Supplementary Material

Construction of Solvent Mediated Supramolecular Templated Assembly of Metal Organophosphonate via Crystal-Amorphous-Crystal Transformation

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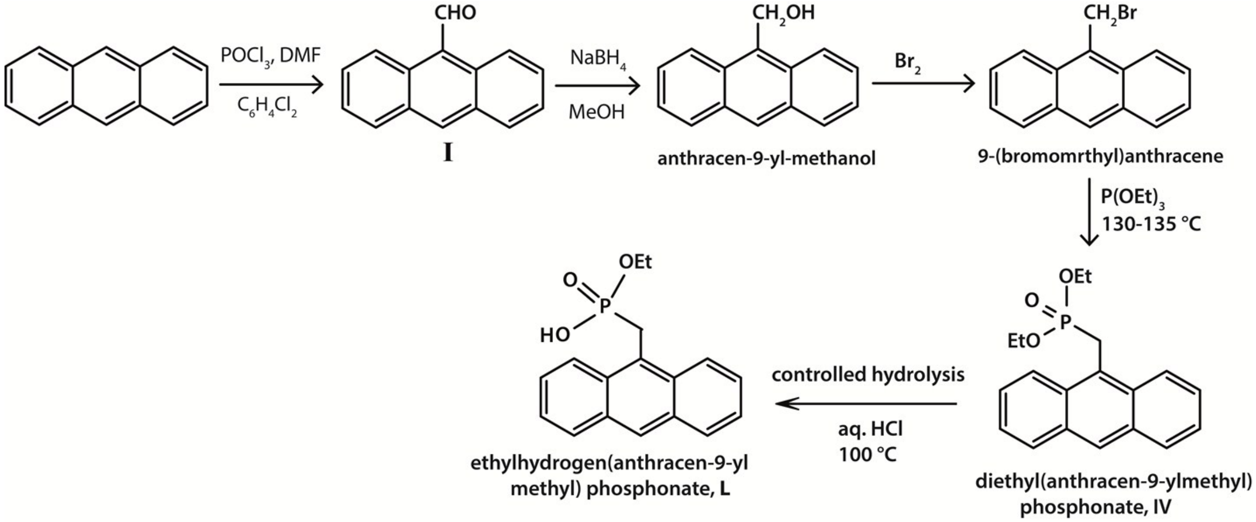
Section S1: Experimental Section:

Flexible anthracene-based ligand, ethyl hydrogen(anthracen-9-ylmethyl)phosphonate (**L**) is synthesized as shown in Scheme S1. The reaction between 9-(bromomethyl)anthracene and triethylphosphite afforded the corresponding diethylphosphonate ester by the Michealis Arbuzov reaction[1] and further on controlled hydrolysis led to **L** in good yield. The combination of **L** with equivalent ratio of $Cu(NO_3)_2.3H_2O$ and 2,2'-bipyridine in acetonitrile/methanol mixed solvent system in presence of triethylamine afforded the zero dimensional discrete system $[Cu_2(\mu_2\text{-}L)_2(^{2,2'}BPy)_2(H_2O)_2](NO_3)_2.S$ (**1**), as green crystals (Scheme 1), whereas the same organic ligands with same metal ion but this time in absence of acetonitrile afforded another discrete molecular system $[Cu_2(\mu_2\text{-}L)_2(^{2,2'}BPy)_2(NO_3)_2].MeOH$ (**2**) as green crystals.



Scheme S1: Synthesis of ethyl hydrogen (anthracen-9-ylmethyl)phosphonate (**L**)

Synthesis:

Herein, we report the modular assembly of produced from solvent mediated supramolecular reactions of monophosphonoester and $^{2,2'}$BPy with $Cu(NO_3)_2$, in which three Cu organophosphonate such as complexes **1-3** supramolecular solids are observed. To the best of our knowledge, there is no report on the use of monoester for the formation of solvent mediated supramolecular isomers of metal phosphonate yet.

Supramolecular complex **1** was synthesized by a reaction carried out between equimolar amounts of phosphonomonoester and $^{2,2'}$BPy with $Cu(NO_3)_2$ in mixed solvents of methanol and acetonitrile at 60 °C for 2 days. Complex **1** was crystallized as green crystals and suitable for X-ray structure analysis. Yield: 0.05 g, 42%.

Elemental Anal. Calcd. for $C_{58}H_{68}Cu_2N_6O_{18}P_2$: C, 52.53; H, 5.17; N, 6.34. Found: C, 52.12; H, 5.31; N, 6.83.

Interestingly, when the amorphous state of **1** i.e. **1a** was allowed to be immersed in acetonitrile and methanol then the amorphous phase switched back to the crystalline form of complex **1**, i.e., **1'** (Elemental Anal. Calcd. for $C_{58}H_{68}Cu_2N_6O_{18}P_2$: C, 52.53; H, 5.17; N, 6.34. Found: C, 52.43; H, 5.04; N, 6.48).

Complex 2: When complex **1** was allowed to heat under vacuum at 90 °C, it resulted into green solid which does not show any diffraction pattern, when diffracted by X-rays. The complex **2** was characterized later and found to be amorphous as supported by PXRD and elemental analysis.

Elemental Anal. Calcd. for $C_{56}H_{56}Cu_2N_6O_{14}P_2$: C, 54.86; H, 4.60; N, 6.85. Found: C, 54.52; H, 4.43; N, 6.68.

IR (KBr, cm^{-1}): 3386, 3242, 2925, 2645, 2495, 2027, 1982, 1892, 1747, 1602, 1316, 1043, 878, 771.

Complex 3: The complex **3** was synthesized by the same procedure as outlined above for complex **1** in methanol only. Green crystals of **3** were isolated from the filtrate. Yield: 0.032 g, 64%.

Elemental Anal. Calcd. for $C_{56}H_{56}Cu_2N_6O_{14}P_2$: C, 57.62; H, 4.44; N, 9.08. Found: C, 57.47; H, 4.72; N, 9.24.

Complex 4: The complex **4** was synthesized by the loss of monophosphonoester from complex **1** in mother liquor, when the mother liquor containing the crystals of latter was allowed to come in contact with air for 10-15 days. The green colored crystals transformed to blue colored.

Elemental Anal. Calcd. for $C_{20}H_{18}CuN_6O_7$: C, 46.38; H, 3.50; N, 16.23. Found: C, 46.25; H, 3.63; N, 16.12.

Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures:

Single crystal data were collected on performed on a Bruker Kappa Apex four circle-CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71070 Å) at 298 K. Suitable size of crystals of all complexes reported in the paper was mounted on nylon CryoLoop.

In the reduction of data Lorentz and polarization corrections, empirical absorption corrections were applied.[2] Crystal structures were solved by direct method. Structure solution, refinement and data output were carried out with the SHELXTL program.[3-4] Non-hydrogen atoms were refined anisotropically. Structure was examined using the *ADDSYM* subroutine of *PLATON*[5] to assure that no additional symmetry could be applied to the models.

Refine_special_details:

Some restraints[6] like EQIV, DFIX and SIMU were used for disordered nitrate anion in complex **1, 1'** and **3** to refine the anisotropic parameters for a better configuration on the structure. In complex **1** and **1'**, it was found that the solvent modeling during structure refinement was inaccessible using conventional discrete-atom models because of eminently disordered solvent molecule; consequently, the segment of partial solvent electron densities was overruled by the SQUEEZE[7] program in PLATON and the solvent molecule is tentatively designated based on TGA and SQUEEZE results. The solvent accessible void was found to be 153.1 Ang^3 and the squeeze result gave ~ 70 electrons/unit cell which corresponds to four methanol molecules per unit cell, which was in agreement with the TGA results as well. Notably, the SQUEEZE treated structure is very stable with minimal IUCr checkcif problems, less R factor and goodness of fit.

The selected bond lengths are given in Table S2 and S3, additionally, these supramolecular isomers **1-3** also displayed some non – classical C⋯O and C⋯N interactions[5] such as C9–H9⋯N3, 2.758(11) Å; C11–H11⋯O7A, 2.997(14) Å; C21–H21⋯O7A, 2.909(18) Å; C21–H21⋯N3, 2.462(17) Å; C21–H21⋯O5, 2.487(12) Å; C24–H24⋯O7A, 2.841(16) Å; C24–H24⋯O5, 2.987(10) Å in complex **1;** C4–H4⋯O2, 2.495(3) Å; C7–H7⋯O5, 2.785(8) Å; C9–H9⋯O6, 2.742(11) Å; C16–H16A⋯O1, 2.695(3) Å; C18–H18⋯O1, 2.582(4) Å; C20–H20⋯O7A, 2.936(19) Å; C21–H21⋯O5, 2.452(21) Å, C24–H24⋯O5, 2.702(9) Å in complex **1';** C5–H5⋯O6, 2.667(2) Å; C11–H11⋯O7, 2.717(2) Å; C12–H12⋯O6, 2.677(2) Å; C21–H21⋯O4, 2.336(2) Å; C26–H26⋯O7, 2.404(2) Å in complex **2;** C6–H6⋯O8, 2.506(1) Å; C11–H11⋯O8, 2.831(1) Å; C13–H13⋯O4, 2.579(1) Å; C13–H13⋯O6, 2.716(1) Å; C18–H18⋯O7, 2.588(1) Å; C21–H21⋯π, 2.886 Å; C24–H24⋯π, 2.830 Å; C29–H29⋯O1, 2.537(1) Å; C31–H31⋯O7, 2.566(1) Å in complex **3** and C3–H3⋯O6, 2.439(4) Å; C4–H4⋯O1, 2.355(2) Å; C8–H8⋯O2, 2.424(2) Å; C11–H11⋯O3, 2.522(2) Å; C12–H12⋯N5, 2.803(2) Å; C18–H18⋯O4, 2.700(3) Å; C20–H20⋯O6, 2.674(4) Å in complex **4**. Moreover, the various π···π interactions involved in complexes **1-4** and **1'**, accountable for the extension of 1D to 3D architecture, are mentioned in Table S4.

The IR spectra were recorded as KBr pellets on a Thermo Nikolet Nexus FT-IR spectrometer. C, H, and N elemental analyses were performed on an Elementar Vario ELIII analyzer. The powder X-ray diffraction (PXRD) data were collected on a Bruker Advanced D8 diffractometer using CuKα radiation. The TG analyses were carried out on Pyris Diamond thermogravimetry analyzer under air with a heating rate of 10 °C min^{-1}. Crystallographic data (excluding structure factors) for the structures and ligands reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as deposition nos. CCDC 1042812-1042815, 1433403 and 1044127.

Crystal description of ethyl hydrogen (anthracen-9-ylmethyl)phosphonate (L):

The ligand, **L** is crystallized in monoclinic space group, *C*2/*c* and contained one molecule of the phosphonomonoester. Unlikely in others phosphonic system, no phosphonic homodimer was observed in this case. Structural analysis revealed that one of the P–OH units in one molecule acts as a donor and is hydrogen bonded to the other molecule, which acts as an acceptor. Remarkably, the hydrogen, H2A on O2 and H3A on O3 lies on the twofold axis and on an inversion centre respectively which strikingly shares half occupancy each, therefore, both oxygen showed intermolecular interactions with another molecule of phosphonomonoester. Thereby, this has led to the formation of ladder like structure in 1D. The intermolecular hydrogen bonding interaction i.e. O···O distance lies in the range of 2.439-2.441 Å. The crystallographic data of **L** is given in Table S1.

Table S1: Crystallographic table for **L, 1-4** and **1'**

Parameters	**L**	**1. nX solvent included**	**1'.nX solvent included**	**2**	**3 (included H on water)**	**4 (included H on water)**
Emprical formula	$C_{17}H_{17}O_3P$	$C_{58}H_{68}Cu_2N_6O_{18}P_2$	$C_{58}H_{68}Cu_2N_6O_{18}P_2$	$C_{56}H_{56}Cu_2N_6O_{14}P_2$	$C_{37}H_{36}CuN_5O_8P$	$C_{20}H_{18}CuN_6O_7$
Formula weight	300.28	1324.3	1324.3	1226.11	773.21	517.95
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	*C2/c*	*P*-1	*P*-1	$P2_1/c$	*P*-1	*P*-1
a/ Å	31.662(16)	11.543(2)	11.397(12)	11.129(3)	11.461(3)	7.260(7)
b/ Å	8.649(4)	11.603(2)	11.533(12)	14.638(4)	12.537(3)	9.959(10)
c/ Å	11.434(6)	12.615(2)	12.584(13)	16.334(4)	14.271(3)	15.082(15)
α/ °	90.00	69.352(10)	117.067(4)	90	111.461(11)	73.778(5)
β/ °	102.53(5)	63.370(10)	101.070(4)	90.251(10)	111.204(12)	87.900(5)
γ/ °	90.00	78.518(12)	101.147(4)	90	92.332(13)	89.707(5)
V / Å^3	3057(3)	1411.6(5)	1369.1(2)	2660.8(12)	1743.5(7)	1046.5(18)
Z	8	1	1	2	2	2
D_{calc} (g cm^{-3})	1.305	1.560	1.61	1.530	1.476	1.644
μ/mm^{-3}	0.187	0.892	0.920	0.934	0.734	1.102
θ range/ °	2.45-26.00	2.23-26.00	2.34- 26.00	2.30-28.62	2.36-26.54	2.13- 28.42
Reflections collected	2973	5469	5127	6702	7155	5124
Independent reflections	1589	3738	4340	4775	4868	4454
Parameters/ Restraints	191/0	348/41	348/41	365/0	472/0	307/0
GOF (F^2)	1.008	1.014	1.147	1.023	1.161	0.983
R_1; wR_2 [$I>2\sigma(I)$]	0.1302; 0.1750	0.0573; 0.1574	0.0564; 0.1566	0.0398 ; 0.0835	0.0426; 0.0975	0.0418; 0.1297
R_1; wR_2 (all data)	0.0608; 0.1529	0.0852; 0.1685	0.0654, 0.1610	0.0718; 0.0952	0.0726; 0.1100	0.0498; 0.1396
$\Delta\rho_{max}$; $\Delta\rho_{min}$	0.358; -0.287	0.720; -0.847	0.531, -1.398	0.808; -0.796	0.753; -0.486	1.530; -0.777
CCDC number	1044127	1042812	1433403	1042813	1042814	1042815

$^aR_1$=P‖Fo| - |Fc‖ /P|Fo|, wR_2={P[w(Fo^2- Fc^2)^2]/Pw(Fo^2)^2}$^{1/2}$.

Table S2: Bond distances and Angles for **1-4**

$[Cu_2(\mu_2\text{-}C_{15}H_{12}PO_3)_2(^{2,2'}BPy)_2(H_2O)_2]((NO_3)_2.X)$ (1)			
Bond Distances			
Cu1—O3	1.932(14)	Cu1—O1$^{\#1}$	1.945(13)
Cu1—N1	2.004(15)	Cu1—N2	2.015(9)
Cu1—O4	2.245(13)		
Bond Angles			i
O3—Cu1—O1$^{\#1}$	94.25(15)	O3—Cu1—N1	168.63(16)
O1$^{\#1}$—Cu1—N1	93.36(17)	O3—Cu1—N2	90.31(16)
O1$^{\#1}$—Cu1—N2	165.65(14)	N1—Cu1—N2	80.35(17)
O3—Cu1—O4	93.98(15)	O1$^{\#1}$—Cu1—O4	93.79(16)
N1—Cu1—O4	93.92(15)	N2—Cu1—O4	99.47(16)

Symmetry codes for Complex 1: 1-x, -y, 1-z (#1)

$[Cu_2(\mu_2\text{-}C_{15}H_{12}PO_3)_2(^{2,2'}BPy)_2(H_2O)_2]((NO_3)_2.X)$ (1')			
Bond Distances			
Cu1—O3$^{\#1}$	1.942(6)	Cu1—O1	1.946(7)
Cu1—N1	2.010(7)	Cu1—N2	2.012(7)
Cu1—O4	2.238(6)		
Bond Angles			
O3$^{\#1}$—Cu1—O1	93.67(15)	O3$^{\#1}$—Cu1—N1	168.96(18)
O1—Cu1—N1	94.08(17)	O3$^{\#1}$—Cu1—N2	90.58(17)
O1—Cu1—N2	165.82(16)	N1—Cu1—N2	80.07(19)

O3$^{\#1}$—Cu1—O4	93.23(16)	O1—Cu1—O4	91.65(16)
N1—Cu1—O4	94.39(18)	N2—Cu1—O4	101.62(18)

Symmetry codes for Complex 1': 1-x, 2-y, -z (#1)

$[Cu_2(\mu_2\text{-}C_{15}H_{12}PO_3)_2(^{2,2'}BPy)_2(NO_3)_2].MeOH$ (2)			
Bond Distances			
Cu1—O3	1.931(9)	Cu1—O1	1.957(3)
Cu1—N2	1.988(9)	Cu1—N1	1.994(2)
Cu1—O4	2.285(8)		
Bond Angles			
O3$^{\#1}$—Cu1—O1	93.70(7)	O3$^{\#1}$—Cu1—N1	90.94(7)
O1—Cu1—N1	166.91(7)	O3$^{\#1}$—Cu1—N2	171.80(7)
O1—Cu1—N2	93.78(7)	N2—Cu1—N1	81.26(8)
O3$^{\#1}$—Cu1—O4	91.62(7)	O1—Cu1—O4	88.72(6)
N1—Cu1—O4	103.54(7)	N2—Cu1—O4	92.67(7)

Symmetry codes for Complex 2: -x, 1-y, -z (#1)

$[Cu(C_{17}H_{16}PO_3)(^{2,2'}BPy)_2](NO_3).(H_2O)_2$ (3)			
Bond Distances			
Cu1—N2	1.978(19)	Cu1—N1	2.056(11)
Cu1—N4	1.990(19)	Cu1—N3	2.112(12)
Cu1—O2	1.994(5)		
Bond Angles			

N2—Cu1—N4	177.47(8)	O2—Cu1—N1	131.70(9)
N2—Cu1—O2	92.16(9)	N2—Cu1—N3	98.77(9)
N4—Cu1—O2	90.31(9)	N4—Cu1—N3	79.64(9)
N2—Cu1—N1	80.21(9)	O2—Cu1—N3	114.90(9)
N4—Cu1—N1	98.56(9)	N1—Cu1—N3	113.40(1)
$[Cu(^{2,2'}BPy)_2.(NO_3)].NO_3. H_2O$ (4)			
Bond Distances			
Cu1—N2	2.056(2)	Cu1—N1	1.978(6)
Cu1—N4	1.988(7)	Cu1—N3	2.021(7)
Cu1—O1	2.261(6)		
Bond Angles			
N1—Cu1—N4	170.67(8)	N4—Cu1—N3	81.18(8)
N1—Cu1—N3	99.34(8)	N1—Cu1—N2	81.41(8)
N4—Cu1—N2	104.26(8)	N3—Cu1—N2	140.01(8)
N1—Cu1—O1	85.32(8)	N4—Cu1—O1	87.06(8)
N3—Cu1—O1	127.88(8)	N2—Cu1—O1	92.11(7)

Table S3. Non-covalent interactions and angles for 1-4 (Å and ^{o}):

1					
D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<(D-H···A)>**	**symmetry codes**
O4-H4A···O5	0.94	1.93	2.862(10)	170	-x+1, -y+1, -z+1
1'					
D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<(D-H···A)>**	**symmetry codes**
O4-O6A	-	-	2.852(16)	-	-
2					
D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<(D-H···A)>**	**symmetry codes**

O7-H7A···O5	0.82	1.94	2.748(4)	168	x+1,+y,+z
3					
D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<(D-H···A)>**	**symmetry codes**
O7-H7W···O6	0.87(5)	2.05(5)	2.841(6)	150(4)	-x+1, -y+1, -z+1
O7-H8W···O5	0.78(5)	2.16(5)	2.892(5)	157(5)	x-1, +y-1, +z
4					
D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<(D-H···A)>**	**symmetry codes**
O7-O5	-	-	2.956(5)	-	x, -1+y, -1+z

Table S4. Various π- π interactions involved in complexes 1-4 and 1' (Å) :

Complexes	**π- π interaction**	**Detail of the interaction**
Complex 1	π(anthryl)- π(anthryl), 3.898 Å	along *ac* plane between two composite units
	π($^{2,2'}$BPy)- π($^{2,2'}$BPy), 3.651 Å	along *ac* plane between two composite units
	π($^{2,2'}$BPy)- π($^{2,2'}$BPy), 3.647 Å	along *ab* plane between two different 2D sheets
Complex 1'	π(anthryl)- π(anthryl), 3.727 Å	along *ac* plane between two composite units
	π($^{2,2'}$BPy)- π($^{2,2'}$BPy), 3.610 Å	along *ac* plane between two composite units
	π($^{2,2'}$BPy)- π($^{2,2'}$BPy), 3.484 Å	along *ab* plane between two different 2D sheets
Complex 2	π($^{2,2'}$BPy)- π(anthryl), 3.202 Å	Interlayer distance along *ac* plane
	π($^{2,2'}$BPy)- π(anthryl), 3.625 Å	Intralayer distance
	CH(methanol)- π(anthryl), 2.896 Å	Along *ac* plane
Complex 3	π($^{2,2'}$BPy)- π($^{2,2'}$BPy), 3.632 Å	Along *ab* plane
	π ($^{2,2'}$BPy)- π(anthryl), 2.886 Å	T-shaped π- π stacking along *ac* plane
	CH(OC_2H_5 group on anthryl)- π(anthryl), 2.869 Å	Interlayer distance between -OCH_2CH_3 and anthryl ring
Complex 4	π ($^{2,2'}$BPy)- π(anthryl), 3.446 Å	T-shaped π- π stacking along *ab* plane
	π($^{2,2'}$BPy)- π($^{2,2'}$BPy), 3.737 Å	Along *ac* plane
	π($^{2,2'}$BPy)- π($^{2,2'}$BPy), 2.900 Å	Parallel to *bc* plane

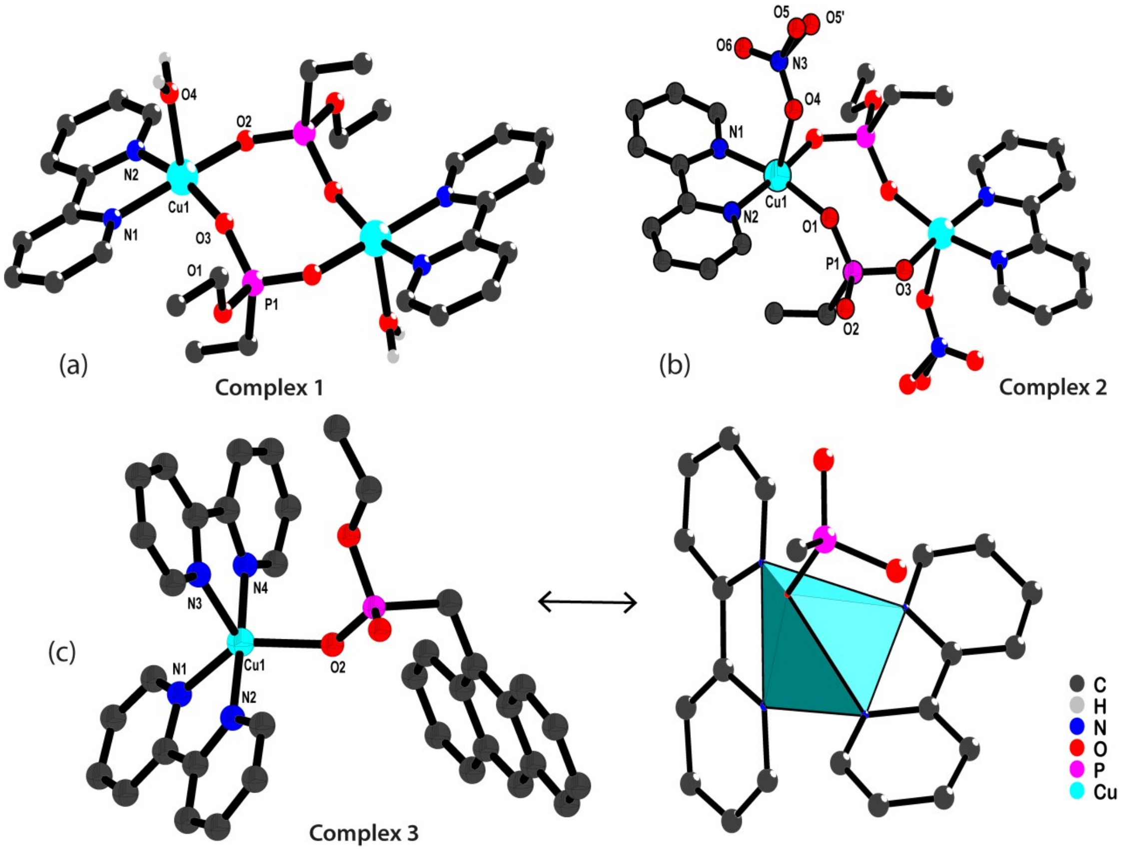


Fig. S1: Coordination environment around Cu(II) center in (a) complex **1;** (b) complex **2**; (c) complex **3**

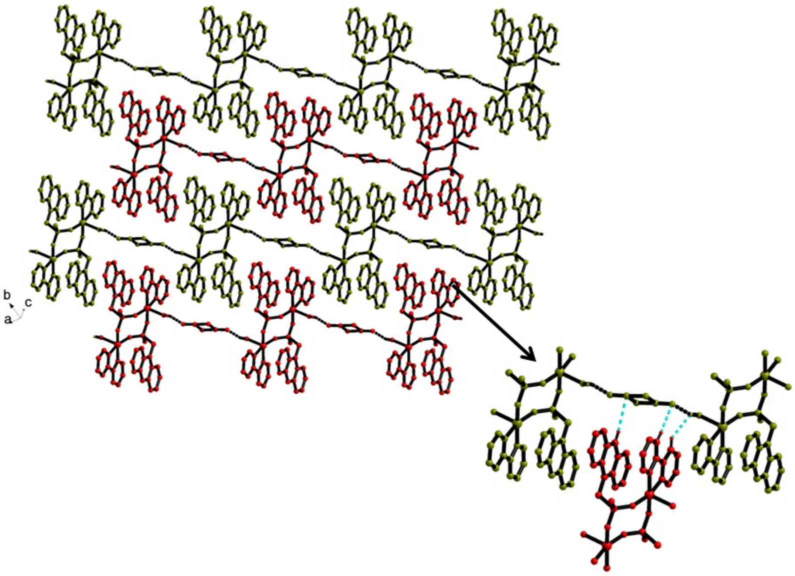


Fig. S2: View of interdigitated parallel 1D chains of composite unit and nitrate anion in *ac*-plane interacting through C–H···O and N–H···O interaction in **1**

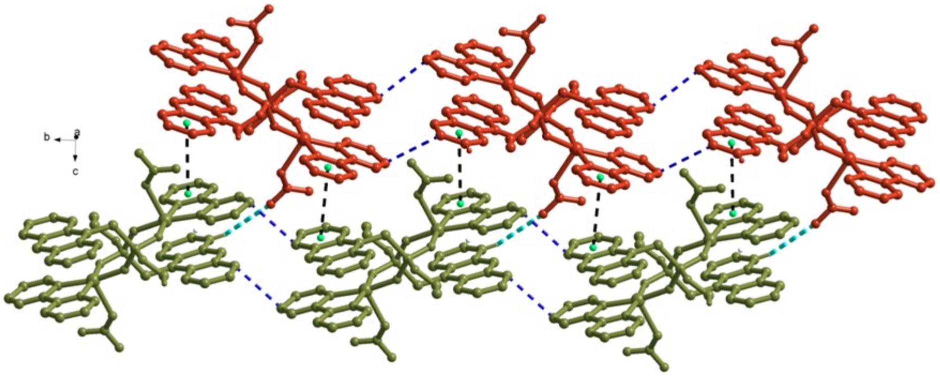


Fig. S3: Parallel stacking of 2D sheets interlinked by various secondary intermolecular interactions such as C–H···O, C–H···π and π···π along *a*-axis in **2**

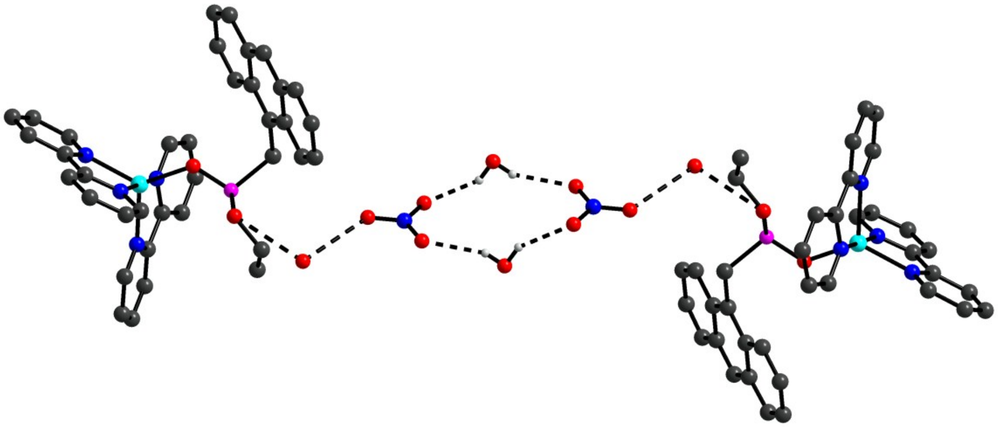


Fig. S4: Formation of cluster in **3**

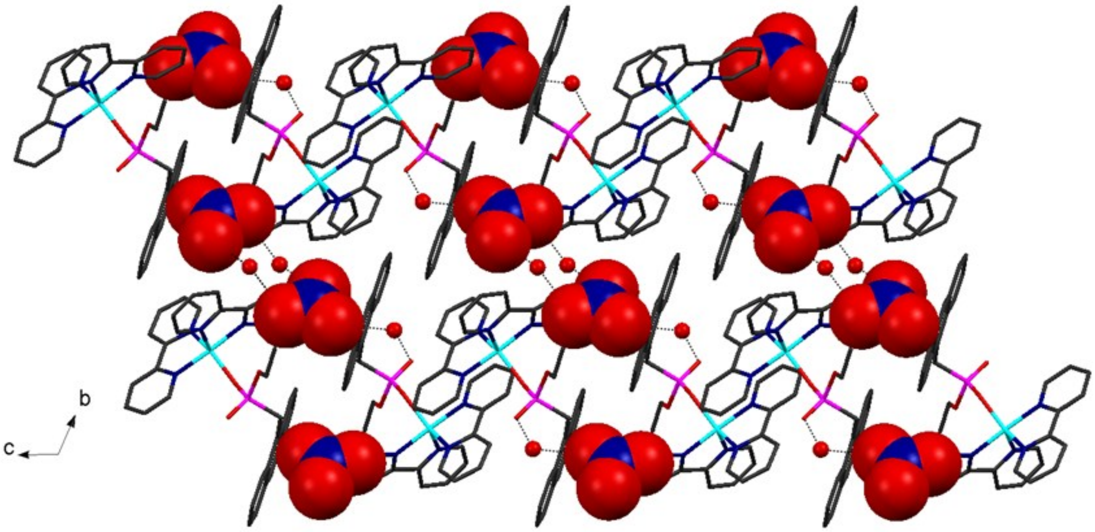


Fig. S5: Representation of 2D sheet along a-axis in **3**

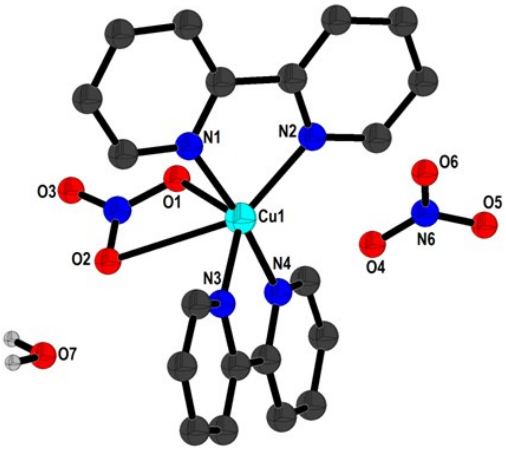


Fig. S6: Crystal structure of $[Cu(^{2,2'}BPy)_2(NO_3)].NO_3.H_2O$ (**4**)

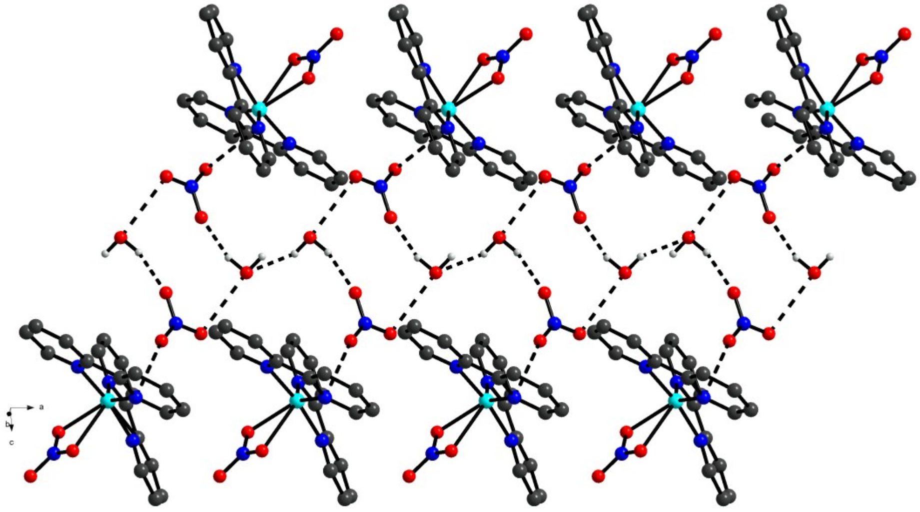


Fig. S7: Representation of 2D sheet along b-axis in **4**

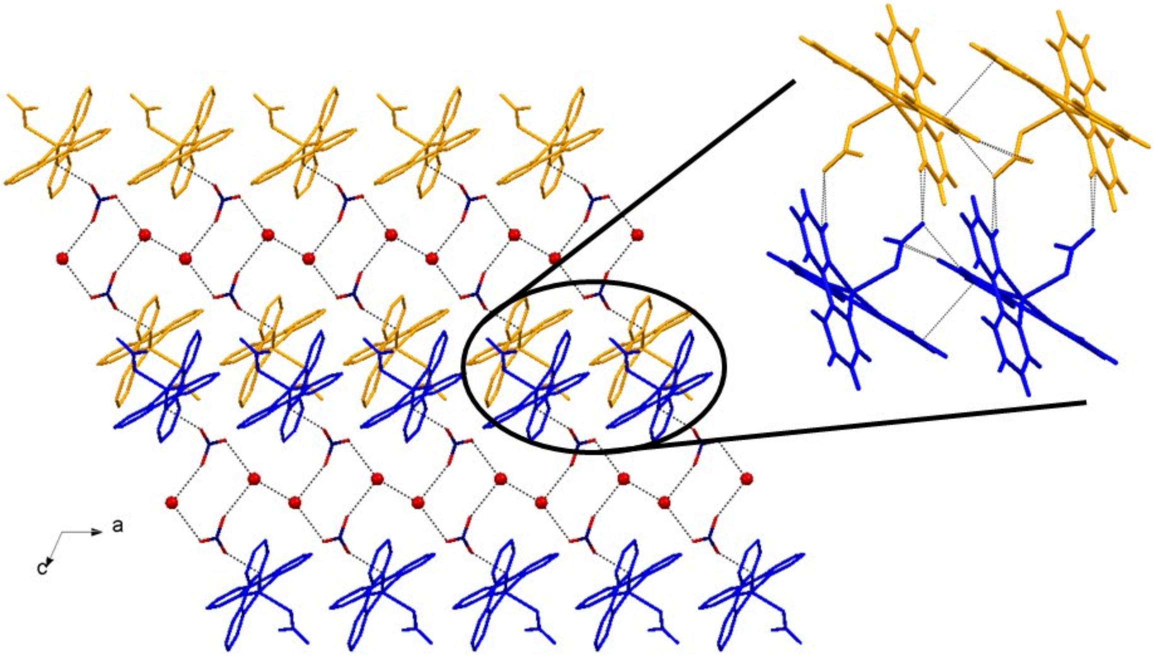


Fig. S8: Representation of 2D sheet along b-axis in **4**

References:

1. A. K. Bhattacharya and G.Thyagarajan, "Michaelis–Arbuzov rearrangement", *Chem. Rev.*, 1981, **81**, 415.
2. G. M. Sheldrick, SADABS, 1996**,** University of Göttingen. Göttingen, Germany.
3. G. M. Sheldrick, *Acta Cryst.*, 1990, **A46**, 467-473.
4. G. M. Sheldrick, SHELXTL-NT 2000 version 6.12, reference manual, University of Göttingen, Göttingen, Germany.
5. A. L. Spek, "PLATON, *A Multipurpose Crystallographic Tool*", **2005**, Utrecht University, Utrecht, The Netherlands.
6. G. M. Sheldrick, SHELXL-93, "A Program for the Refinement of Crystal Structures".
7. A. L. Spek, "PLATON/SQUEEZE—an effective tool for taking the contribution of disordered solvent into account in crystal structure refinement", 2004, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands.