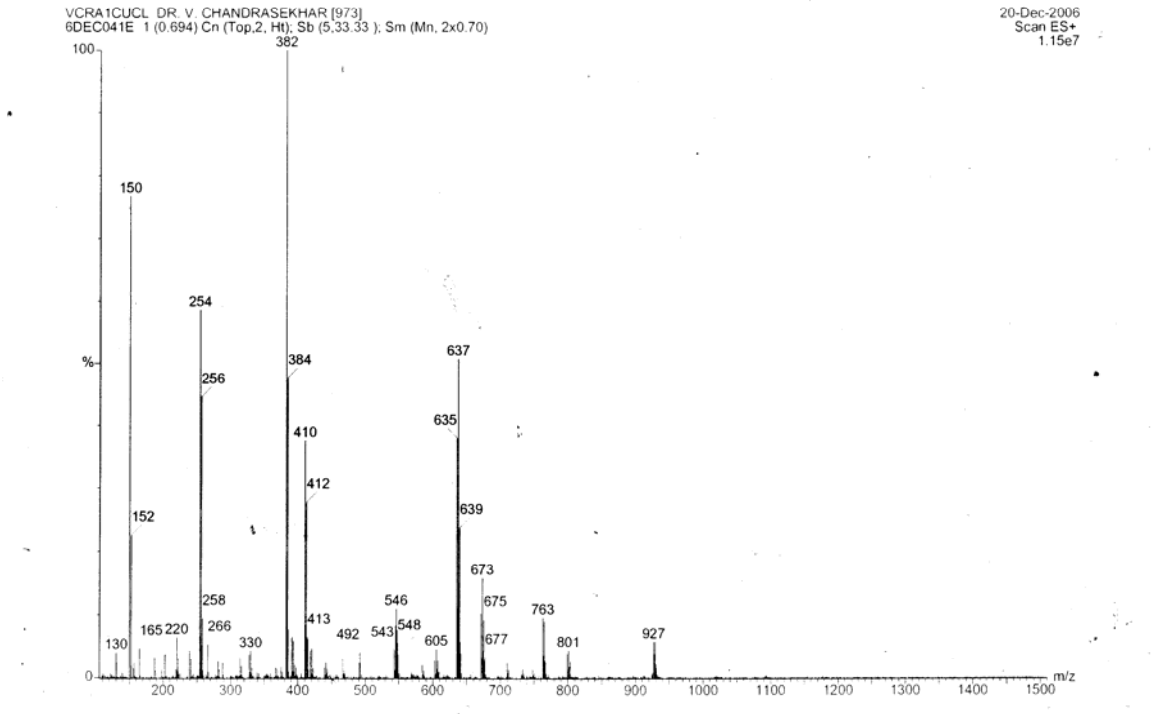


Figure: S1 ESI-MS spectra of compound **1**

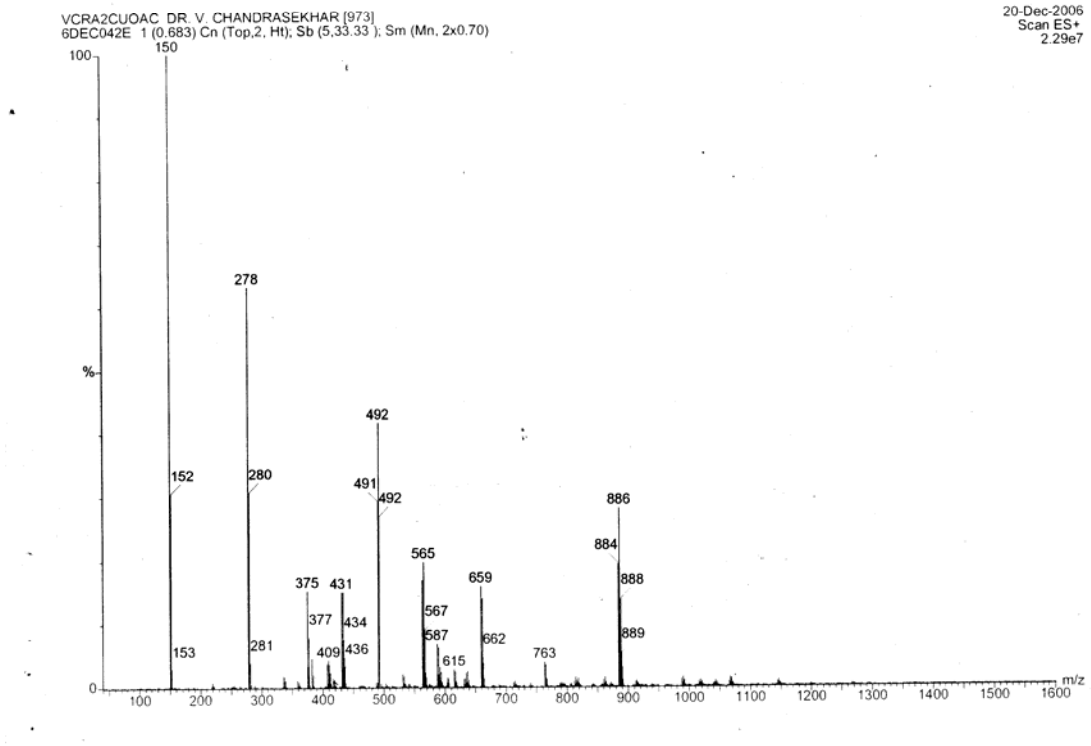


Figure: S2 ESI-MS Spectra of compound **2**

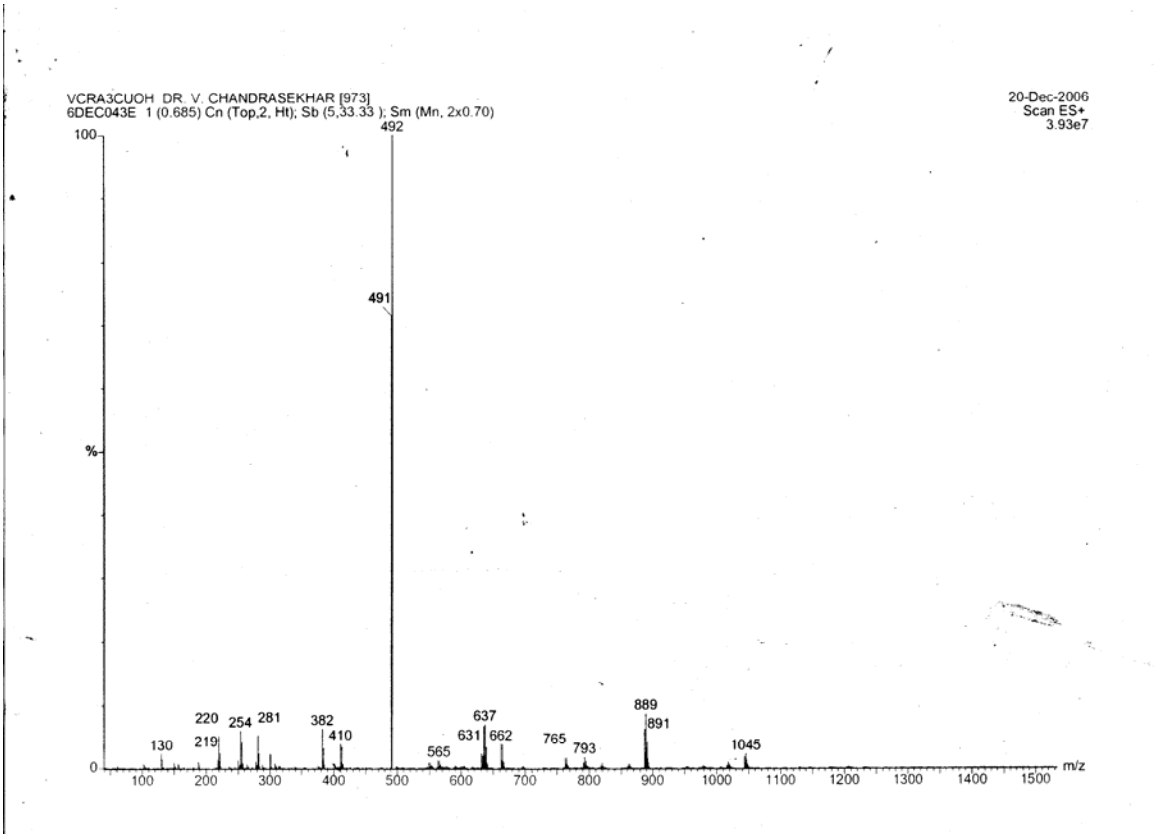


Figure: S3 ESI-MS Spectra of compound **3**

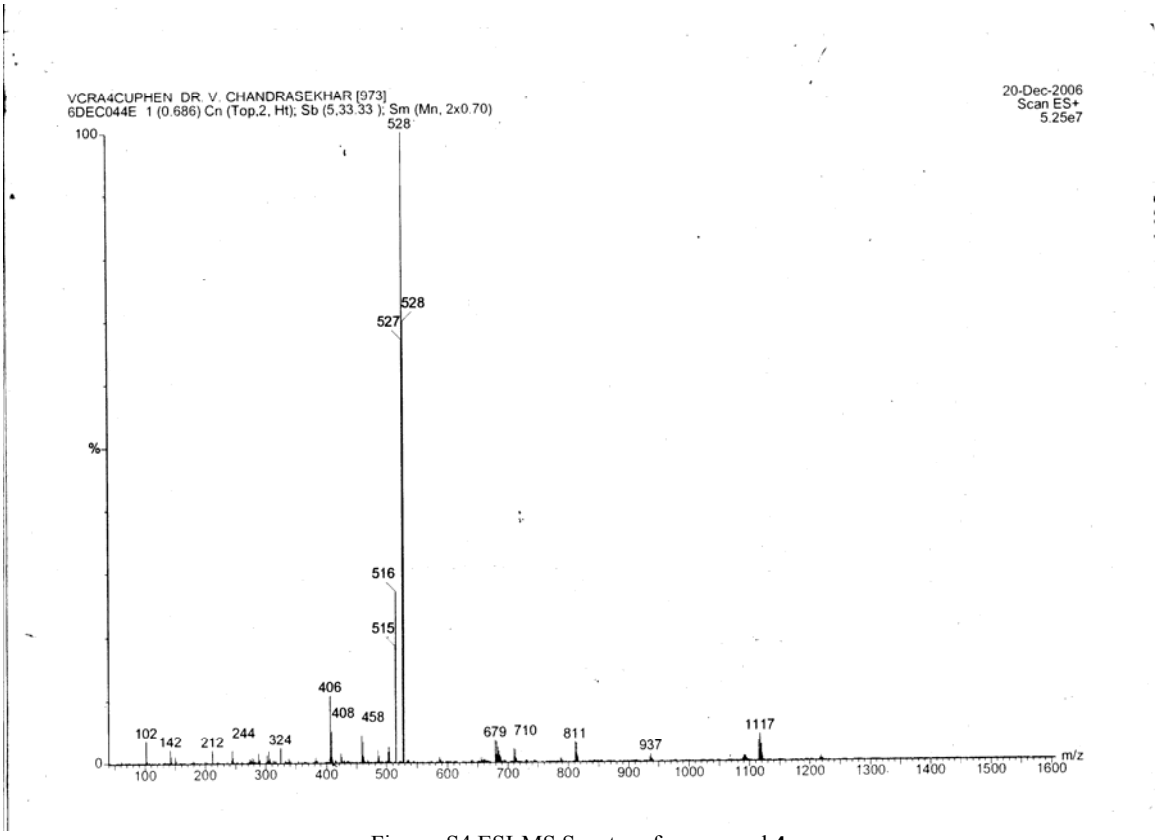


Figure: S4 ESI-MS Spectra of compound **4**

Table S1(a). Selected Bond Length and Bond Angles for **1**

Bond Length / Å or Bond Angles / º		
Cu(1)-O(1) 1.914(4)	Cu(2)-O(2) 1.885(4)	Cu(1)-Cu(2) 3.338
Cu(1)-O(3*) 1.969(4)	Cu(2)-O(3*) 2.396(4)	Cu(1)-Cu(2*) 4.047
Cu(1)-N(1) 2.007(5)	Cu(2)-N(3) 1.980(5)	Cu(1)-Cu(1*) 5.059
Cu(1)-N(2) 2.007(5)	Cu(2)-N(4) 2.030(5)	Cu(2)-Cu(2*) 5.428
Cu(1)-Cl(1) 2.707(2)	Cu(2)-Cl(1) 2.3520(19)	P-O_{avg} 1.531(5)
N(1)-Cu(1)-O(1) 169.60(19)	O(1)-Cu(1)-Cl(1) 94.45(14)	O(2)-Cu(2)-O(3*) 91.58(17)
N(2)-Cu(1)-O(3*) 167.5(2)	O(3*)-Cu(1)-Cl(1) 83.25(14)	N(3)-Cu(2)-Cl(1) 95.97(16)
N(1)-Cu(1)-N(2) 80.38(19)	N(3)-Cu(2)-O(2) 168.5(2)	N(4)-Cu(2)-Cl(1) 150.23(16)
O(1)-Cu(1)-O(3*) 96.19(16)	N(4)-Cu(2)-O(3*) 126.07(18)	O(2)-Cu(2)-Cl(1) 95.39(14)
N(1)-Cu(1)-Cl(1) 91.36(15)	N(3)-Cu(2)-N(4) 80.0(2)	O(3*)-Cu(2)-Cl(1) 83.25(11)
N(2)-Cu(1)-Cl(1) 107.32(16)		

*Symmetry transformations used to generate equivalent atoms: 1 -x,-y+2,-z+1

Table S1(b). Selected Bond Length and Bond Angles for **2.**

Bond Length / Å or Bond Angles / º		
Cu(1)-O(1) 1.902(7)	Cu(2)-O(2) 1.898(7)	Cu(1)-Cu(2) 3.255
Cu(1)-O(3*) 1.954(7)	Cu(2)-O(3*) 2.409(8)	Cu(1)-Cu(2*) 4.138
Cu(1)-N(1) 1.978(9)	Cu(2)-N(3) 1.982(10)	Cu(1)-Cu(1*) 5.071
Cu(1)-N(2) 2.022(9)	Cu(2)-N(4) 2.023(9)	Cu(2)-Cu(2*) 5.452
Cu(1)-O(4) 2.344(9)	Cu(2)-O(4) 1.977(8)	P-O_{avg} 1.547(8)
N(1)-Cu(1)-O(1) 168.2(4)	O(1)-Cu(1)-O(4) 90.9(3)	O(2)-Cu(2)-O(3*) 92.4(3)
N(2)-Cu(1)-O(3*) 172.3(4)	O(3*)-Cu(1)-O(4) 80.6(3)	N(3)-Cu(2)-O(4) 93.9(4)
N(1)-Cu(1)-N(2) 80.8(4)	N(3)-Cu(2)-O(2) 172.1(4)	N(4)-Cu(2)-O(4) 165.8(4)
O(1)-Cu(1)-O(3*) 95.6(3)	N(4)-Cu(2)-O(3*) 114.3(3)	O(2)-Cu(2)-O(4) 93.4(3)
N(1)-Cu(1)-O(4) 98.0(3)	N(3)-Cu(2)-N(4) 80.0(4)	O(3*)-Cu(2)-O(4) 78.5(3)
N(2)-Cu(1)-O(4) 105.2(3)		

*Symmetry transformations used to generate equivalent atoms: -x+1,-y+1,-z+1

Table S1(c). Selected Bond Length and Bond Angles for **3**

Bond Length / Å or Bond Angles / º					
Molecule 1					
Cu(1)-O(2)	1.935(4)	Cu(2)-O(33)	2.492(4)	Cu(4)-O(9)	1.884(4)
Cu(1)-O(6)	1.949(4)	Cu(3)-O(3)	1.955(3)	Cu(2)-Cu(4)	3.299
Cu(1)-N(1)	1.996(5)	Cu(3)-O(4)	1.949(4)	Cu(3)-Cu(4)	3.438
Cu(1)-N(2)	2.011(4)	Cu(3)-N(5)	2.001(4)	Cu(1)-Cu(2)	3.598
Cu(1)-O(7)	2.389(4)	Cu(3)-N(6)	2.007(5)	Cu(1)-Cu(3)	4.388
Cu(2)-O(1)	1.931(4)	Cu(3)-O(8)	2.260(4)	Cu(1)-Cu(4)	5.148
Cu(2)-O(6)	2.648(4)	Cu(4)-O(3)	2.487(4)	Cu(2)-Cu(3)	5.163
Cu(2)-N(3)	1.996(5)	Cu(4)-O(5)	1.921(4)	$P\text{-}O_{avg}$	1.537(4)
Cu(2)-N(4)	2.017(5)	Cu(4)-N(7)	2.011(5)		
Cu(2)-O(9)	1.928(4)	Cu(4)-N(8)	2.008(5)		
N(1)-Cu(1)-O(2)	169.17(17)	N(3)-Cu(2)-N(4)	80.37(19)	O(3)-Cu(3)-O(4)	94.64(15)
N(2)-Cu(1)-O(6)	165.71(16)	O(1)-Cu(2)-O(9)	93.85(16)	N(7)-Cu(4)-O(9)	160.34(16)
N(1)-Cu(1)-N(2)	80.76(19)	O(6)-Cu(2)-O(33)	171.50(12)	N(8)-Cu(4)-O(5)	171.61(17)
O(2)-Cu(1)-O(6)	94.53(15)	N(5)-Cu(3)-O(3)	168.26(17)	N(7)-Cu(4)-N(8)	80.31(18)
N(3)-Cu(2)-O(1)	169.39(18)	N(6)-Cu(3)-O(4)	164.53(16)	O(5)-Cu(4)-O(9)	89.54(17)
N(4)-Cu(2)-O(9)	169.51(16)	N(5)-Cu(3)-N(6)	80.47(18)		

Table S1(d). Selected Bond Length and Bond Angles for **4.**

Bond Length / Å or Bond Angles / º					
Cu(1)-O(1)	2.428(4)	Cu(2)-O(1)	1.961(4)	Cu(1)-Cu(2)	3.506
Cu(1)-O(2*)	1.914(4)	Cu(2)-O(3*)	1.945(4)	Cu(1)-Cu(1*)	3.249
Cu(1)-N(1)	2.002(5)	Cu(2)-N(3)	2.019(5)	Cu(2)-Cu(2*)	4.283
Cu(1)-N(2)	2.028(5)	Cu(2)-N(4)	2.007(5)	Cu(1)-Cu(2*)	5.093
Cu(1)-O(4)	1.906(3)	Cu(2)-O(5)	2.280(5)	$P\text{-}O_{avg}$	1.534(4)
N(1)-Cu(1)-O(2*)	172.0(2)	O(2*)-Cu(1)-O(1)	90.19(15)	O(1)-Cu(2)-O(3*)	92.81(16)
N(2)-Cu(1)-O(4)	165.2(2)	O(1)-Cu(1)-O(4)	103.29(16)	N(3)-Cu(2)-O(5)	96.79(19)
N(1)-Cu(1)-N(2)	81.6(2)	N(3)-Cu(2)-O(3*)	165.39(19)	N(4)-Cu(2)-O(5)	95.82(19)
O(4)-Cu(1)-O(2*)	92.19(15)	N(4)-Cu(2)-O(1)	165.04(18)	O(1)-Cu(2)-O(5)	98.44(17)
N(1)-Cu(1)-O(1)	89.75(17)	N(3)-Cu(2)-N(4)	81.2(2)	O(3*)-Cu(2)-O(5)	95.83(17)
N(2)-Cu(1)-O(1)	91.23(16)				

*Symmetry transformations used to generate equivalent atoms: -x,y,-z+1/2

Table S2. Coordination environment, Value of τ (degree of trigonality), Deviation from the mean plane for the each copper atom in complexes **1** – **4**.

Compound	Atom Label	Coordination Environment	Value of τ^a	Deviation from plane / Å
1	Cu1	2N,2O,Cl	0.035	0.000
	Cu2	2N,2O,Cl	0.707	0.000
2	Cu1	2N,3O	0.068	0.000
	Cu2	2N,3O	0.105	0.000
3	Cu1	2N,3O	0.058	-0.147
	Cu2	2N,4O	------	0.199
	Cu3	2N,3O	0.062	0.156
	Cu4	2N,3O	0.188	-0.207
	Cu5	2N,3O	0.053	-0.137
	Cu6	2N,4O	------	0.188
	Cu7	2N,3O	0.017	0.144
	Cu8	2N,3O	0.242	-0.195
4	Cu1	2N,3O	0.113	-0.203
	Cu2	2N,3O	0.006	0.153

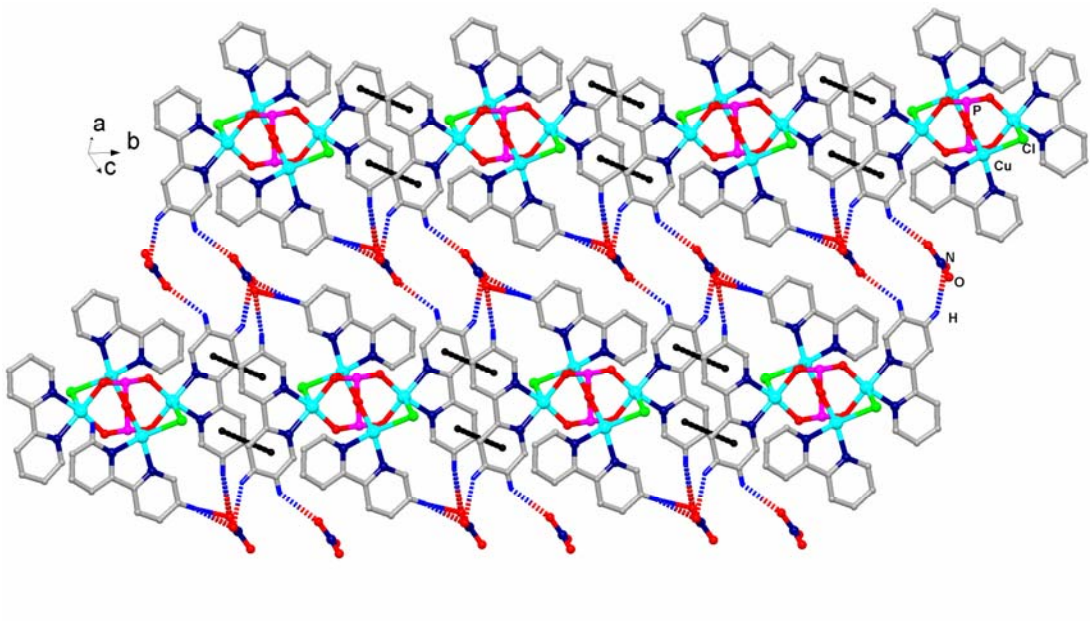
Supramolecular Structures of 1- 4:

The supramolecular architectures of **1-4** are dominated by intermolecular π-π and C-H---O interactions involving the planar bipyridyl/phenanthroline ligands. These interactions are aided by the counter anions and guest molecules also in some instances as outlined below. All the metric parameters involved in the supramolecular interactions in compounds **1-4** are summarized in Table 4.Compound **1** shows slipped π-π interactions[1] between the 2,2'-bipyridine ligands of the adjacent molecules leading to the formation of a 1D *tape-like* structure. The distances associated in these contacts (between the centroid of the rings) range between 3.8897(14) to 3.9385(16) Å [(Figure: S5(a)]. Adjacent 1-D tapes are interconnected via C-H---O interactions[2] (bipyridyl C-H and oxygen atom of nitrate anion) to generate a 2-D sheet like structure [Figure: S5(a)]. Further intermolecular π-π interactions involving the bipyridyl ligands between the 2-D sheets generates a three-dimensional supramolecular structure where the guest dichloromethane molecules efficiently occupy the free space between the adjacent layers. The guest molecules are non-innocent and they are involved in intermolecular C-H---O interaction with nitrate anion. The metric parameters involved in these interactions are summarized in Table **4**.

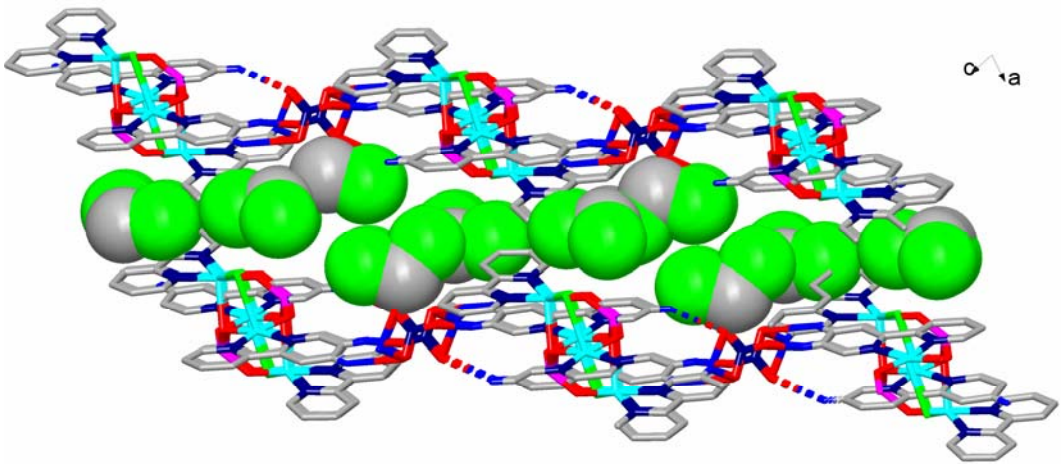
Intermolecular C-H---O interactions between the oxygen atom of the acetate anion and the C-H of bipyridyl moiety of the cationic cluster in **2** leads to the formation of a two dimensional helical layered structure [Figure: S6(a)]. Lattice water molecules connect adjacent helical layers via C-H---O interactions to generate a 3-D structure [Figure: S6(b)].

The asymmetric unit cell of **3** contains two crystallographicaly distinct molecules (molecule A and molecule B), six water molecules and six nitrate anions. The supramolecular architecture in this compound results from an interaction of all of these chemical entities. We have not considered the disordered nitrate and water molecules for an analysis of the supramolecular organization in 3. The supramolecular formation in **3** can be understood in a step-wise manner as follows. The intermolecular C-H---O interaction (oxygen of metal bound nitrate and C-H of the bipyridyl ring) between neighboring molecules (molecules A) generates a dimeric unit. Adjacent dimers are interconnected by one of the six nitrate anion to forming a 1-D zig-zag ribbon[3] [Figure: S7(a) and S7(b)]. Similarly another 1-D zig-zag ribbon arises from the interaction between molecules B. These resultant ribbons (A and B) alternate with each other and are inter connected by intermolecular O-H---O interaction (metal bound water molecule and the hydrogen atom of the bipyridyl moiety) [Figure: S7(a) and S7(b)]. Nitrate anions and neutral water molecules occupy the voids formed because of this interconnection. Further interaction between the two-dimensional sheets leads to a three-dimensional architecture (not shown).

Intermolecular C-H---O interaction (metal bound water and C-H of phenanthroline) between the adjacent molecules of **4** generates a helical chain [Figure: S8(a)]. Slipped π---π interaction between the phenanthroline rings of the adjacent helices generates a 2D sheet like structure. Adjacent 2D sheets are interconnected *via* C-H-O interactions (lattice water and C-H of phenonthroline) to afford a three- dimensional structure [Figure: S8(b)].

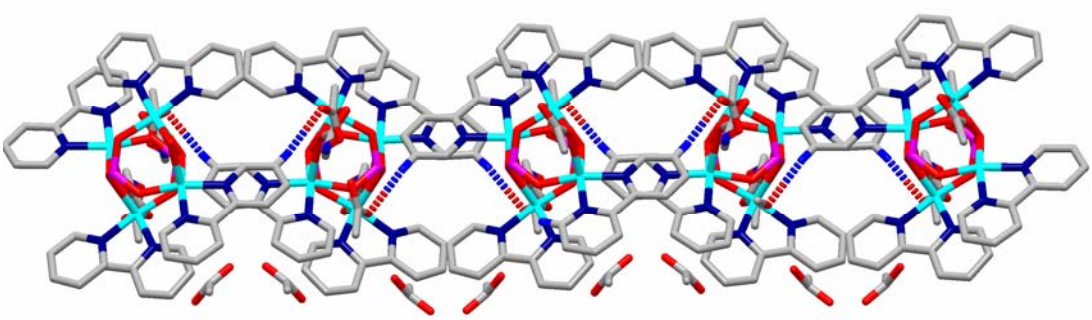


(a)



(b)

Figure: S5. a) 2D layer structure of 1 formed through intermolecular π-π and C-H---O interactions b) 3D supramolecular structure of **1**. Guest chloroform molecules are shown in space-filling model.



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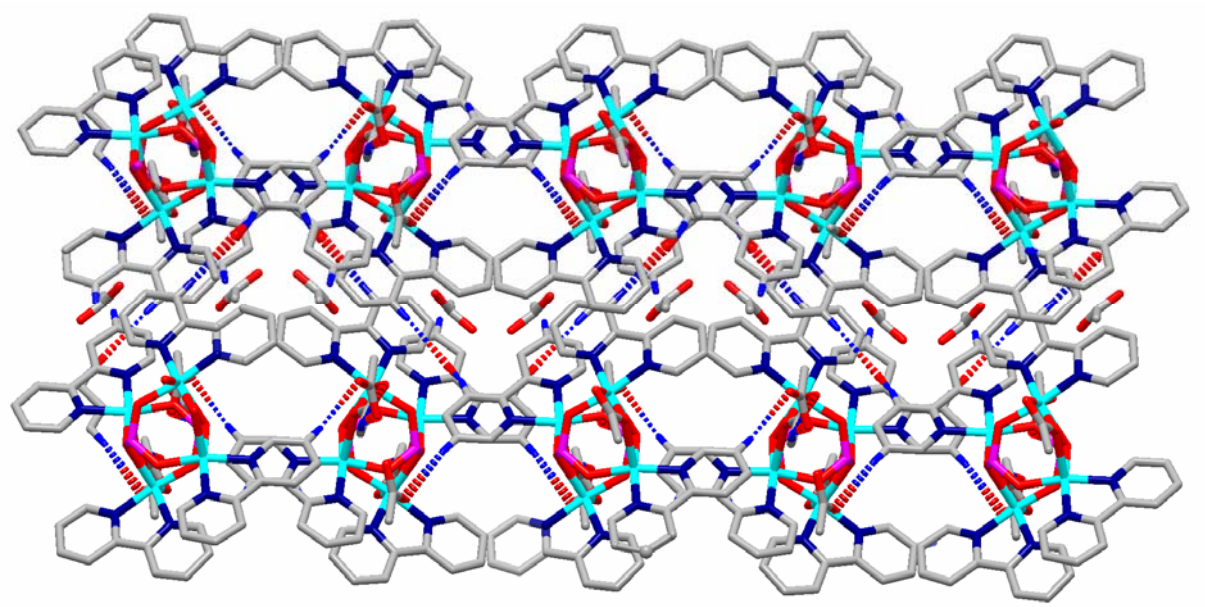
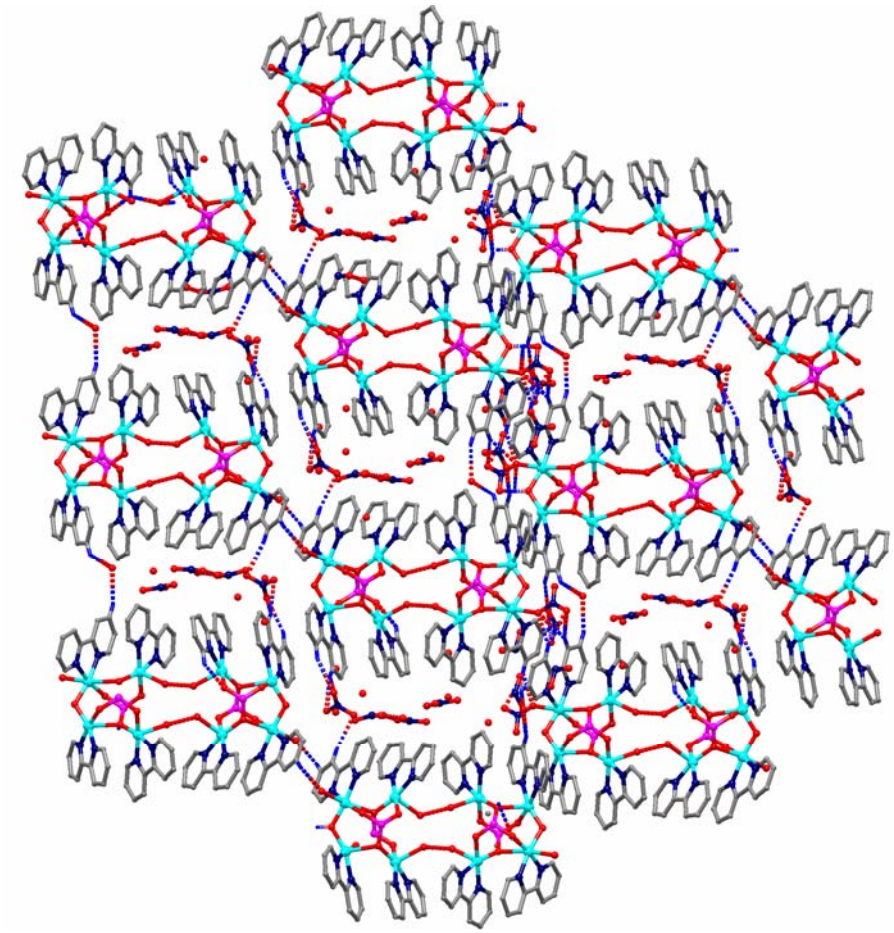


(b)

Figure: S6. a) 2D helical-layered structure of **2** in the crystallographic ab plane. b) 3D supramolecular structure of **2**.



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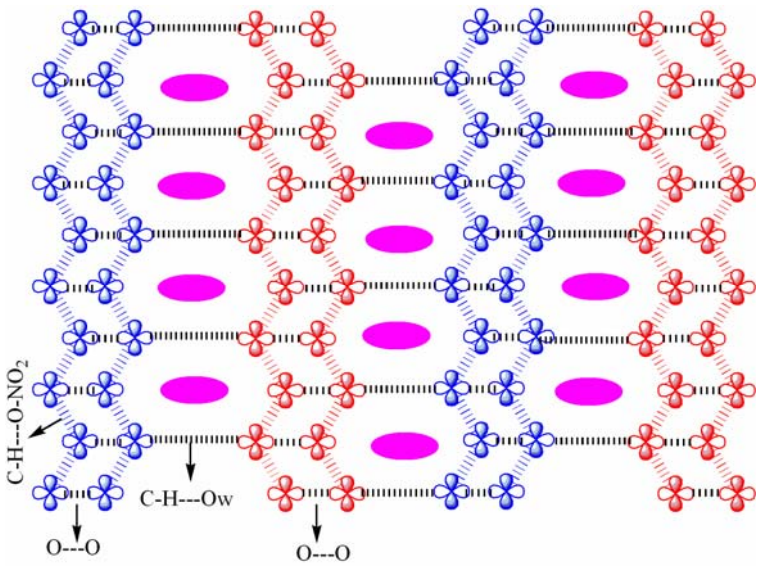
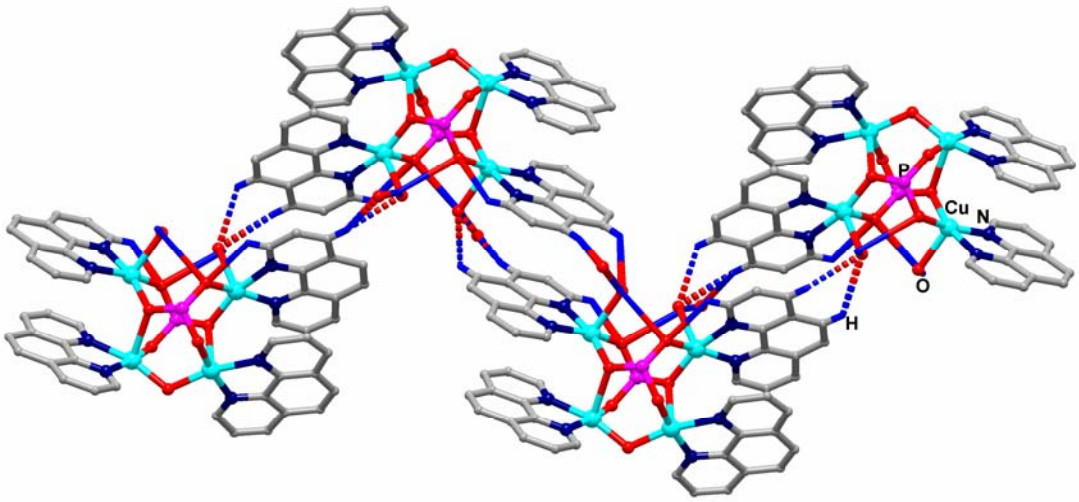
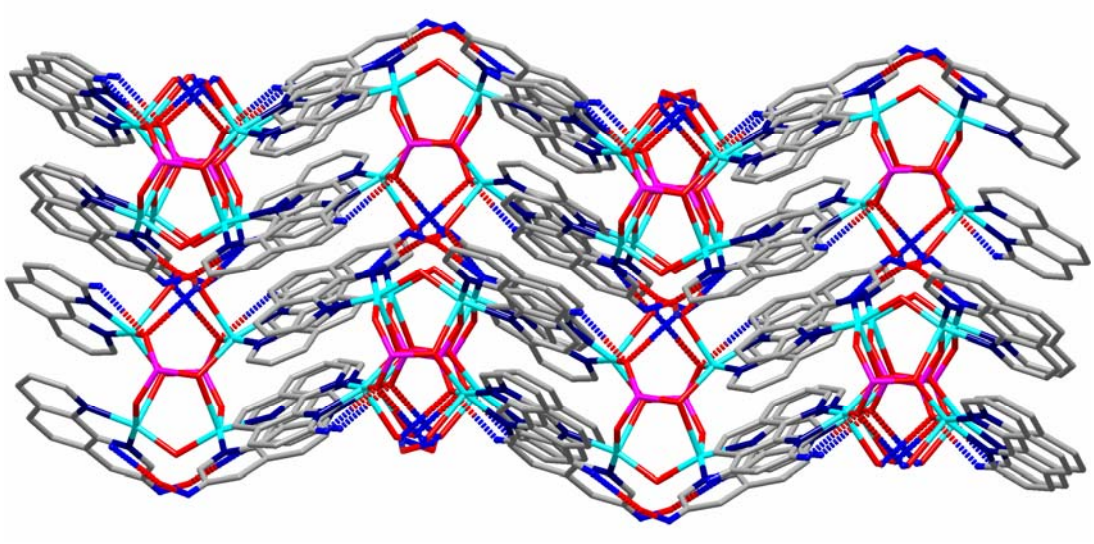


(b)

Figure: S7. a) Two-dimensional supramolecular architecture of **3**. b) Cartoon representation of the two-dimensional architecture of **3**. Alternating inter-connected zig-zag ribbons are shown generating voids which are filled up with nitrate anions and water molecules (shown in the cartoon as elliptical structures).



(a)



(b)

Figure: S8. a) Supramolecular helical chain-like structure of 4. b) 3-D Supramolecular structure of **4**.

Table S3. Selected metric parameters for Hydrogen-bonding interactions in the Supramolecular Structures of 1-4

$[Cu_4(\mu\text{-}Cl)_2(\mu_3\text{-}C_6H_{11}PO_3)_2(bpy)_4](NO_3)_2$ (1)		$[Cu_4(\mu\text{-}CH_3COO)_2(\mu_3\text{-}C_6H_{11}PO_3)_2(bpy)_4](CH_3COO)_2$ (2)	
D---A Bond Distance (Å)	D---A Bond Angle (º)	D---A Bond Distance (Å)	D---A Bond Angle (º)
H12---O13 : 2.596	C12-H12---O13 152.33	H12A---O41 : 2.380	C12–H12A---O41 163.56
H18---O11 : 2.568	C18–H18---O12 141.32	H17---O70 : 2.435	C17–H17---O70 151.77
H19---O12 : 2.651	C19–H19---O12 137.77	H19---O61 : 2.580	C19–H19---O61 160.34
H22---O11 : 2.449	C22–H22---O11 147.49	H24---O70 : 2.371	C20–H19---O61 144.14
H22---O13 : 2.611	C22–H22---O13 163.33	H27---O70 : 2.659	C24–H24---O70 157.19
		H32B---O5 : 2.529	C27–H27---O70 159.35
		H32B---O62 : 2.678	
$[Cu_4(\mu\text{-}OH)(\mu_3\text{-}C_6H_{11}PO_3)_2(bpy)_4(H_2O)_2](NO_3)_3$ (3)		$[Cu_4(\mu\text{-}OH)(\mu_3\text{-}C_6H_{11}PO_3)_2(phen)_4(H_2O)_2](NO_3)_3$ (4)	
H33---O31 : 2.736	C33–H33---O31 162.90	H5W---O3 : 2.977	C8–H8---O10 131.57
H33---O33 : 2.430	C33–H33---O33 147.75	H5W---O5 : 0.849	C24–H24---O5 134.59
H36---O31 : 2.881	C36-H36---O31 156.51	H5W---O10 : 1.972	C26–H26---O5 135.01
H37---O27 : 2.656	C47–H41---O42 146.18	H8---O10 : 3.194	C26–H26---O10 156.72
H47---O42 : 2.372	C47–H47---O42 146.18	H26---O10 : 2.638	
H92---O19 : 2.576	C92–H92---O19 152.14		
H93---O83 : 2.696	C93–H93---O83 169.06		
H103---O81 : 2.739	C103–H103---O81 159.25		

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