Electronic Supplementary Information (ESI)

Molecular and Polymeric Zinc(II) Phosphonates: Isolation of an Octanuclear Ellipsoidal Ensemble

Dipankar Sahoo[a], Ramakirushnan Suriyanarayanan[a], Ramesh K. Metre[a] and Vadapalli Chandrasekhar*[a,b]

[a] Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur - 208016, India.

[b] National Institute of Science Education and Research, Institute of Physics Campus, Sachivalaya Marg, Sainik School Road, Bhubaneshwar-751 005, Orissa, India

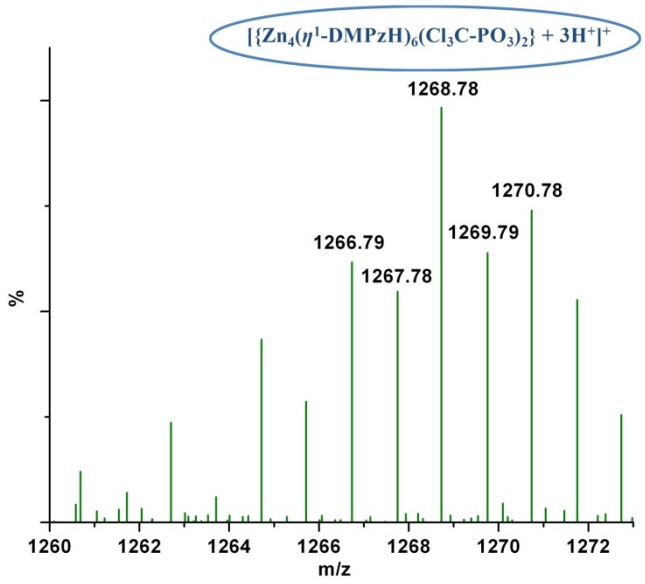


Figure S1. ESI-MS of **2**.

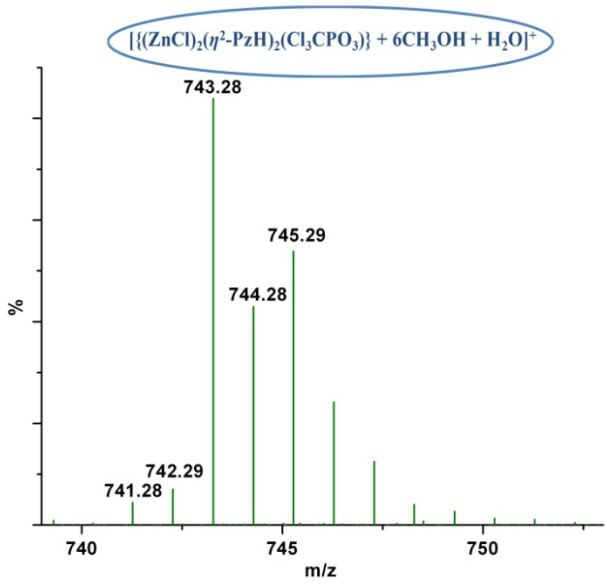


Figure S2. ESI-MS of **3**.

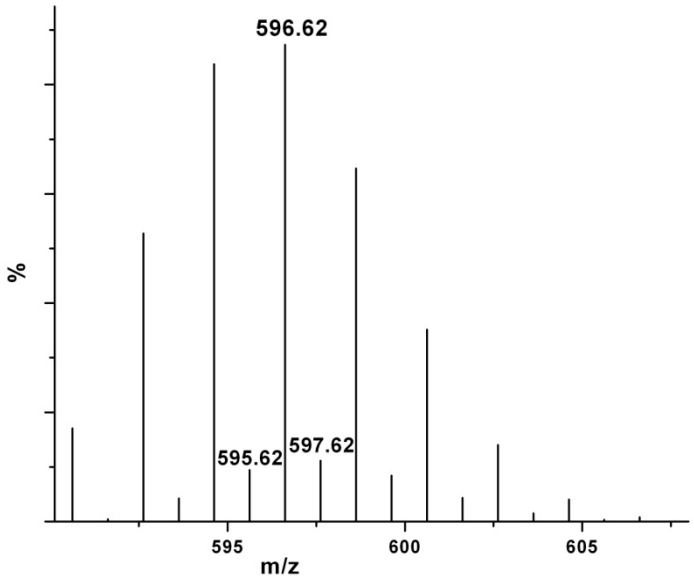


Figure S3. Simulated ESI-MS of **1**.

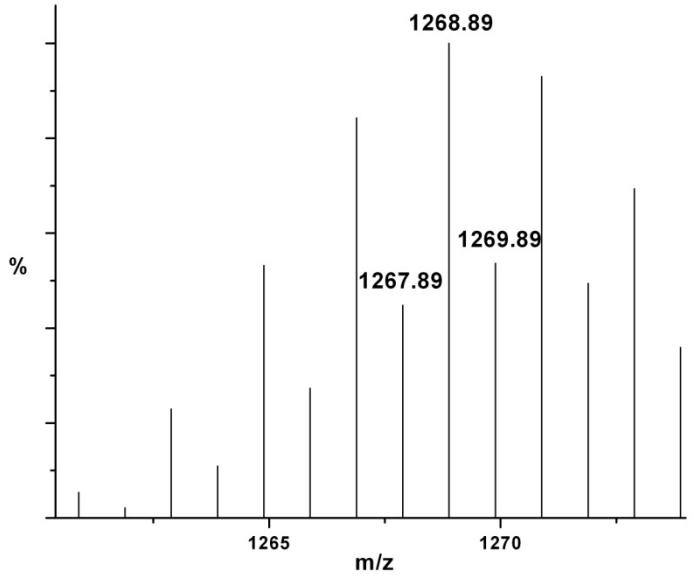


Figure S4. Simulated ESI-MS of **2**.

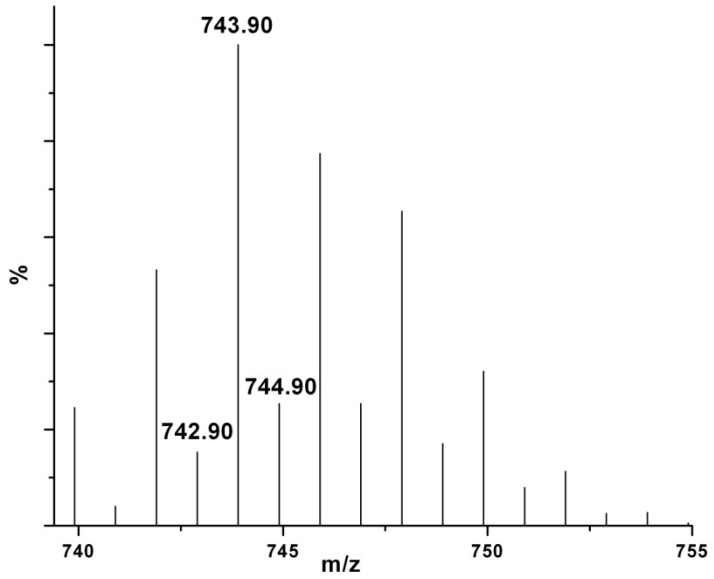


Figure S5. Simulated ESI-MS of **3**.

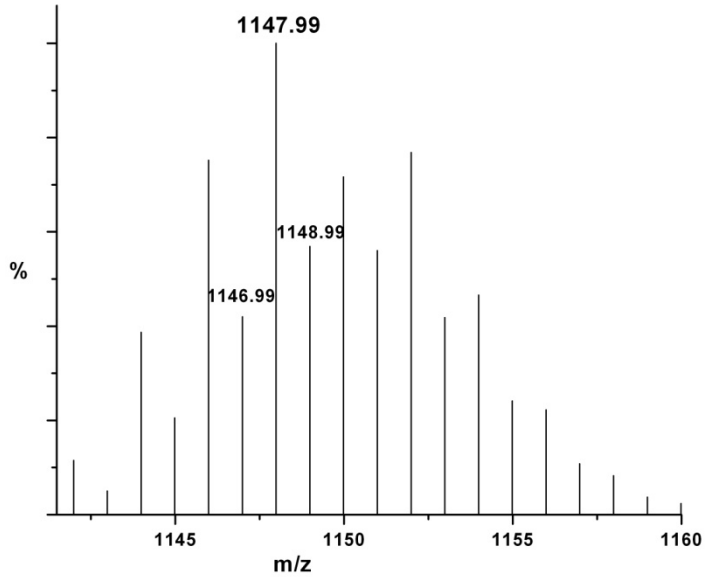


Figure S6. Simulated ESI-MS of **4**.

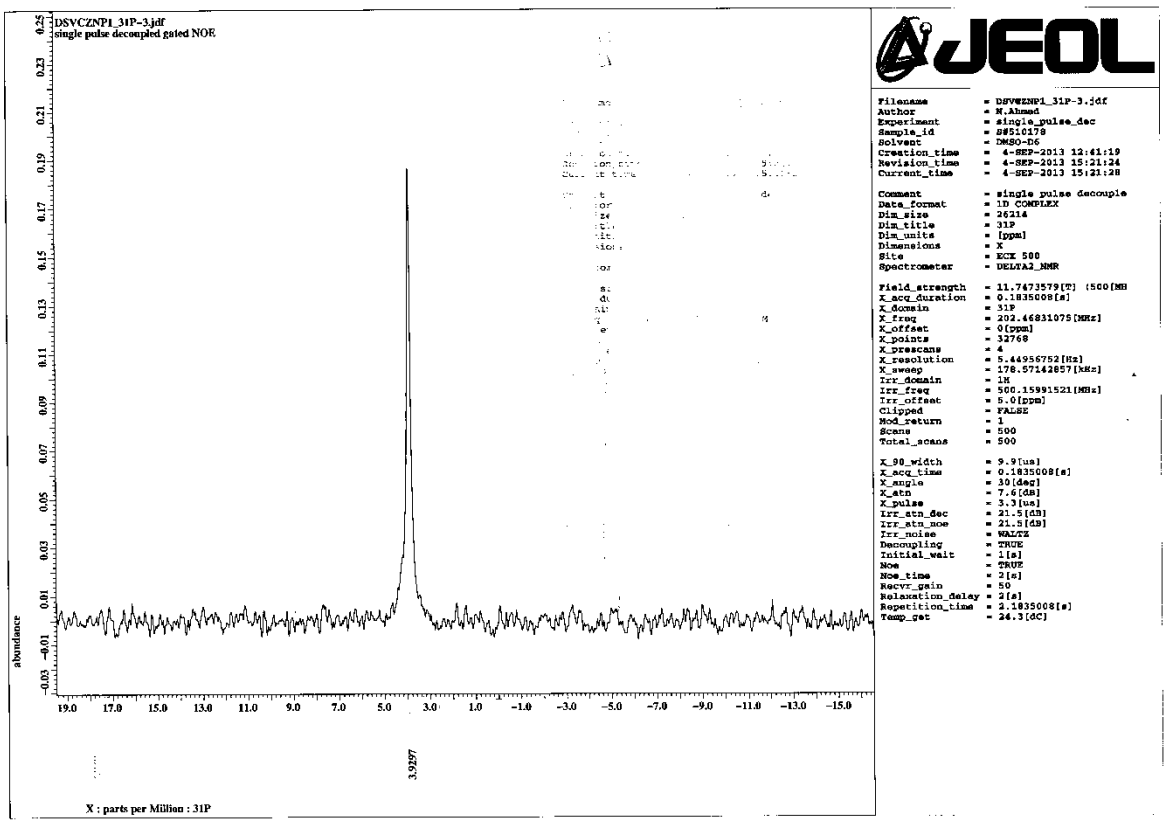


Figure S7. ^{31}P NMR of **1**.

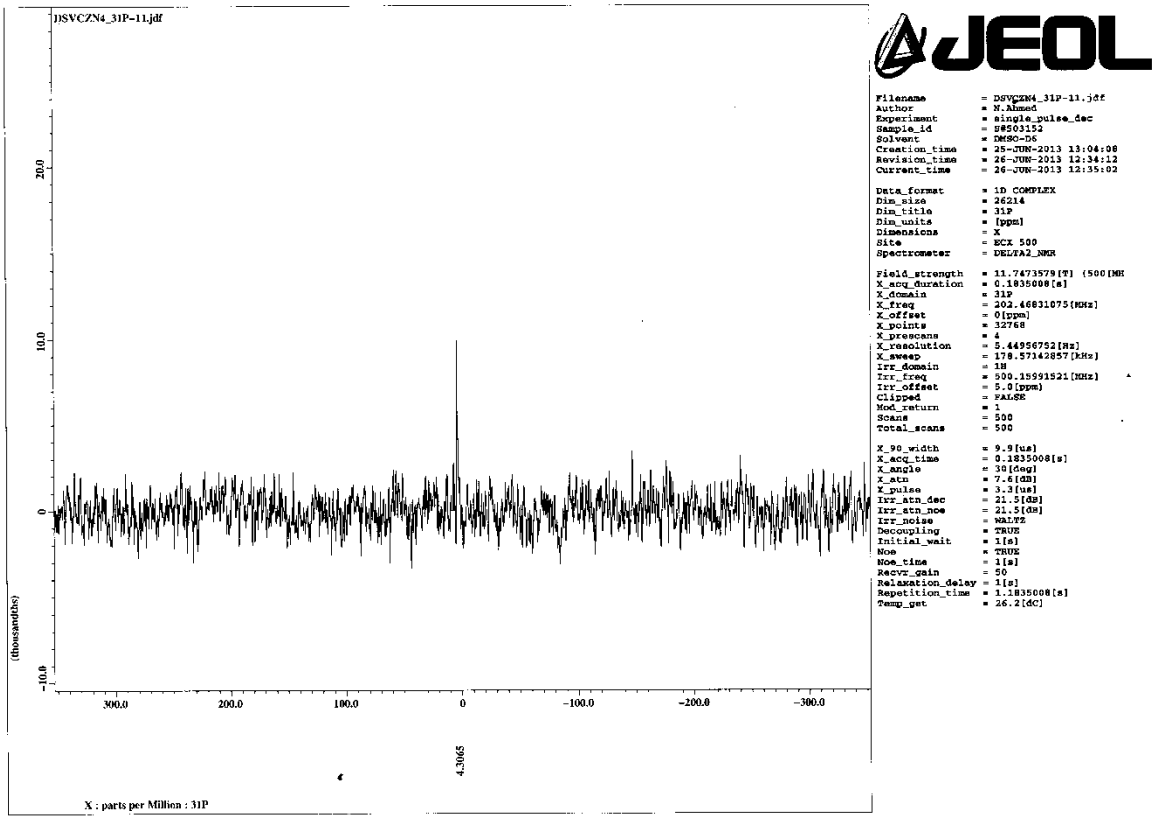


Figure S8. ^{31}P NMR of **2**.

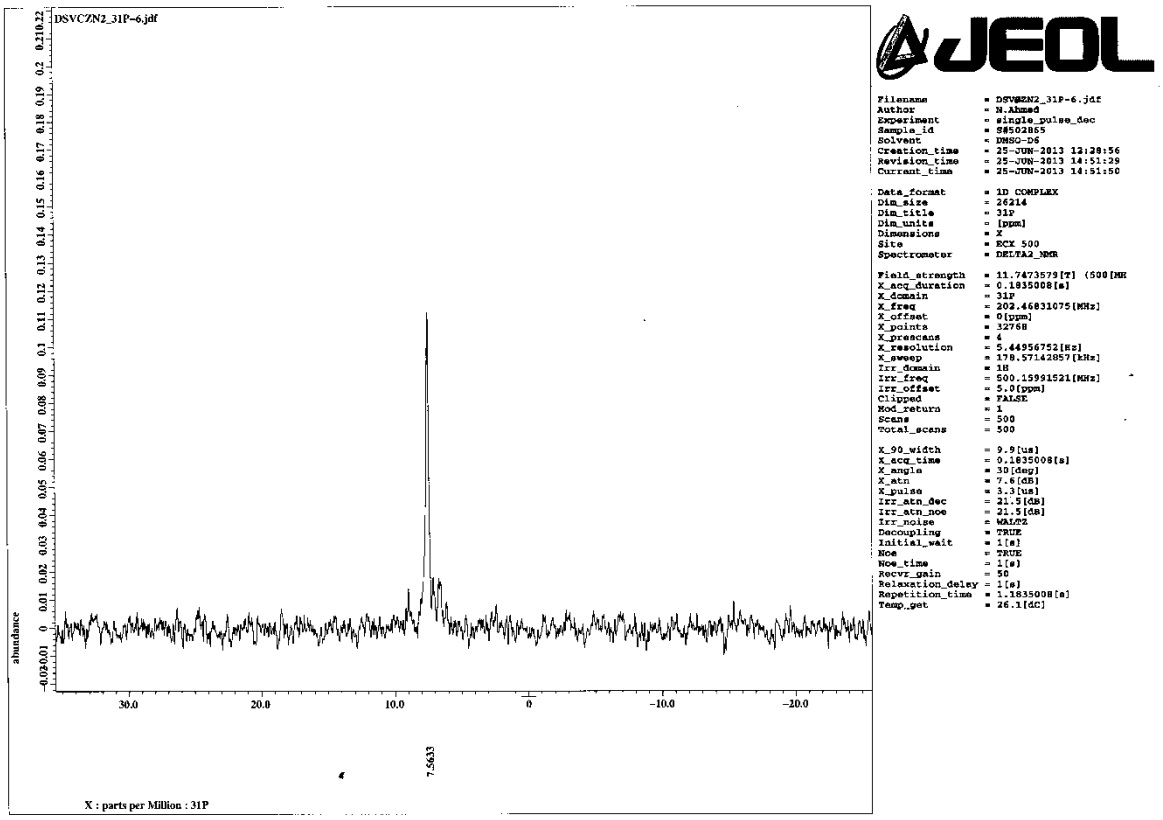


Figure S9. ^{31}P NMR of **3**.

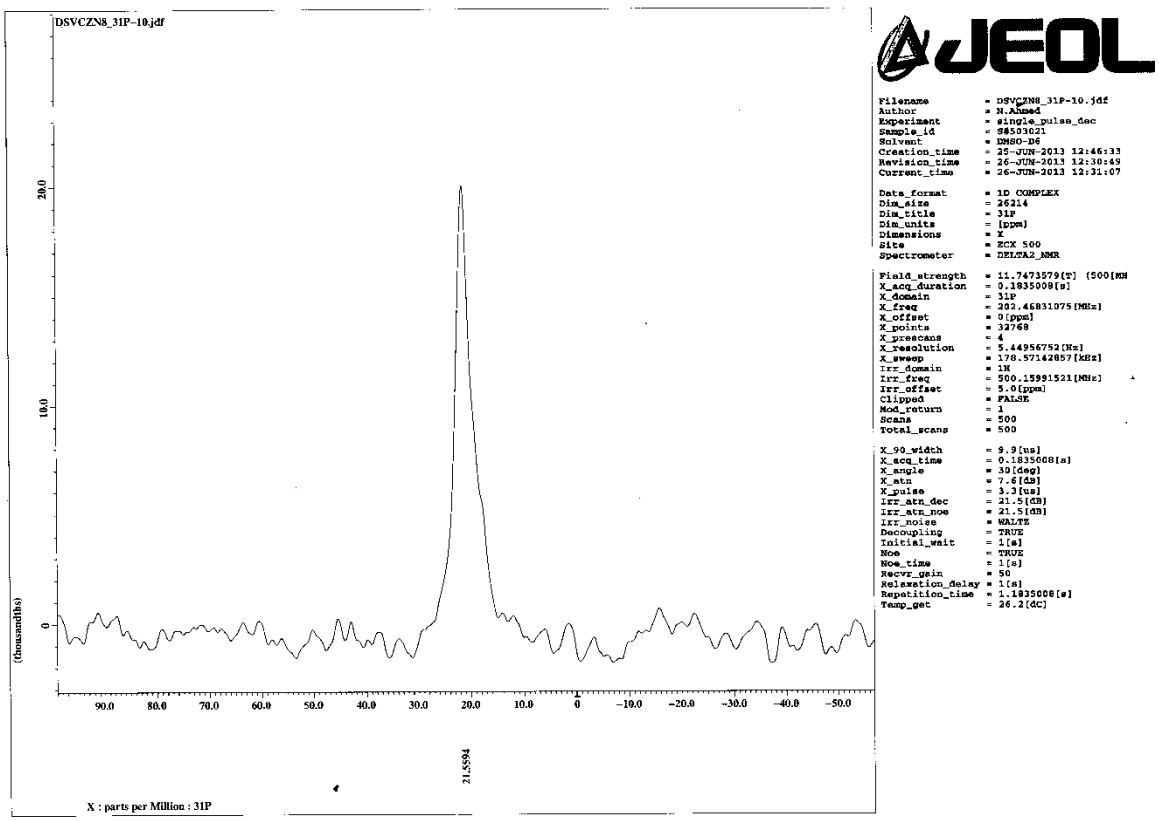


Figure S10. ^{31}P NMR of **4**.

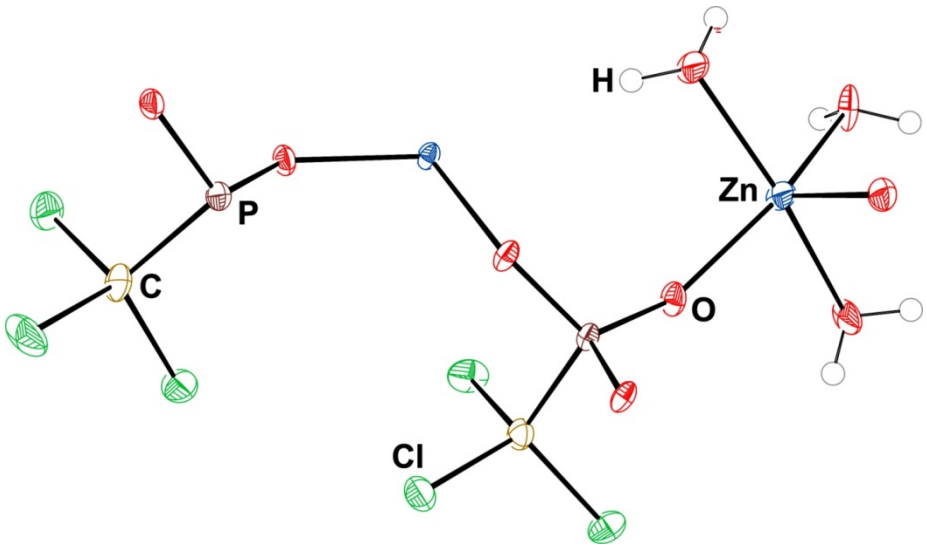


Figure S11. *ORTEP* diagram of **1** with 50 % thermal ellipsoids.

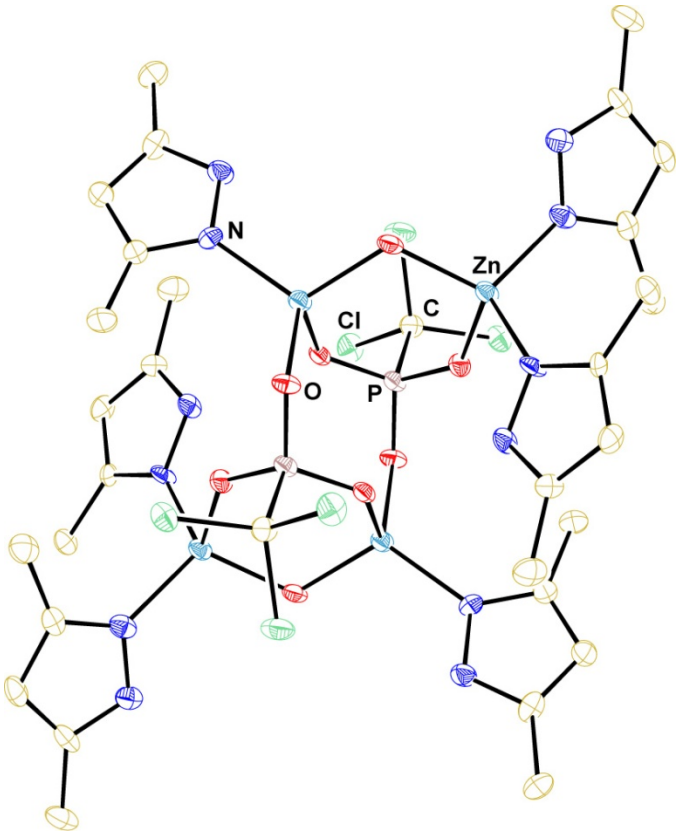


Figure S12. *ORTEP* diagram of **2** with 50 % thermal ellipsoids. All H atoms and two ClO_4^- anions have been deleted for clarity.

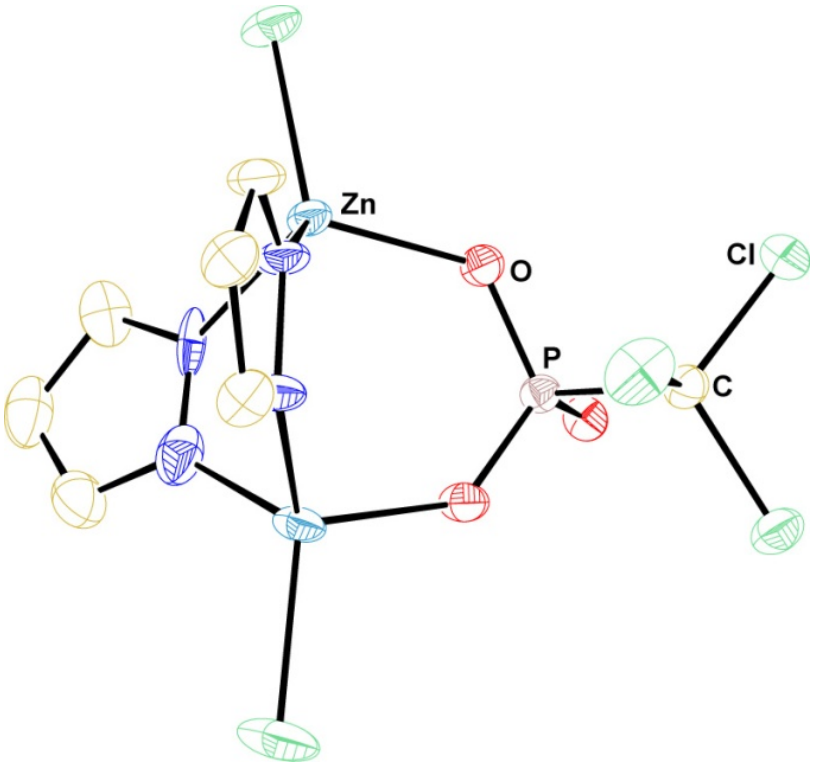


Figure S13. *ORTEP* diagram of **3** with 50 % thermal ellipsoids. All H atoms and two Et_3NH^+ cations have been deleted for clarity.

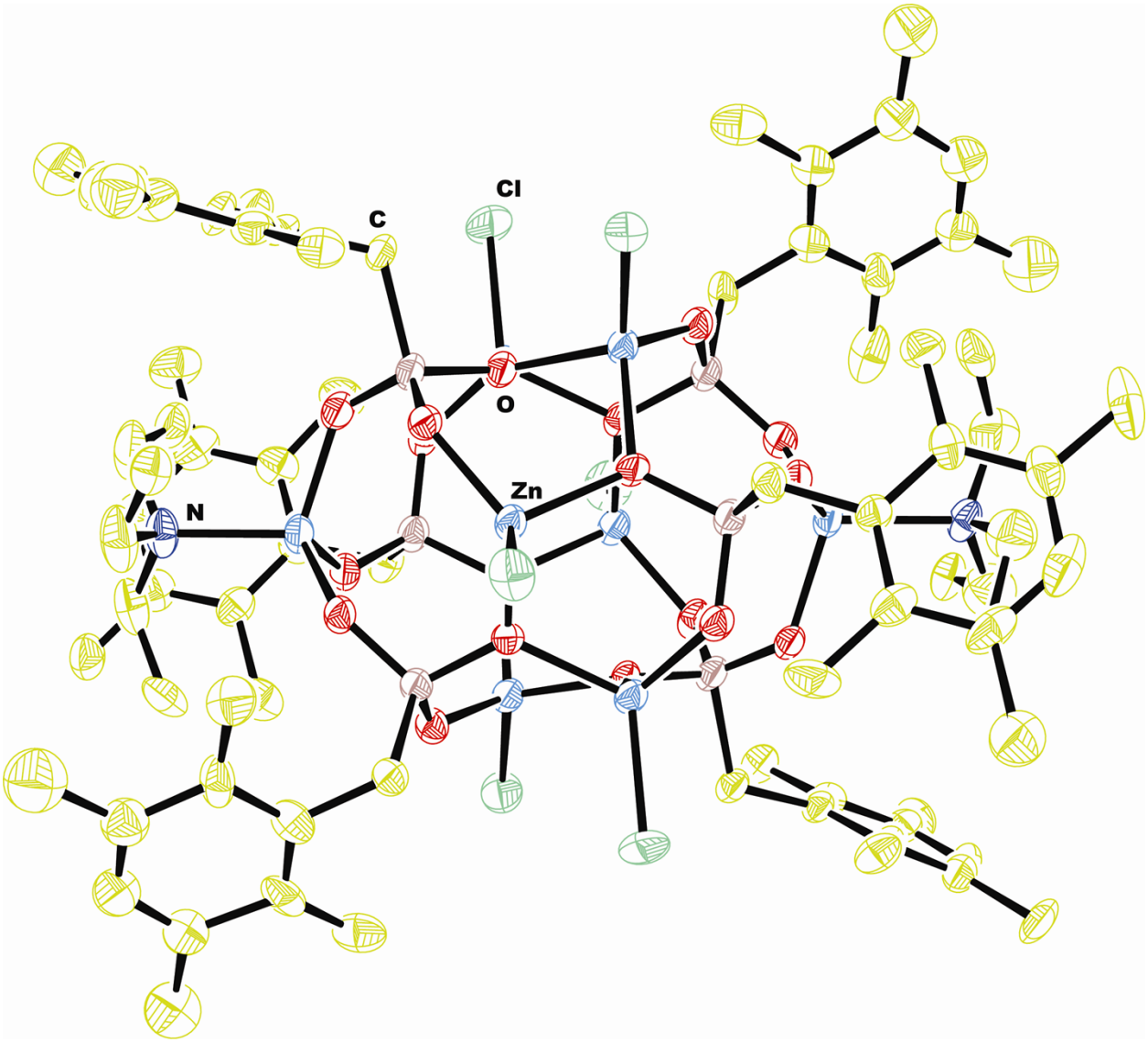


Figure S14. *ORTEP* diagram of **4** with 50% thermal ellipsoids. All H atoms , water and Et_3NH^+ cations are not shown for clarity

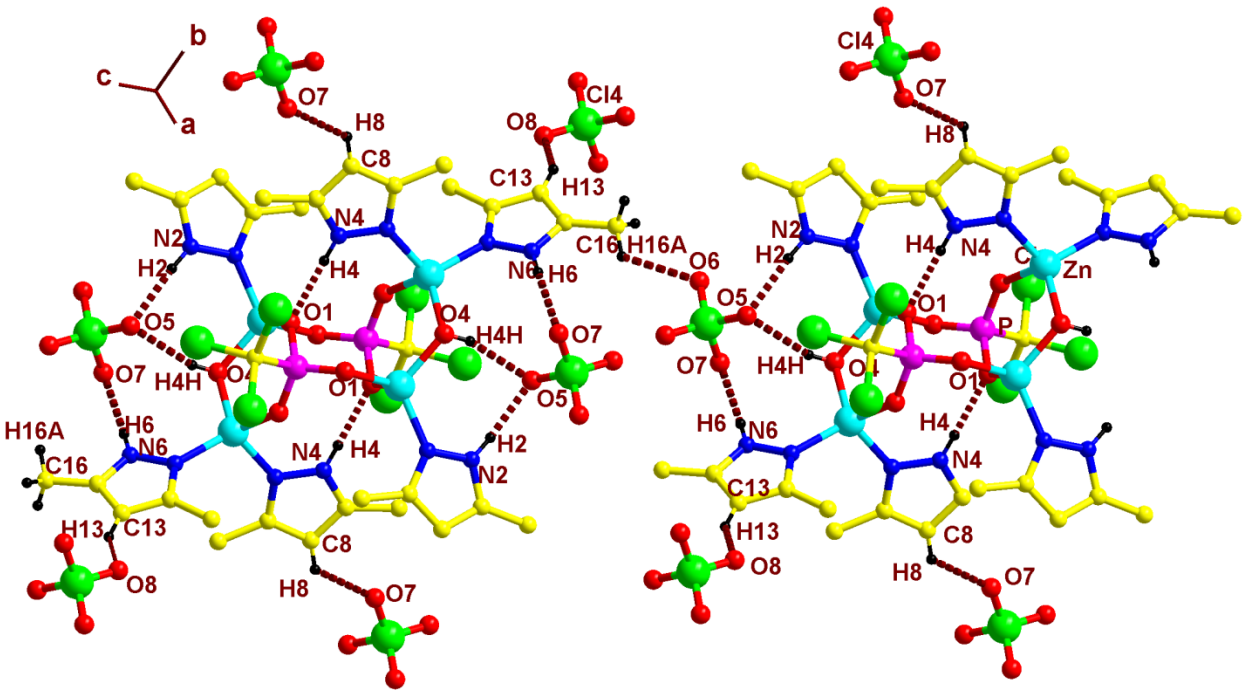


Figure S15. H-bond interactions in **2** (Table S1).

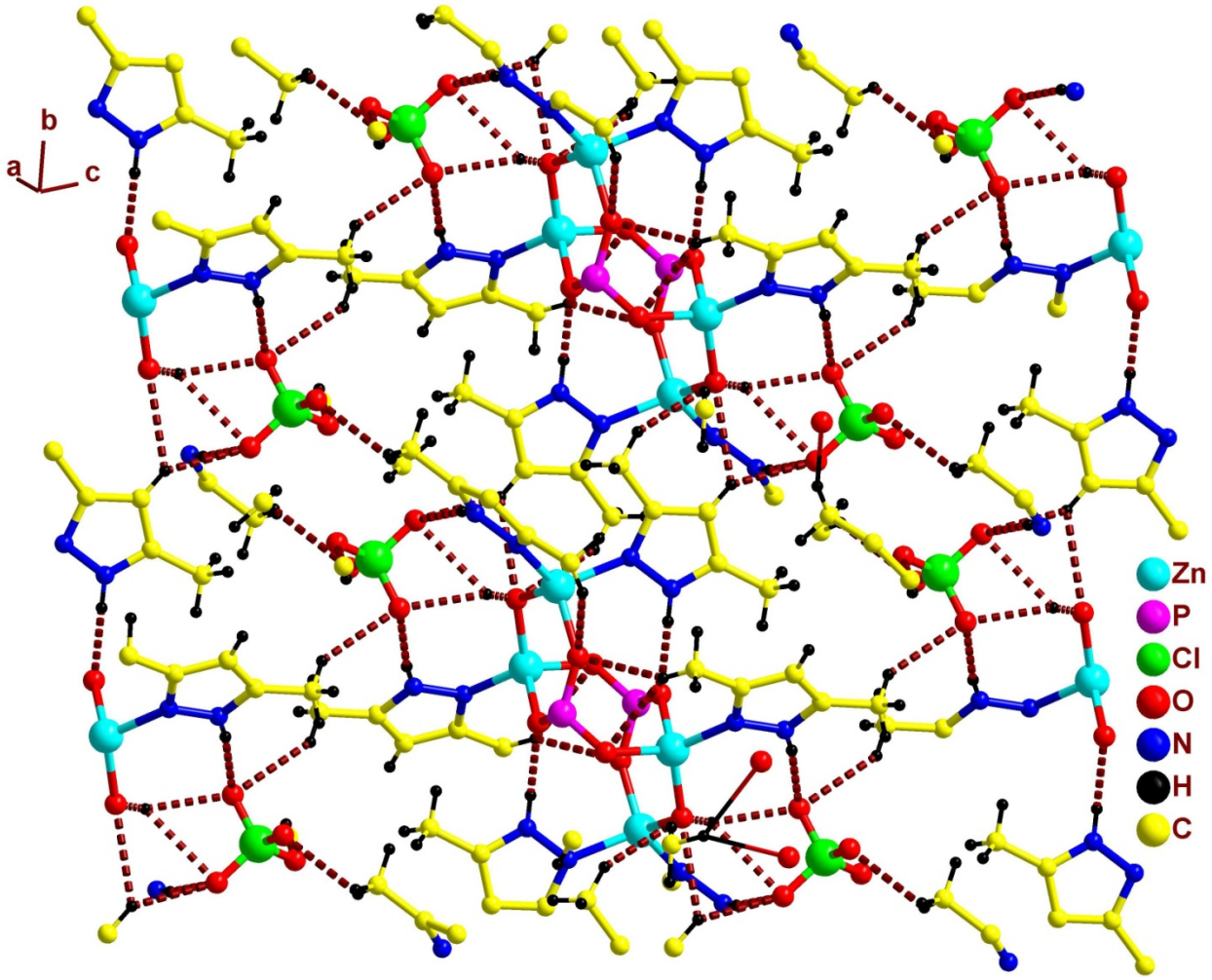


Figure S16. Supramolecular assembly along the *a*-axis of **2**.

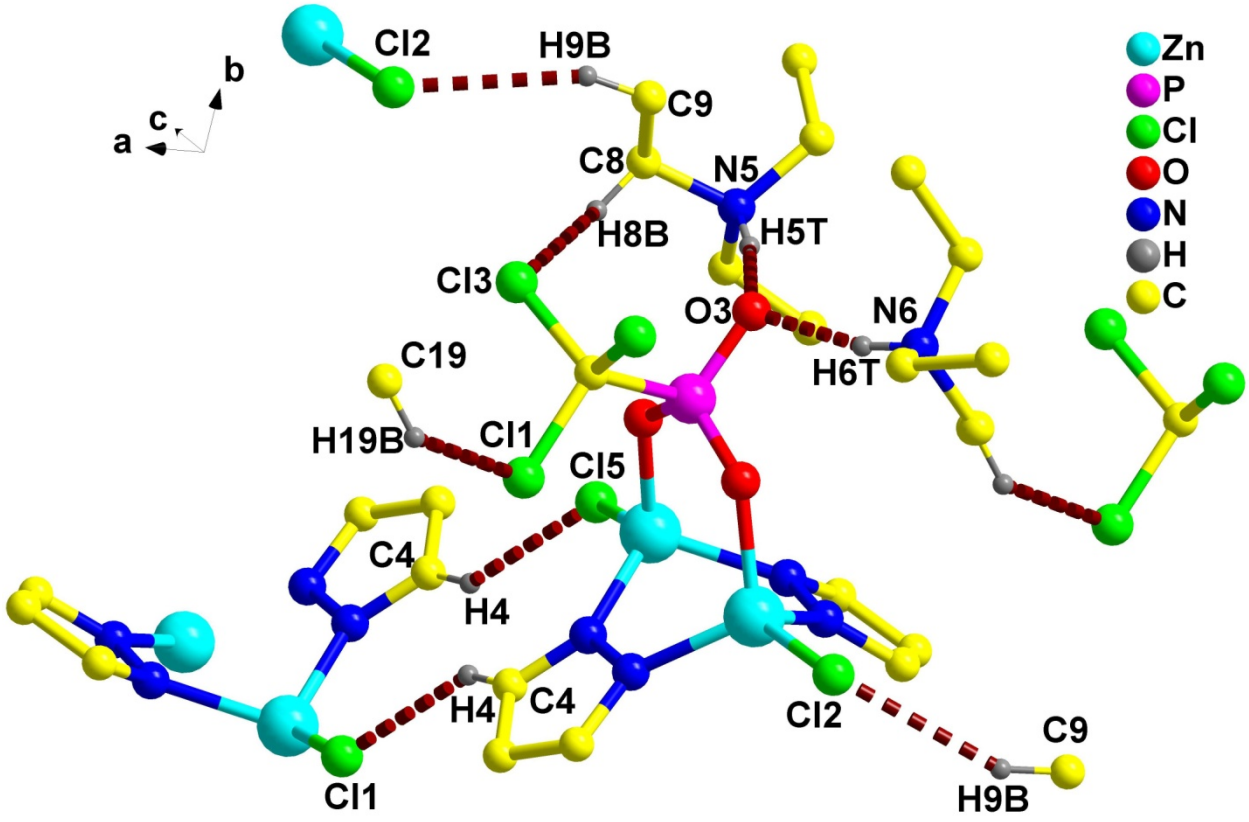


Figure S17. H-bonds interactions in **3** (Table S2). Some H atoms have been omitted for clarity.

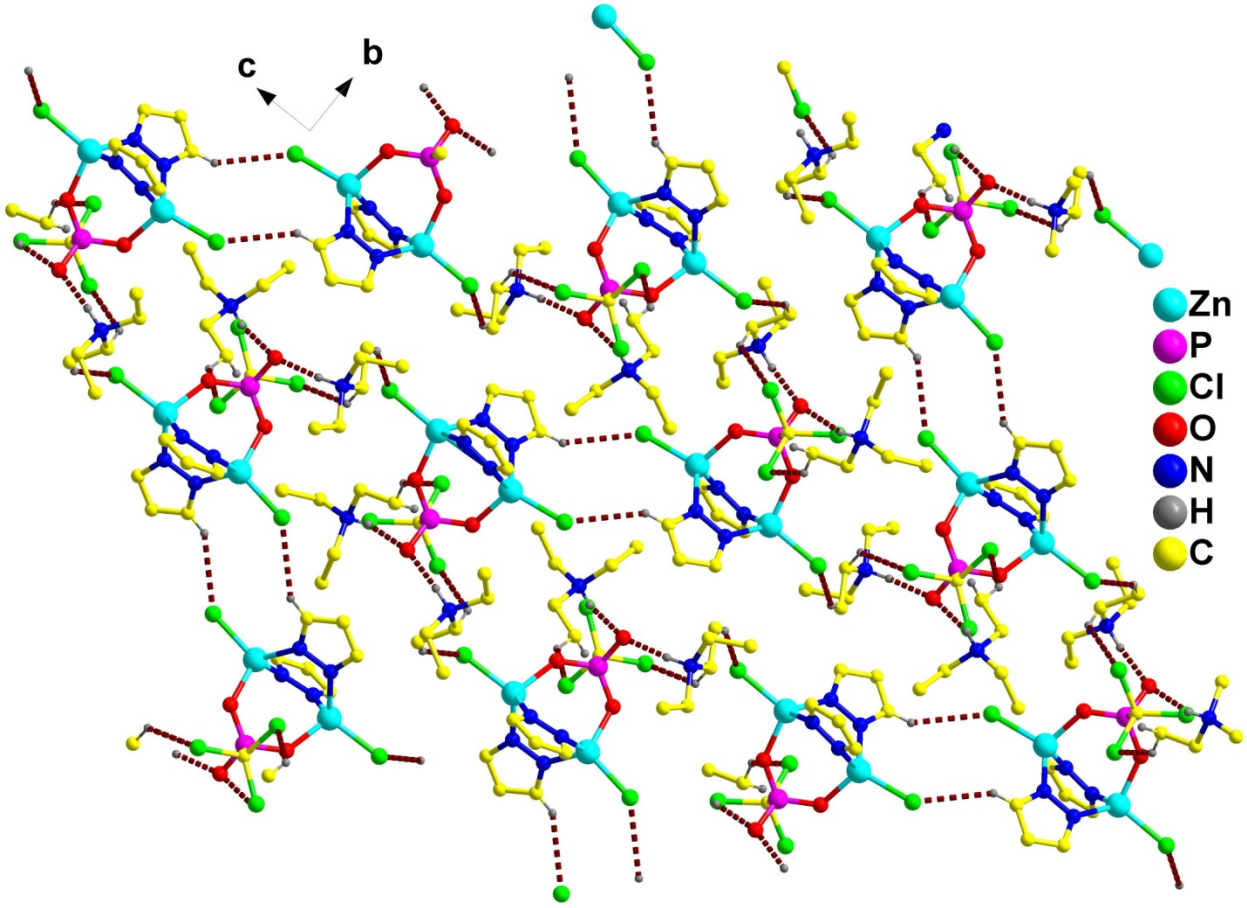
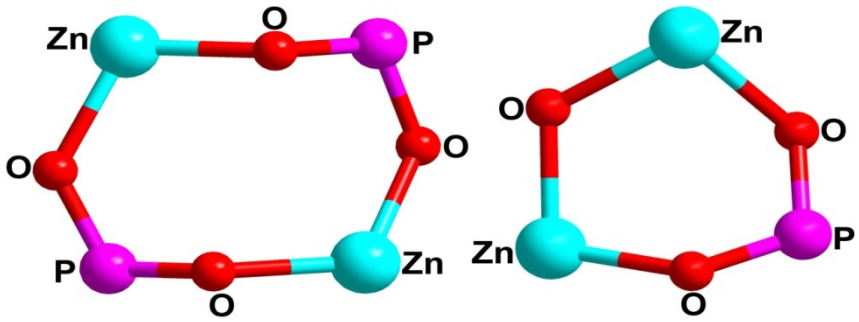


Figure S18. 3D-supramolecular assembly of **3** by H-bond interactions.



(a) (b)

Figure S19. (a) Eight membered $Zn_2P_2O_4$ ring (b) Six membered Zn_2O_3P ring of of **4**.

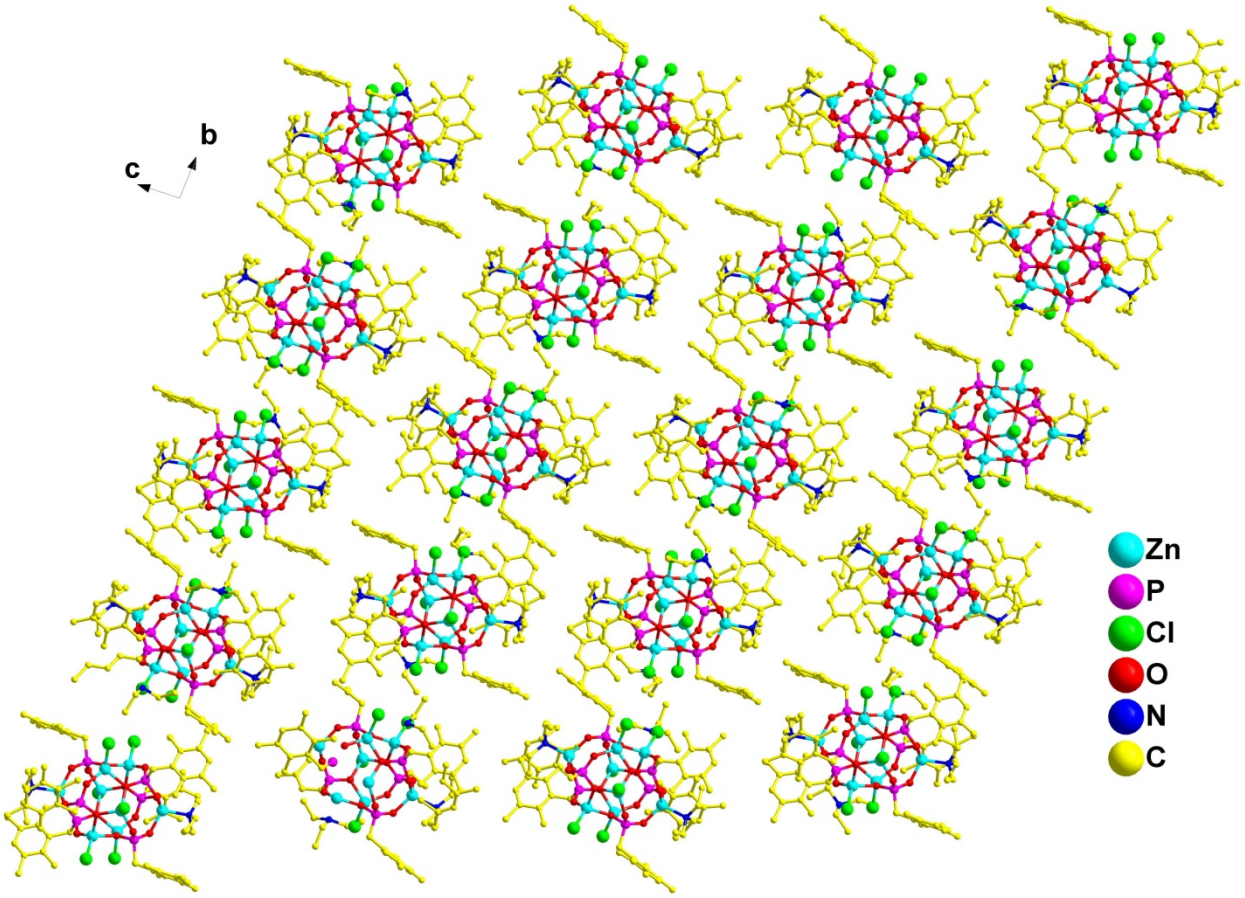


Figure S20. Supramolecular assembly along the *a*-axis of **4**.

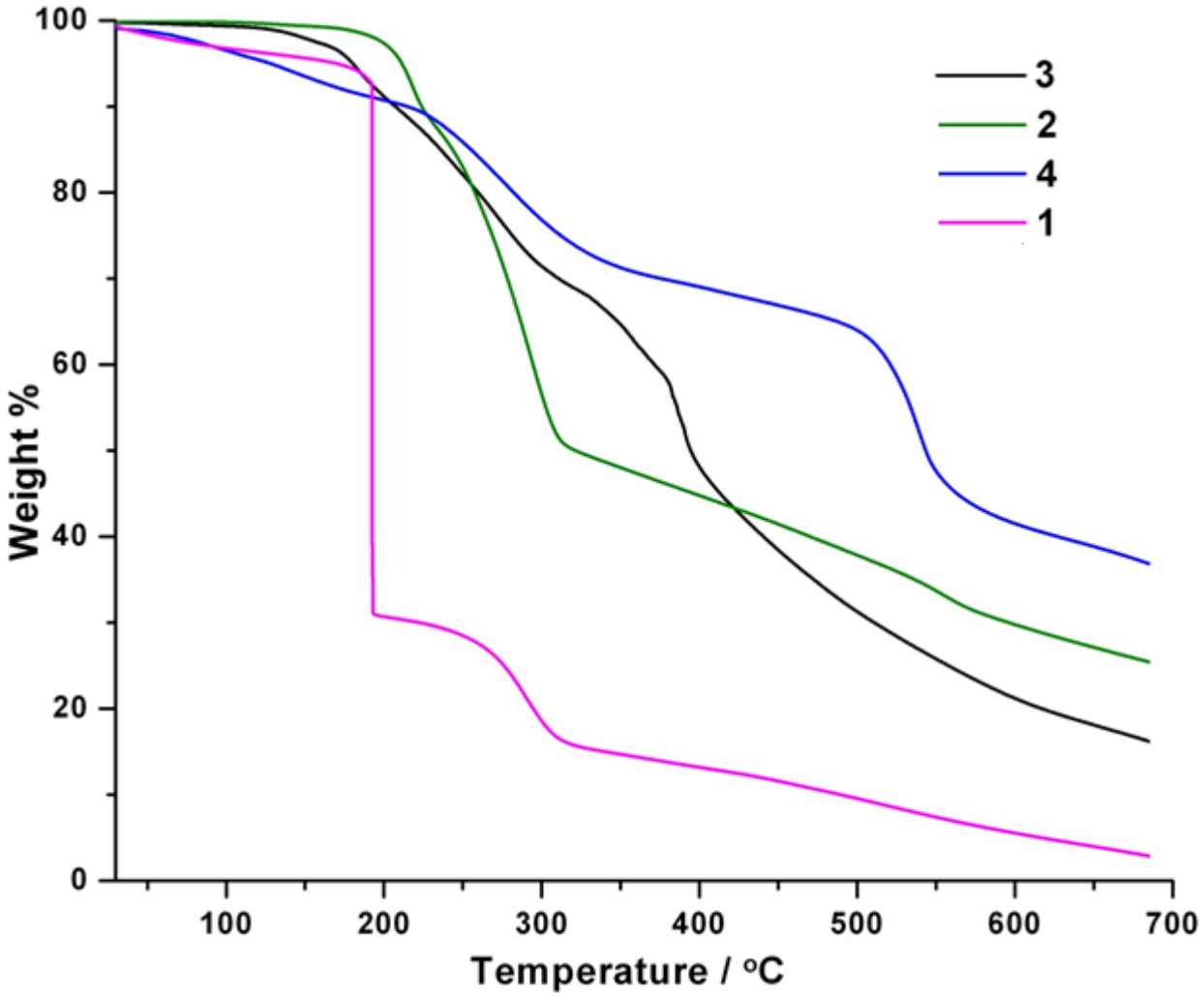
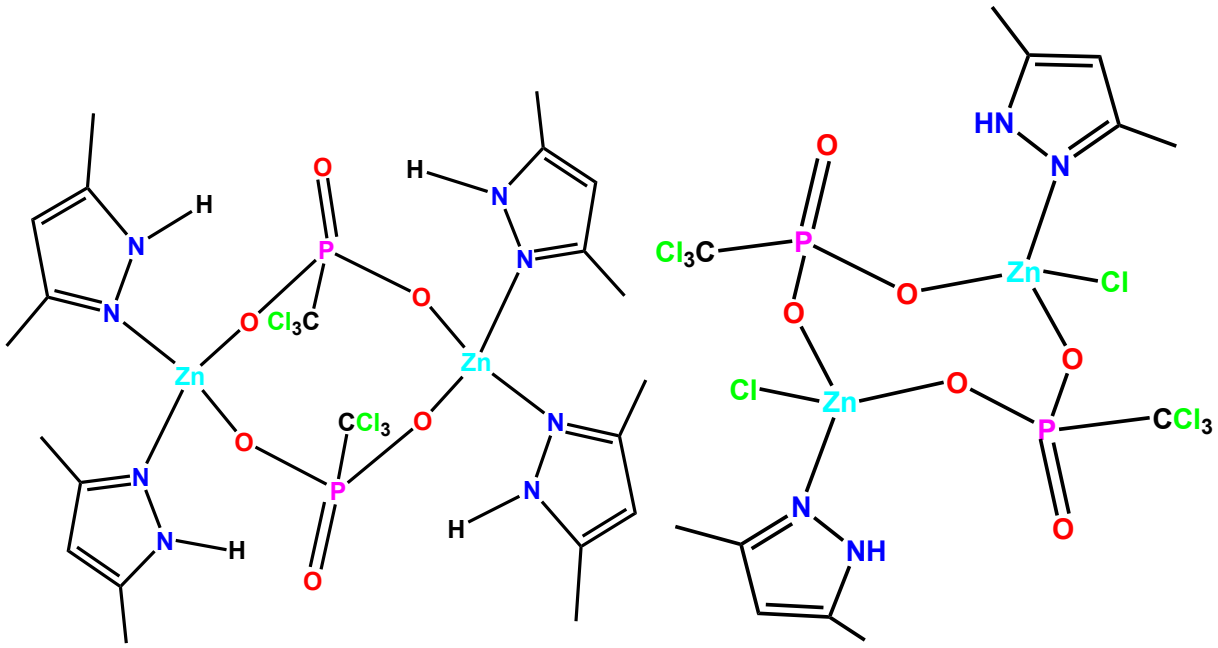
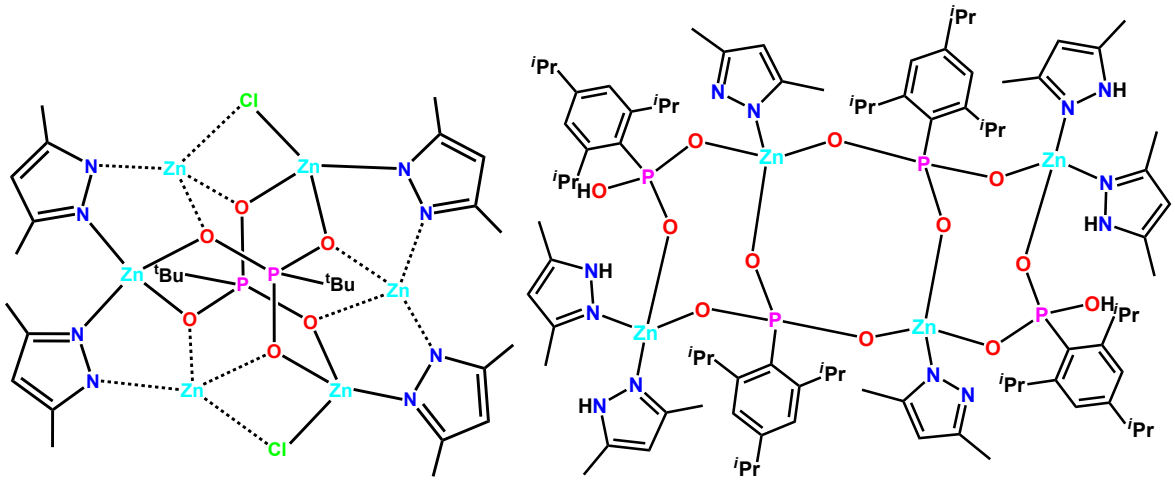


Figure S21. TGA plots of **1-4**.



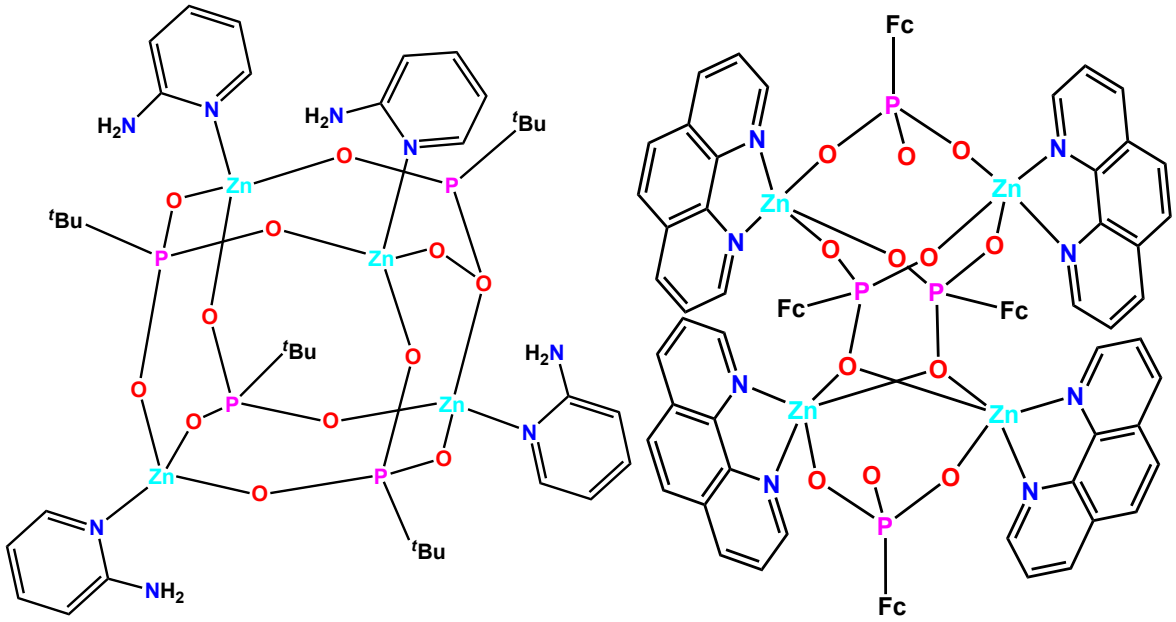
(a) (b)

Reference: V. Chandrasekhar, D. Sahoo and R. K. Metre, *Cryst. Eng. Comm*. 2013, **15**, 7419.



(c) (d)

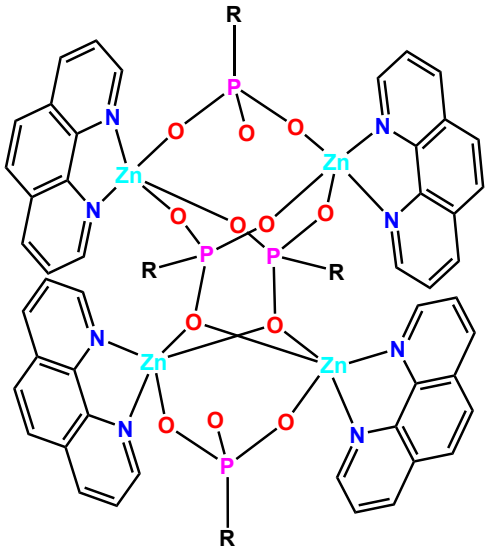
Reference: (c) V. Chandrasekhar, S. Kingsley, B. Rhatigan, M. K. Lam and A. L. Rheingold, *Inorg. Chem*. 2002, **41**, 1030; (d) V. Chandrasekhar, P. Sasikumar, R. Boomishankar and G. Anantharaman, *Inorg. Chem*. **2006**, *45*, 3344.



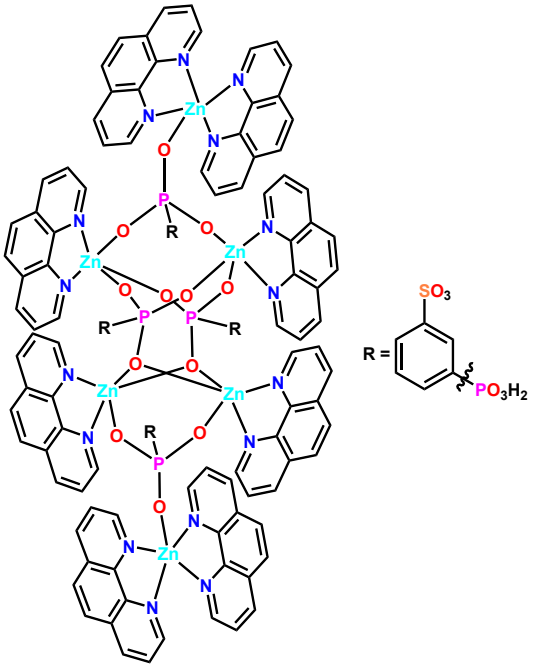
(e) (f)

Reference: (e) R. Murugavel and S. Shanmugam, *Chem. Commun*. **2007**, 1257. Murugavel, R.; Shanmugan, S. *Dalton Trans.* 2008, 5358.

(f) J. Wu, Y. Song, E. Zhang, H. Hou, Y. Fan, and Y. Zhu, *Chem.-Eur. J*. 2006, **12**, 5823.

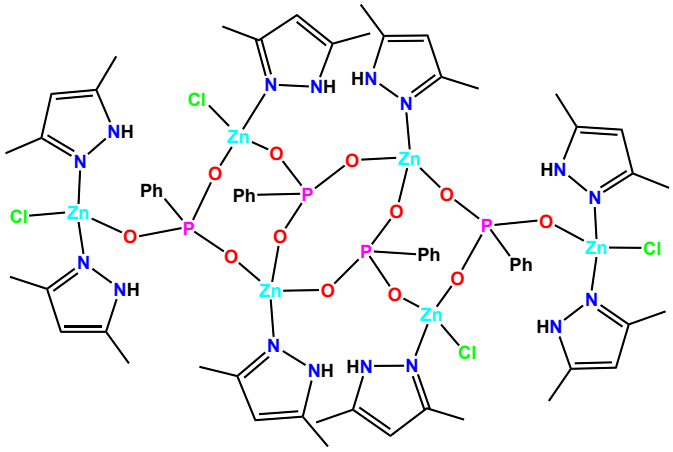


(g)



(h)

Reference: Z. -Y. Du, H. -B. Xu and J. -G. Mao, *Inorg. Chem*. 2006, **45**, 6424.



(i)

Reference: V. Chandrasekhar, S. Kingsley, B. Rhatigan, M. K. Lam and A. L. Rheingold, *Inorg. Chem*. 2002, **41**, 1030.

Chart S1. Molecular zinc(II) phosphonates known in literature (references are given below each structure)

Table S1. H-bond parameters of **1** (Figure 4c).

Donor (D)	H atom	Acceptor (A)	Symmetry of A	D...H (in Å)	H...A (in Å)	D…A (in Å)	< D-H···A (in deg)
O1	H1A	O7	0.5-x, 0.5-y, 1-z	0.857(3)	1.909(3)	2.740(4)	162.92(24)
O1	H1B	O8	x, y, 1+z	0.858(4)	2.287(4)	3.065(6)	150.77(27)
O3	H3A	O6	0.5-x, 0.5-y, 1-z	0.851(3)	2.055(3)	2.816(4)	148.64(20)
O3	H3B	O5	0.5-x, 0.5+y, 0.5-z	0.851(3)	2.525(4)	3.118(5)	127.57(22)
O3	H3B	O4	0.5-x, -0.5-y, -z	0.851(3)	2.545(4)	3.303(5)	148.94(24)
O4	H4B	O9	0.5-x, -0.5+y, 0.5-z	0.853(4)	2.199(3)	2.759(4)	123.05(21)

Table S2. H-bond parameters of **2** (Figure S9).

Donor (D)	H atom	Acceptor (A)	Symmetry of A	D...H (in Å)	H...A (in Å)	D…A (in Å)	< D-H···A (in deg)
O4	H4H	O5	x, y, z	0.783(6)	2.298(6)	3.051(5)	161.78(62)
N2	H2	O5	x, y, z	0.860(5)	2.001(4)	2.850(6)	168.59(38)
N6	H6	O7	x, y, z	0.860(5)	2.068(5)	2.907(7)	164.73(38)
N4	H4	O1	x, y, z	0.860(4)	2.008(3)	2.861(5)	171.87(31)
O4	H4H	O5	x, y, z	0.783(6)	2.298(6)	3.051(9)	161.78(62)
C8	H8	O7	x, 1+y, z	0.930(6)	2.558(6)	3.257(9)	132.22(39)
C13	H13	O8	x, 1+y, -1+z	0.930(7)	2.641(6)	3.395(9)	138.73(45)
C16	H16A	O6	1+x, 1+y, -1+z	0.960(7)	2.662(5)	3.324(8)	126.48(45)

Table S3. H-bond parameters of **3** (Figure S11).

Donor (D)	H atom	Acceptor (A)	Symmetry of A	D...H (in Å)	H...A (in Å)	D…A (in Å)	< D-H···A (in deg)
N5	H5T	O3	1-x, 1-y, -z	0.909(8)	1.829(8)	2.721(6)	166.36(73)
N6	H6T	O3	1-x, 1-y, -z	0.909(8)	1.889(8)	2.776(7)	164.58(72)
C8	H8B	Cl3	1-x, 1-y, -z	0.971(6)	2.842(2)	3.555(7)	130.98(72)
C9	H9B	Cl2	1.5-x, 0.5+y, 0.5-z	0.960(8)	2.739(2)	3.621(8)	153.23(48)
C4	H4	Cl5	1-x, 1-y, -z	0.931(6)	2.892(2)	3.710(6)	147.39(39)
C19	H19B	Cl1	1+x, y, z	0.960(8)	2.889(2)	3.615(8)	133.16(47)
C4	H4	Cl1	1+x, y, z	0.931(6)	2.892(2)	3.710(6)	147.39(39)

Table S4. Coordination geometries, bond distances (Å) and bond angles (°) of **1**.

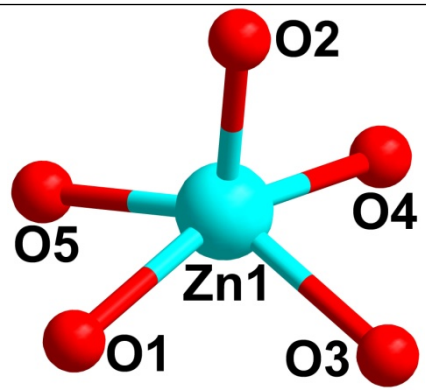
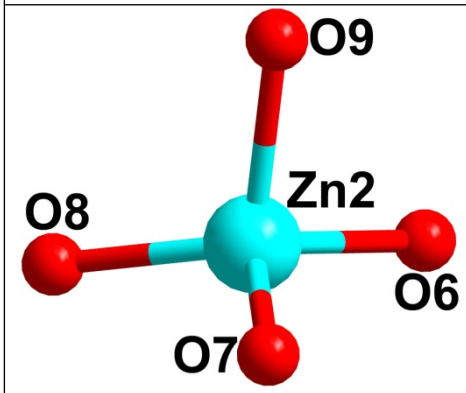
	Bond Angle (in Å)		Bond distance (in °)	
 **Square Pyramidal**	Zn(1)-O(2)	1.965(8)	O(2)-Zn(1)-O(5)	110.0(3)
	Zn(1)-O(5)	1.972(8)	O(2)-Zn(1)-O(3)	103.3(3)
	Zn(1)-O(3)	2.048(8)	O(5)-Zn(1)-O(3)	145.0(3)
	Zn(1)-O(4)	2.050(8)	O(2)-Zn(1)-O(4)	102.5(4)
	Zn(1)-O(1)	2.131(9)	O(5)-Zn(1)-O(4)	97.9(3)
			O(3)-Zn(1)-O(4)	84.8(3)
			O(2)-Zn(1)-O(1)	96.0(3)
			O(5)-Zn(1)-O(1)	81.9(3)
			O(3)-Zn(1)-O(1)	84.3(3)
			O(4)-Zn(1)-O(1)	160.3(4)
 **Tetrahedral**	Zn(2)-O(8)	1.942(8)	O(8)-Zn(2)-O(7)	109.2(3)
	Zn(2)-O(7)	1.936(7)	O(8)-Zn(2)-O(6)$^{\#1}$	119.8(3)
	Zn(2)-O(6)$^{\#1}$	1.949(7)	O(7)-Zn(2)-O(6)$^{\#1}$	119.3(3)
	Zn(2)-O(9)$^{\#2}$	1.987(8)	O(8)-Zn(2)-O(9)$^{\#2}$	108.7(3)
			O(7)-Zn(2)-O(9)$^{\#2}$	96.9(3)
			O(6)$^{\#1}$-Zn(2)-O(9)$^{\#2}$	99.0(3)

Table S5. Coordination geometries, bond distances (Å) and bond angles (°) of **2**.

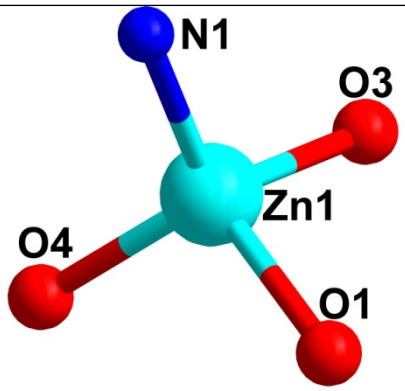
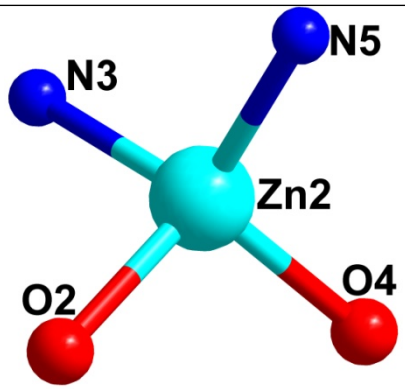
	Bond Distances (Å)		Bond Angles (°)	
 **Tetrahedral**	Zn(1)-O(4)	1.927(6)	O(4)-Zn(1)-O(3)#1	106.6(3)
	Zn(1)-O(3)#1	1.952(6)	O(4)-Zn(1)-N(1)	115.1(3)
	Zn(1)-N(1)	1.981(7)	O(3)#1-Zn(1)-N(1)	117.5(3)
	Zn(1)-O(1)	2.003(6)	O(4)-Zn(1)-O(1)	110.2(3)
			O(3)#1-Zn(1)-O(1)	103.6(2)
			N(1)-Zn(1)-O(1)	103.2(3)
 **Tetrahedral**	Zn(2)-O(2)	1.937(6)	O(2)-Zn(2)-O(4)	104.3(3)
	Zn(2)-O(4)	1.938(7)	O(2)-Zn(2)-N(3)	97.7(3)
	Zn(2)-N(3)	1.997(8)	O(4)-Zn(2)-N(3)	117.0(3)
	Zn(2)-N(5)	1.998(7)	O(2)-Zn(2)-N(5)	114.1(3)
			O(4)-Zn(2)-N(5)	111.6(3)
			N(3)-Zn(2)-N(5)	111.3(3)

Table S6. Coordination geometries, bond distances (Å) and bond angles (°) of **3**.

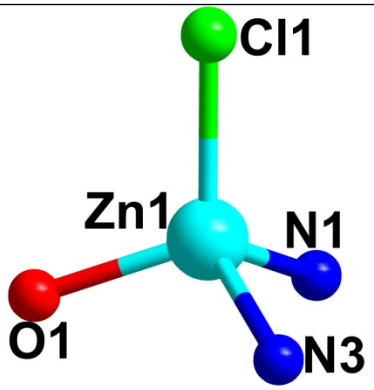
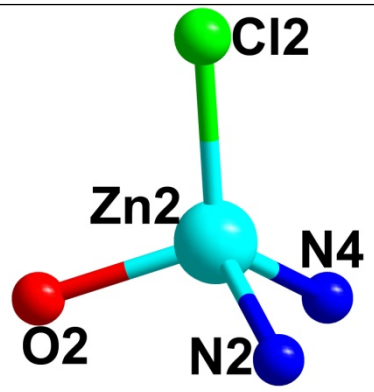
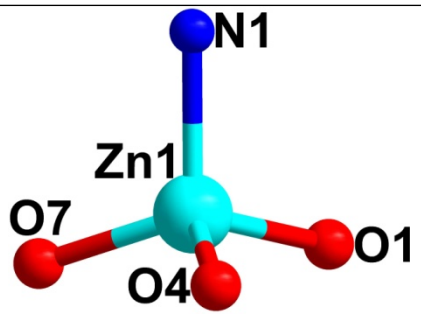
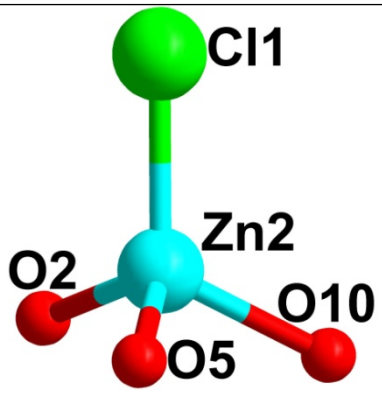
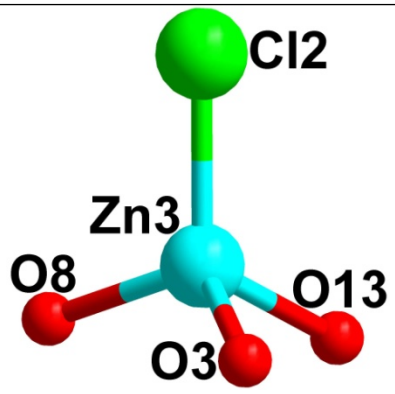
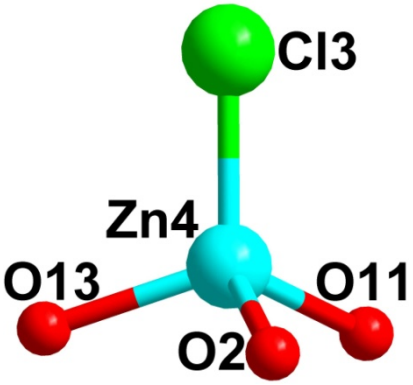
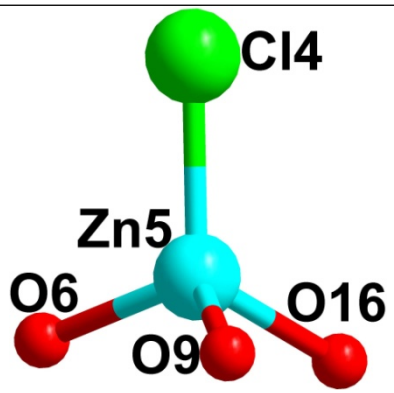
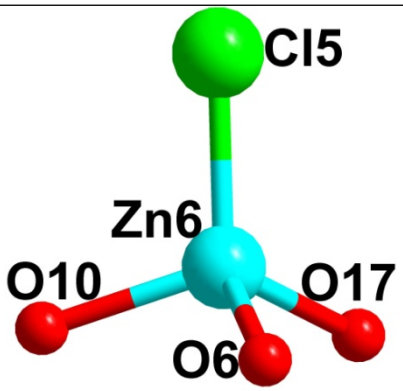
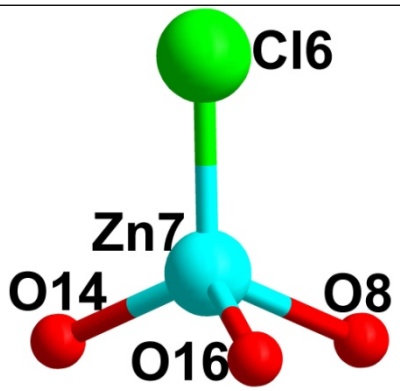
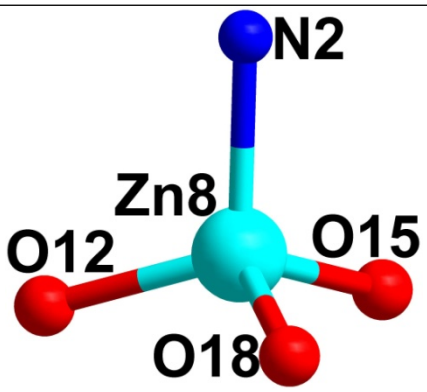
	Bond Distances (Å)		Bond Angles (°)	
 **Tetrahedral**	Zn(1)-O(1)	1.961(4)	O(1)-Zn(1)-N(3)	106.19(17)
	Zn(1)-N(3)	1.995(5)	O(1)-Zn(1)-N(1)	108.90(17)
	Zn(1)-N(1)	2.042(5)	N(3)-Zn(1)-N(1)	101.97(19)
	Zn(1)-Cl(1)	2.2137(2)	O(1)-Zn(1)-Cl(1)	110.07(12)
			N(3)-Zn(1)-Cl(1)	117.97(13)
			N(1)-Zn(1)-Cl(1)	111.17(16)
 **Tetrahedral**	Zn(2)-O(2)	1.954(4)	O(2)-Zn(2)-N(4)	110.63(17)
	Zn(2)-N(4)	1.996(5)	O(2)-Zn(2)-N(2)	102.98(19)
	Zn(2)-N(2)	2.004(6)	N(4)-Zn(2)-N(2)	100.4(2)
	Zn(2)-Cl(2)	2.2164(2)	O(2)-Zn(2)-Cl(2)	105.69(12)
			N(4)-Zn(2)-Cl(2)	121.05(14)
			N(2)-Zn(2)-Cl(2)	114.79(17)

Table S7. Coordination geometries, bond distances (Å) and bond angles (°) of **4**.

	Bond Distances (Å)	Bond Angles (°)
 **Tetrahedral**	Zn(1)-O(7) 1.928(8) Zn(1)-O(4) 1.923(8) Zn(1)-O(1) 1.933(8) Zn(1)-N(1) 2.011(1)	O(7)-Zn(1)-O(4) 110.5(4) O(7)-Zn(1)-O(1) 112.5(3) O(4)-Zn(1)-O(1) 112.6(3) O(7)-Zn(1)-N(1) 109.8(4) O(4)-Zn(1)-N(1) 106.6(4) O(1)-Zn(1)-N(1) 104.4(4)
 **Tetrahedral**	Zn(2)-O(5) 1.894(8) Zn(2)-O(2) 1.994(9) Zn(2)-O(10) 2.019(7) Zn(2)-Cl(1) 2.203(4)	O(5)-Zn(2)-O(2) 118.5(3) O(5)-Zn(2)-O(10) 100.9(3) O(2)-Zn(2)-O(10) 97.6(4) O(5)-Zn(2)-Cl(1) 112.5(3) O(2)-Zn(2)-Cl(1) 108.6(3) O(10)-Zn(2)-Cl(1) 118.2(2)
	Zn(3)-O(3) 1.943(8) Zn(3)-O(8) 2.005(7) Zn(3)-O(13) 2.013(7) Zn(3)-Cl(2) 2.206(4)	O(3)-Zn(3)-O(8) 119.7(4) O(3)-Zn(3)-O(13) 100.0(3) O(8)-Zn(3)-O(13) 96.5(3) O(3)-Zn(3)-Cl(2) 112.7(3) O(8)-Zn(3)-Cl(2) 110.2(3) O(13)-Zn(3)-Cl(2) 116.6(3)

Tetrahedral		
 **Tetrahedral**	Zn(4)-O(11) 1.921(8) Zn(4)-O(13) 2.007(8) Zn(4)-O(2) 2.018(8) Zn(4)-Cl(3) 2.200(4)	O(11)-Zn(4)-O(13) 121.0(3) O(11)-Zn(4)-O(2) 100.7(4) O(13)-Zn(4)-O(2) 98.6(3) O(11)-Zn(4)-Cl(3) 111.6(3) O(13)-Zn(4)-Cl(3) 107.8(3) O(2)-Zn(4)-Cl(3) 116.8(2)
 **Tetrahedral**	Zn(5)-O(9) 1.903(8) Zn(5)-O(6) 1.979(8) Zn(5)-O(16) 1.980(8) Zn(5)-Cl(4) 2.202(4)	O(9)-Zn(5)-O(6) 118.9(3) O(9)-Zn(5)-O(16) 100.8(3) O(6)-Zn(5)-O(16) 99.0(3) O(9)-Zn(5)-Cl(4) 113.1(3) O(6)-Zn(5)-Cl(4) 108.0(3) O(16)-Zn(5)-Cl(4) 116.5(3)
	Zn(6)-O(17) 1.925(8) Zn(6)-O(10) 1.990(8) Zn(6)-O(6) 2.040(7) Zn(6)-Cl(5) 2.220(4)	O(17)-Zn(6)-O(10) 121.8(4) O(17)-Zn(6)-O(6) 99.6(3) O(10)-Zn(6)-O(6) 96.5(3) O(17)-Zn(6)-Cl(5) 112.6(3) O(10)-Zn(6)-Cl(5) 107.2(3) O(6)-Zn(6)-Cl(5) 118.7(3)

Tetrahedral		
 **Tetrahedral**	Zn(7)-O(14) 1.918(8) Zn(7)-O(16) 2.007(9) Zn(7)-O(8) 2.006(8) Zn(7)-Cl(6) 2.216(4)	O(14)-Zn(7)-O(16) 118.8(3) O(14)-Zn(7)-O(8) 101.5(3) O(16)-Zn(7)-O(8) 99.2(3) O(14)-Zn(7)-Cl(6) 114.0(3) O(16)-Zn(7)-Cl(6) 107.6(2) O(8)-Zn(7)-Cl(6) 115.0(2)
 **Tetrahedral**	Zn(8)-O(15) 1.916(8) Zn(8)-O(18) 1.925(7) Zn(8)-O(12) 1.940(9) Zn(8)-N(2) 2.041(9)	O(15)-Zn(8)-O(18) 109.7(3) O(15)-Zn(8)-O(12) 110.6(3) O(18)-Zn(8)-O(12) 112.8(4) O(15)-Zn(8)-N(2) 106.1(4) O(18)-Zn(8)-N(2) 107.9(4) O(12)-Zn(8)-N(2) 109.5(4)