Electronic Supplementary Information

Molecular, 1D and 2D Assemblies from Hexakis(3-pyridyloxy)cyclophosphazene Containing 20-membered Metallamacrocyclic Motifs

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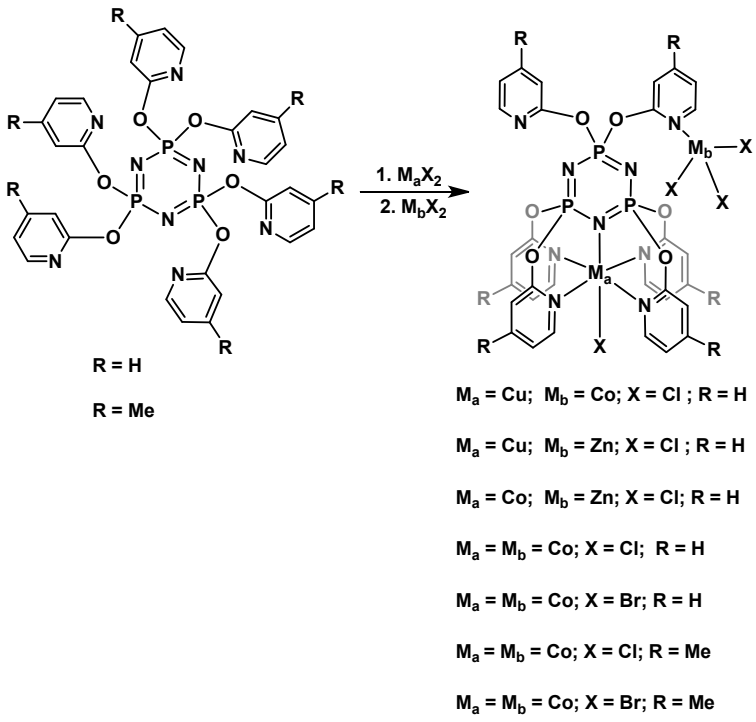
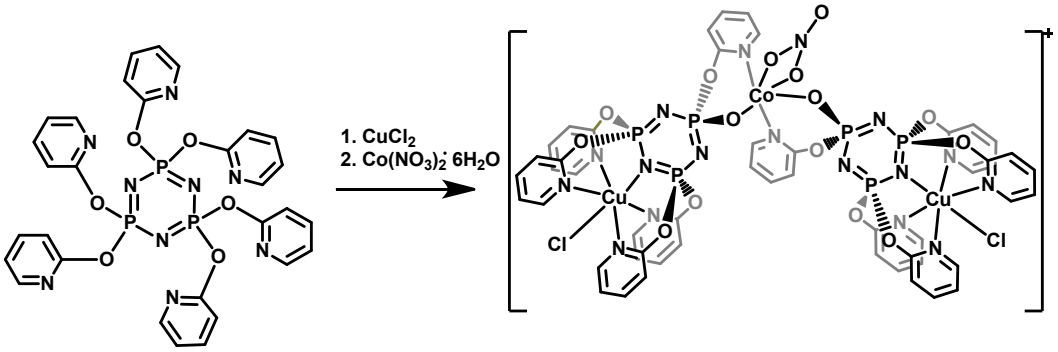


Scheme S1. Hetero and homobimetallic compounds of 2-pyridyloxy cyclophosphazenes (References: 1) G. A. Carriedo, P. G. Elipe, F. J. G. Alonso, L. F. Catuxo, M. R. Díaz and S. G. Granda, *J. Organomet. Chem*., 1995, **498**, 207. 2) G. A. Carriedo, F. J. G. Alonso, J. L. Garcia, R. J. Carbajo and F. L. Ortiz, *Eur. J. Inorg. Chem*., 1999, 1015. 3) Y. Cho, H. Baek and Y. S. Sohn, *Macromolecules*, 1999, **32**, 2167. 4) E. W. Ainscough, A. M. Brodie and C. V. Depree, *J. Chem. Soc., Dalton Trans*., 1999, 4123. 5) E. W. Ainscough, A. M. Brodie, B. Moubaraki, K. S. Murray and C. A. Otter, J. Chem. Soc., *Dalton Trans*., 2005, 3337. 6) E. W. Ainscough, A. M. Brodie, C. V. Depree, G. B. Jameson and C. A. Otter, *Inorg. Chem*., 2005, **44**, 7325. 7) V. Chandrasekhar, B. M. Pandian and R. Azhakar, *Inorg. Chem*., 2006, **45**, 3510. 8) E. W. Ainscough, A. M. Brodie, A. B. Chaplin, A. Derwahl, J. A. Harrison and C. A. Otter, *Inorg. Chem*., 2007, **46**, 2575. 9) V. Chandrasekhar, B. M. Pandian and R. Azhakar*, Polyhedron*, 2008, **27**, 255. 10) E. W. Ainscough, A. M. Brodie, R. J. Davidson, B. Moubaraki, K. S. Murray, C. A. Otter and M. A. Waterland, *Inorg. Chem*., 2008, **47**, 9182. 11) E. W. Ainscough, A. M. Brodie, R. J. Davison and C. A. Otter, *Inorg. Chem. Commun*., 2008, **11**, 171. 12) E. W. Ainscough, A. M. Brodie, P. J. B. Edwards, G. B. Jameson, C. A. Otter and S. Kirk, *Inorg. Chem*., 2012, **51**, 10884.)



Scheme S2. Synthesis of heterometallic compound [{$N_3P_3(OC_5H_4N\text{-}2)_5O$}$_2${CuCl}$_2$ {$Co(NO_3)$}]Cl (Reference: V. Chandrasekhar, B. M. Pandian and R. Azhakar, *Inorg. Chem*., 2006, **45**, 3510)

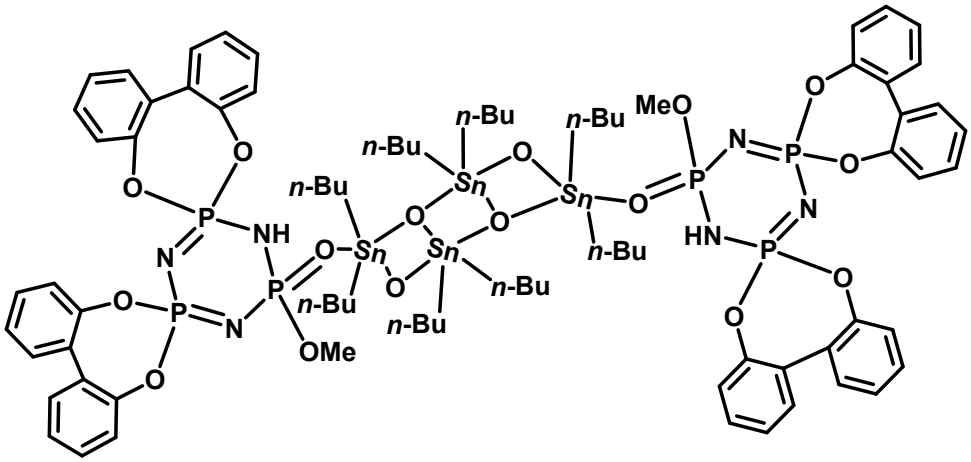


Chart S1. *Dispiro*-{ $P_3N_3(O_2C_{12}H_8)_2O$-*n*-$(Bu_2Sn)_2$(μ-O)(μ-OMe)}.MeOH (Reference: S. Kundu, C. Mohapatra and V. Chandrasekhar, *RSC Adv*., 2014, **4**, 53662.)

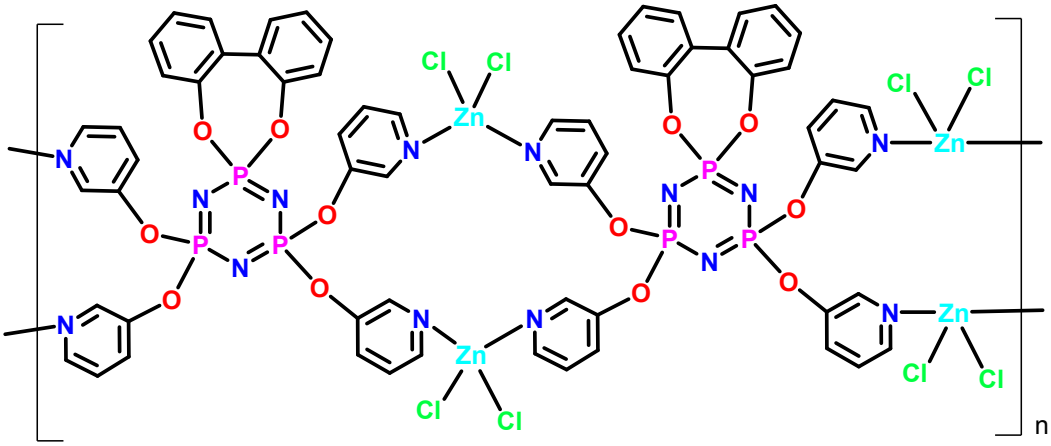
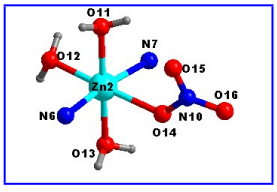
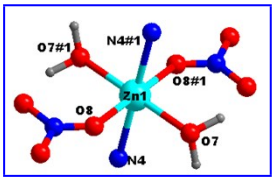
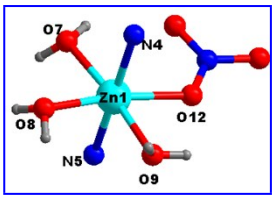
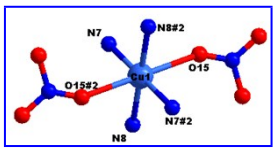
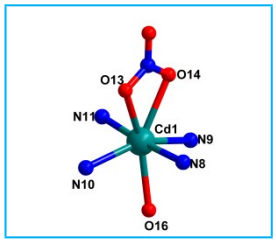
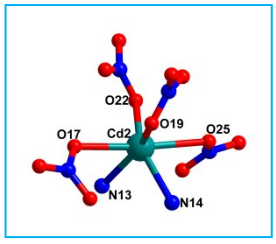


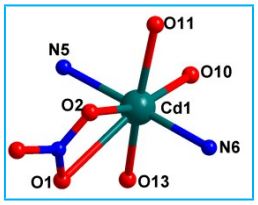
Chart S2. [{*spiro*-$N_3P_3(O_2C_{12}H_8)(O\text{-}C_5H_4N\text{-}3)_4$}{$ZnCl_2$}]$_n$ (Reference: V. Chandrasekhar and R. S. Narayanan, *Dalton Trans*., 2013, **42**, 6619.)

Table S1. Coordination environment around the metal ions in the compounds **1-4**

Compound	**Environment around metal**	**Bond length (Å)**	**Bond angles (°)**
1	Macrocycle part  Octahedral-2N, 4O	Zn(2)-O(11) 2.065(4) Zn(2)-O(13) 2.095(4) Zn(2)-O(12) 2.096(5) Zn(2)-N(6) 2.118(5) Zn(2)-N(7) 2.148(5) Zn(2)-O(14) 2.207(4)	O(11)-Zn(2)-O(13) 175.90(16) O(11)-Zn(2)-O(12) 81.61(19) O(13)-Zn(2)-O(12) 95.93(18) O(11)-Zn(2)-N(6) 92.13(18) O(13)-Zn(2)-N(6) 91.39(18) O(12)-Zn(2)-N(6) 95.80(18) O(11)-Zn(2)-N(7) 89.06(18) O(13)-Zn(2)-N(7) 87.76(17) O(12)-Zn(2)-N(7) 92.36(19)

			N(6)-Zn(2)-N(7) 171.83(18) O(11)-Zn(2)-O(14) 100.35(16) O(13)-Zn(2)-O(14) 81.81(16) O(12)-Zn(2)-O(14) 174.50(17) N(6)-Zn(2)-O(14) 89.28(16) N(7)-Zn(2)-O(14) 82.56(17)
	Connecting part  Octahedral-2N, 4O	Zn(1)-N(4)$^{\#1}$ 2.115(5) Zn(1)-N(4) 2.115(5) Zn(1)-O(7) 2.137(5) Zn(1)-O(7)$^{\#1}$ 2.137(5) Zn(1)-O(8) 2.394(10) Zn(1)-O(8)$^{\#1}$ 2.394(10)	N(4)$^{\#1}$-Zn(1)-N(4) 180.0 N(4)$^{\#1}$-Zn(1)-O(7) 90.5(2) N(4)-Zn(1)-O(7) 89.5(2) N(4)$^{\#1}$-Zn(1)-O(7)$^{\#1}$ 89.5(2) N(4)-Zn(1)-O(7)$^{\#1}$ 90.5(2) O(7)-Zn(1)-O(7)$^{\#1}$ 180.0 N(4)$^{\#1}$-Zn(1)-O(8) 90.0(2) N(4)-Zn(1)-O(8) 90.0(2) O(7)-Zn(1)-O(8) 77.4(2) O(7)$^{\#1}$-Zn(1)-O(8) 102.6(2) N(4)$^{\#1}$-Zn(1)-O(8)$^{\#1}$ 90.0(2) N(4)-Zn(1)-O(8)$^{\#1}$ 90.0(2) O(7)-Zn(1)-O(8)$^{\#1}$ 102.6(2) O(7)$^{\#1}$-Zn(1)-O(8)$^{\#1}$ 77.4(2) O(8)-Zn(1)-O(8)$^{\#1}$ 180.0
2	Macrocycle part  Octahedral-2N, 4O	Zn(1)-N(5) 2.077(5) Zn(1)-N(4) 2.085(5) Zn(1)-O(8) 2.097(5) Zn(1)-O(7) 2.133(4) Zn(1)-O(9) 2.153(5) Zn(1)-O(12) 2.172(6)	N(5)-Zn(1)-N(4) 176.32(18) N(5)-Zn(1)-O(8) 92.45(18) N(4)-Zn(1)-O(8) 89.46(18) N(5)-Zn(1)-O(7) 89.62(18) N(4)-Zn(1)-O(7) 87.45(18) O(8)-Zn(1)-O(7) 83.86(17) N(5)-Zn(1)-O(9) 90.48(19)

			N(4)-Zn(1)-O(9) 92.70(19) O(8)-Zn(1)-O(9) 89.25(19) O(7)-Zn(1)-O(9) 173.10(18) N(5)-Zn(1)-O(12) 87.27(18) N(4)-Zn(1)-O(12) 91.38(18) O(8)-Zn(1)-O(12) 170.11(18) O(7)-Zn(1)-O(12) 106.01(18) O(9)-Zn(1)-O(12) 80.88(19)
	Connecting part  Octahedral-4N, 2O	Cu(1)-N(7) 2.023(5) Cu(1)-N(7)$^{\#2}$ 2.023(5) Cu(1)-N(8)$^{\#2}$ 2.025(5) Cu(1)-N(8) 2.025(5) Cu(1)-O(15) 2.513(7) Cu(1)-O(15)$^{\#2}$ 2.513(7)	N(7)-Cu(1)-N(7)$^{\#2}$ 180.0 N(7)-Cu(1)-N(8)$^{\#2}$ 90.36(19) N(7)#1-Cu(1)-N(8)$^{\#2}$ 89.64(19) N(7)-Cu(1)-N(8) 89.64(19) N(7)$^{\#2}$-Cu(1)-N(8) 90.36(19) N(8)$^{\#2}$-Cu(1)-N(8) 180.0
3	Terminal Cadmium  Pentagonalbipyramid N4, O3	Cd(1)-N(11) 2.304(6) Cd(1)-O(13) 2.466(5) Cd(1)-O(14) 2.506(6) Cd(1)-N(9) 2.368(6) Cd(1)-N(8) 2.333(5) Cd(1)-O(16) 2.472(6) Cd(1)-N(10) 2.418(6)	N(11)-Cd(1)-O(13) 95.315(2) O(13)-Cd(1)-O(14) 51.437(2) O(14)-Cd(1)-N(9) 76.072(2) N(9)-Cd(1)-N(8) 92.801(2) N(8)-Cd(1)-O(16) 78.954(2) O(16)-Cd(1)-N(10) 80.963(2) N(10)-Cd(1)-N(1) 92.368(2)
	Center Cadmium  Octahedral-2N, 4O	Cd(2)-N(13) 2.363(6) Cd(2)-O(17) 2.526(5) Cd(2)-O(22) 2.235(5) Cd(2)-O(19) 2.261(6) Cd(2)-O(25) 2.548(7) Cd(2)-N(14) 2.332(5)	N(13)-Cd(2)-O(17) 94.556(2) O(17)-Cd(2)-O(22) 104.131(2) O(22)-Cd(2)-O(19) 113.485(2) O(19)-Cd(2)-O(25) 99.930(2) O(25)-Cd(2)-N(14) 76.148(2) N(14)-Cd(2)-N(13) 89.450(2) N(13)-Cd(2)-O(17) 77.075(2)

4	 Pentagonalbipyramid 2N, 5O	Cd(1)-O(10) 2.313(6) Cd(1)-O(11) 2.295(8) Cd(1)-N(4) 2.290(7) Cd(1)-N(5) 2.307(6) Cd(1)-O(12) 2.361(7) Cd(1)-O(13) 2.384(6)	N(4)-Cd(1)-O(11) 92.6(3) N(4)-Cd(1)-N(5) 178.1(2) O(11)-Cd(1)-N(5) 89.3(3) N(4)-Cd(1)-O(10) 90.8(2) O(11)-Cd(1)-O(10) 82.9(3) N(5)-Cd(1)-O(10) 89.6(2) N(4)-Cd(1)-O(12) 92.6(2) O(11)-Cd(1)-O(12) 85.1(3) N(5)-Cd(1)-O(12) 87.4(2) O(10)-Cd(1)-O(12) 167.7(2) N(4)-Cd(1)-O(13) 88.1(2) O(11)-Cd(1)-O(13) 160.7(3) N(5)-Cd(1)-O(13) 90.0(2) O(10)-Cd(1)-O(13) 116.3(2) O(12)-Cd(1)-O(13) 75.6(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1, #2 -x+1,-y+1,-z+1

Table S2. P-N and P-O bond distances and P-N-P and N-P-N bond angles for compounds **L**, **1** to **4**

Compound	P-N and P-O bond distance (Å)		P-N-P and N-P-N bond angle (°)
L[1]	P(1)-N(1) 1.568(3) P(1)-N(3) 1.574(3) P(2)-N(1) 1.569(3) P(2)-N(2) 1.574(3) P(3)-N(2) 1.575(3) P(3)-N(3) 1.577(3)	P(1)-O(1) 1.579(2) P(1)-O(2) 1.584(2) P(2)-O(3) 1.577(2) P(2)-O(4) 1.583(2) P(3)-O(5) 1.572(2) P(3)-O(6) 1.575(2)	N(1)-P(1)-N(3) 117.3(3) N(1)-P(2)-N(2) 118.20(13) N(3)-P(3)-N(2) 117.24(13) P(1)-N(1)-P(2) 122.5(2) P(2)-N(2)-P(3) 122.4(2) P(3)-N(3)-P(1) 121.8(2)

1	P(1)-N(1) 1.581(5) P(1)-N(3) 1.573(5) P(2)-N(1) 1.585(5) P(2)-N(2) 1.579(5) P(3)-N(2) 1.580(5) P(3)-N(3) 1.571(5)	O(1)-P(1) 1.588(4) O(2)-P(1) 1.594(5) O(3)-P(2) 1.589(5) O(4)-P(2) 1.595(4) O(5)-P(3) 1.572(5) O(6)-P(3) 1.589(5)	N(1)-P(1)-N(3) 117.5(3) N(1)-P(2)-N(2) 117.9(3) N(3)-P(3)-N(2) 118.5(3) P(1)-N(1)-P(2) 121.4(3) P(2)-N(2)-P(3) 120.8(3) P(3)-N(3)-P(1) 122.2(3)
2	P(1)-N(1) 1.571(6) P(1)-N(3) 1.579(6) P(2)-N(1) 1.590(6) P(2)-N(2) 1.586(6) P(3)-N(2) 1.569(6) P(3)-N(3) 1.581(6)	O(1)-P(1) 1.583(4) O(2)-P(1) 1.592(4) O(3)-P(2) 1.589(4) O(4)-P(2) 1.584(4) O(5)-P(3) 1.600(4) O(6)-P(3) 1.576(6)	N(1)-P(1)-N(3) 117.8(3) N(1)-P(2)-N(2) 115.7(3) N(3)-P(3)-N(2) 118.5(3) P(1)-N(1)-P(2) 122.4(3) P(2)-N(2)-P(3) 121.7(3) P(3)-N(3)-P(1) 120.1(3)
3	P(1)-N(1) 1.583(5) P(1)-N(3) 1.584(5) P(2)-N(1) 1.572(5) P(2)-N(2) 1.586(5) P(3)-N(2) 1.582(5) P(3)-N(3) 1.573(5)	O(1)-P(1) 1.583(4) O(2)-P(1) 1.586(4) O(3)-P(2) 1.581(4) O(4)-P(2) 1.590(4) O(5)-P(3) 1.586(4) O(6)-P(3) 1.579(4)	N(1)-P(1)-N(3) 116.3(3) N(1)-P(2)-N(2) 117.1(3) N(3)-P(3)-N(2) 117.5(3) P(1)-N(1)-P(2) 122.0(3) P(2)-N(2)-P(3) 119.4(3) P(3)-N(3)-P(1) 120.2(3)
4	P(1)-N(1) 1.577(6) P(1)-N(3) 1.585(6) P(2)-N(1) 1.590(6) P(2)-N(2) 1.581(6) P(3)-N(2) 1.583(7) P(3)-N(3) 1.598(6)	O(1)-P(1) 1.602(5) O(2)-P(1) 1.582(5) O(3)-P(2) 1.578(5) O(4)-P(2) 1.582(5) O(5)-P(3) 1.572(5) O(6)-P(3) 1.584(5)	N(1)-P(1)-N(3) 119.1(3) N(1)-P(2)-N(2) 115.6(3) N(3)-P(3)-N(2) 118.5(3) P(1)-N(1)-P(2) 122.0(4) P(2)-N(2)-P(3) 121.0(4) P(3)-N(3)-P(1) 118.5(4)

Reference:

1) Y. Cho, H. Baek and Y. S. Sohn, *Macromolecules*, 1999, **32**, 2167.

Table S3. Mean plane data for compounds **1** to **4**

	Distance from the mean plane (Å)			
	1	**2**	**3**	**4**
P1	0.012	-0.125	-0.057	0.128

P2	0.089	0.080	-0.080	-0.068
P3	-0.046	0.051	0.188	-0.073
N1	-0.084	0.048	0.156	-0.066
N2	-0.025	-0.131	-0.092	0.139
N3	0.053	0.078	-0.115	0.061

Table S4. Olex-2 mask details:

Compound	Masked electron count	Calculated solvent
4	151	MeOH, $2H_2O$ (152)

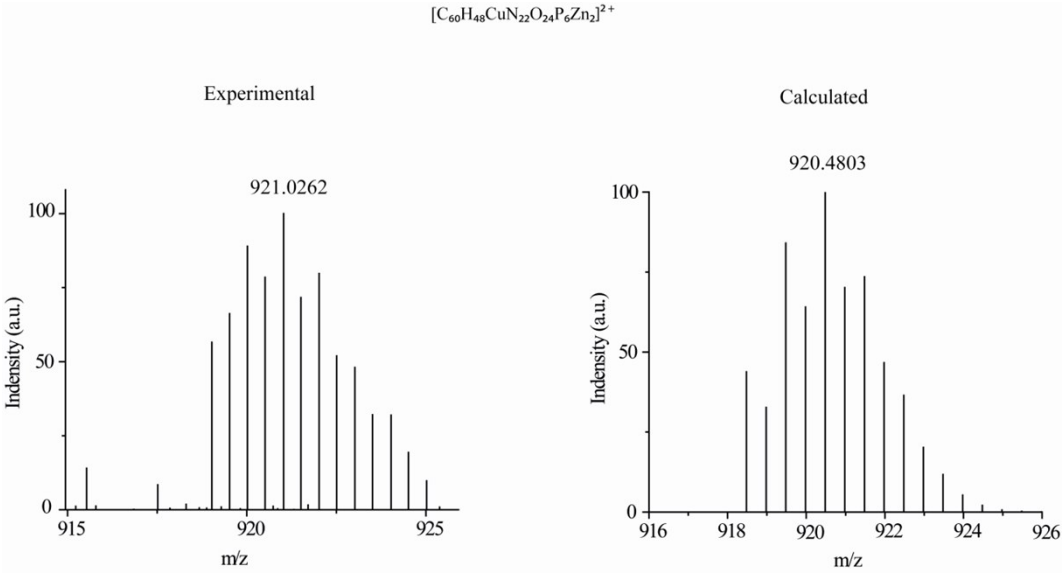


Figure S1. ESI-MS (a) experimental and (b) calculated spectra for the fragment ion [{N_3P_3(O-C_5H_4N-3)$_6$ {$Zn(NO_3)_2$} {$Cu(NO_3)_2$}]

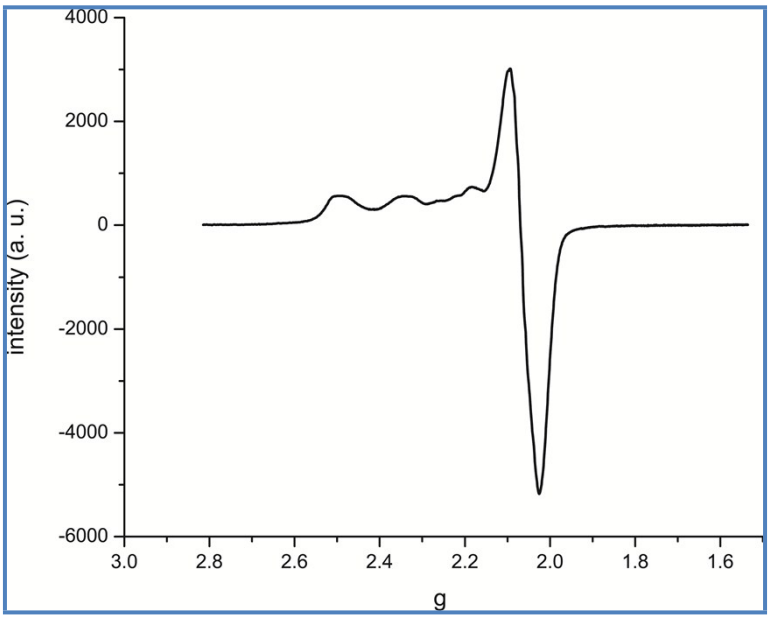


Figure S2: EPR spectrum of compound **2** in DMF-toluene glass at -120 °C

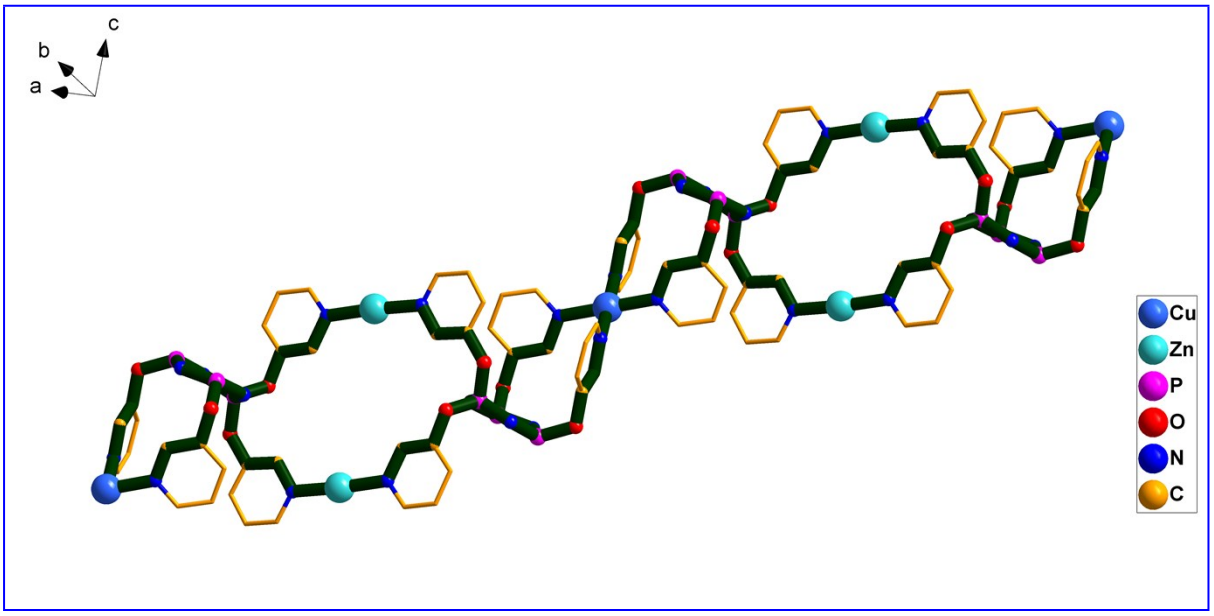


Figure S3. A representation of the double helix like 1D coordination polymer **2**. Hydrogen atoms, non-coordinating pyridyloxy groups, coorninated water and nitrate anions are omitted for clarity

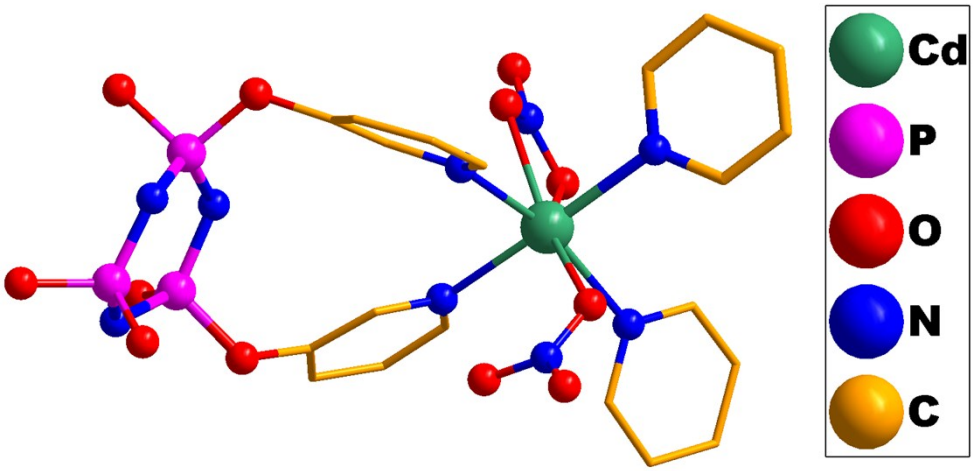


Figure S4. 12 membered metallamacrocycle found in compound **3 (1L; 2 non-gem pyridyloxy + 1Cd): LM**

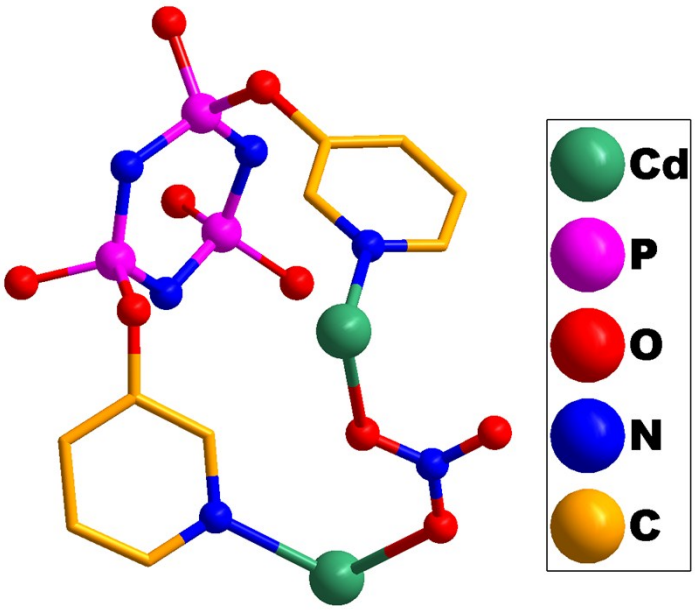


Figure S5. 16- membered metallamacrocycle found in compound **3**

LM_2 (two non-gem pyridyloxy coordinate to two separate Cds. The latter are connected by bridging of nitrate, O-N-O)

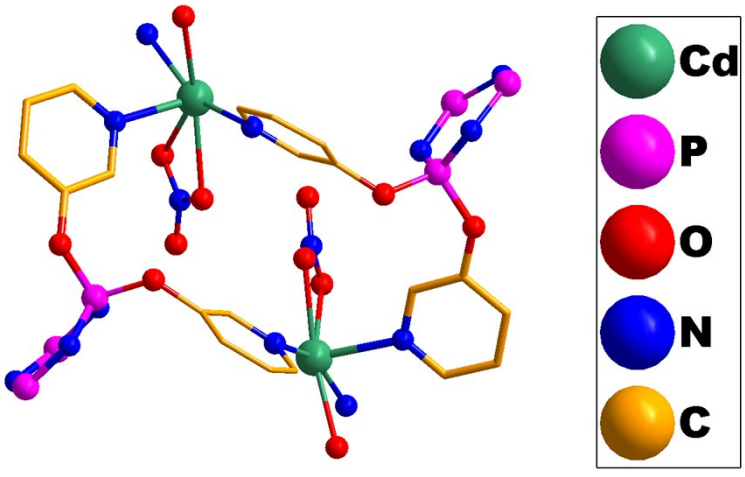


Figure S6. 20-membered metallamacrocycle found in compound **3**

L2M2(A pair of geminal pyridyloxy nirogens)

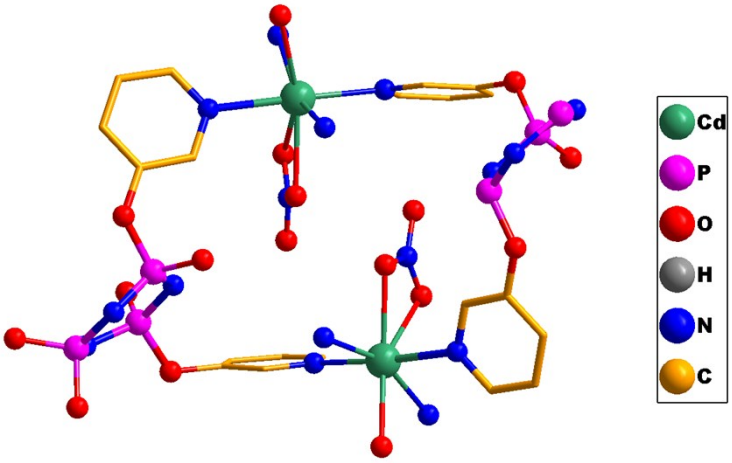


Figure S7. 24 membered metallamacrocycle in compound **3**

L2M2 (A pair of non-geminal pyridyloxy groups)

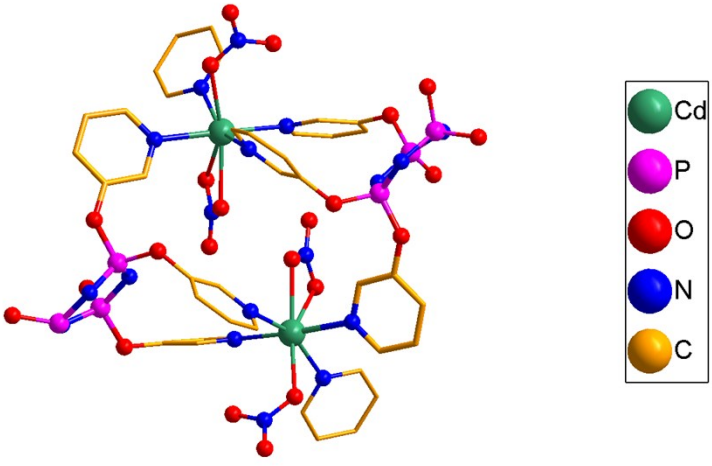


Figure S8. 12, 16, 20 and 24 membered metallamacrocycles in compound **3**

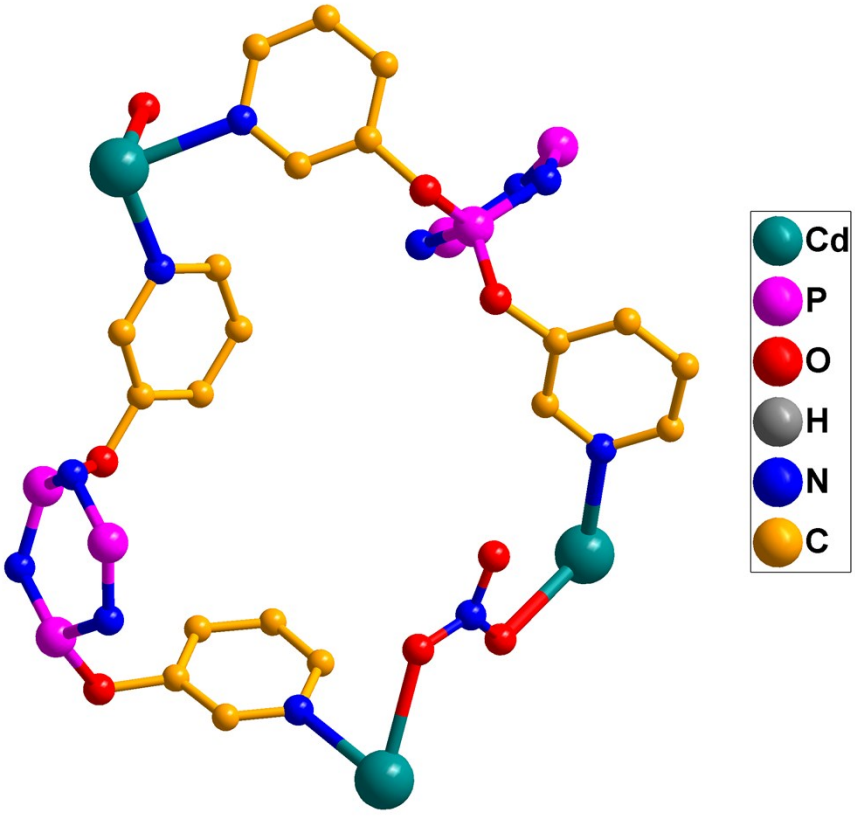


Figure S9. A view of the 26 membered metallamacrocycle **L2M3 (A pair of geminal and non-gem pyridyloxy groups coordinating to two different Cd centers; these are further connected to two other Cds through a nitrate groups: O-N-O)**

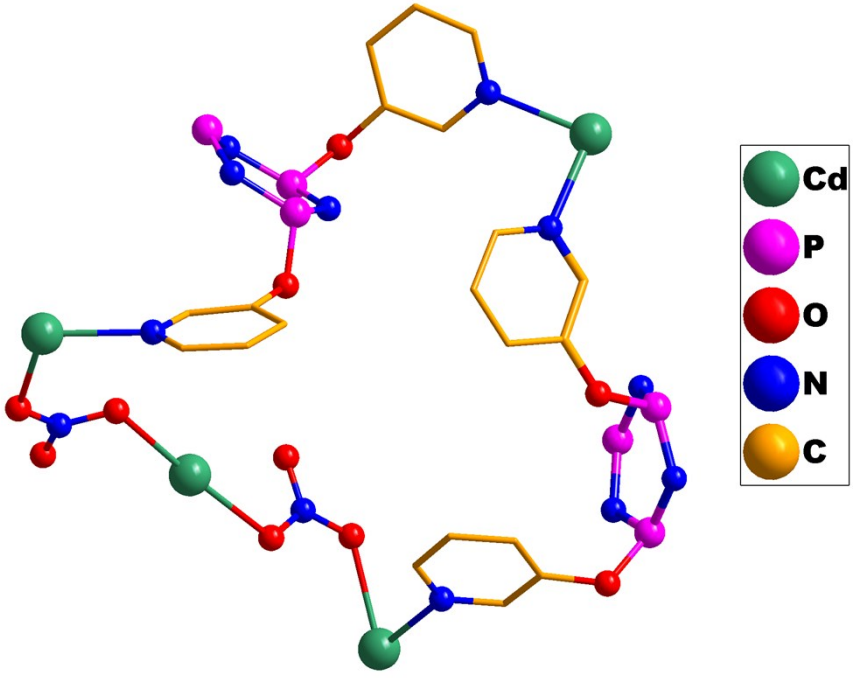


Figure S10. 32 membered metallamacrocycle in compound **3**. **L2M4 (two pairs of non-gem pyridyloxy groups coordinating to two different Cd centers; these are further connected to two other Cds through two nitrate groups: O-N-O)**

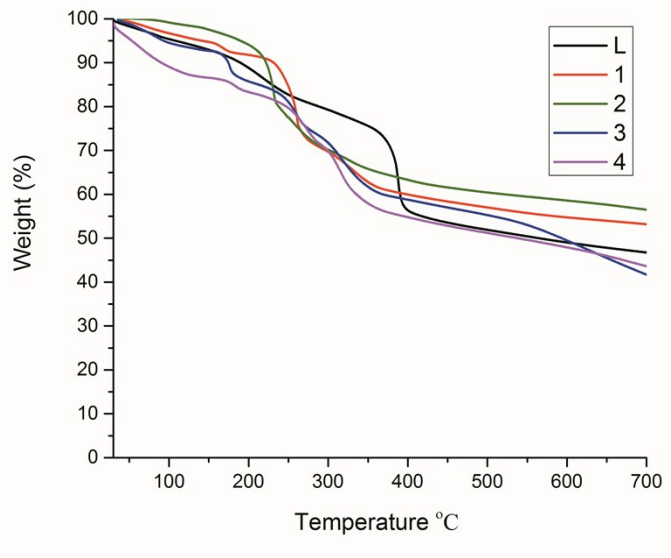


Figure S11: TGA curves for compounds **L**, **1** to **4**

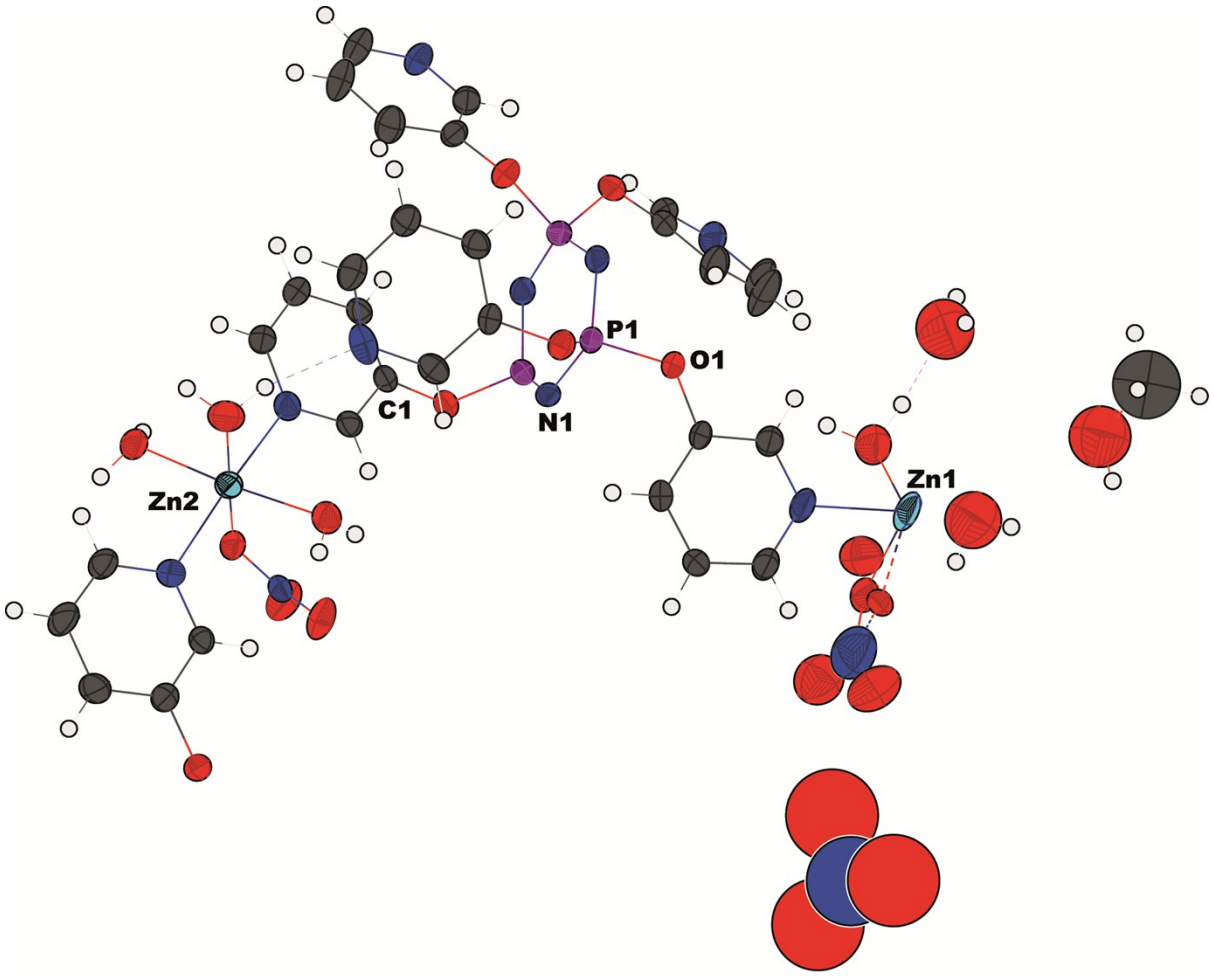


Figure S12. Thermal ellipsoid plot (50 % probability) of asymmetric unit of Compound **1**

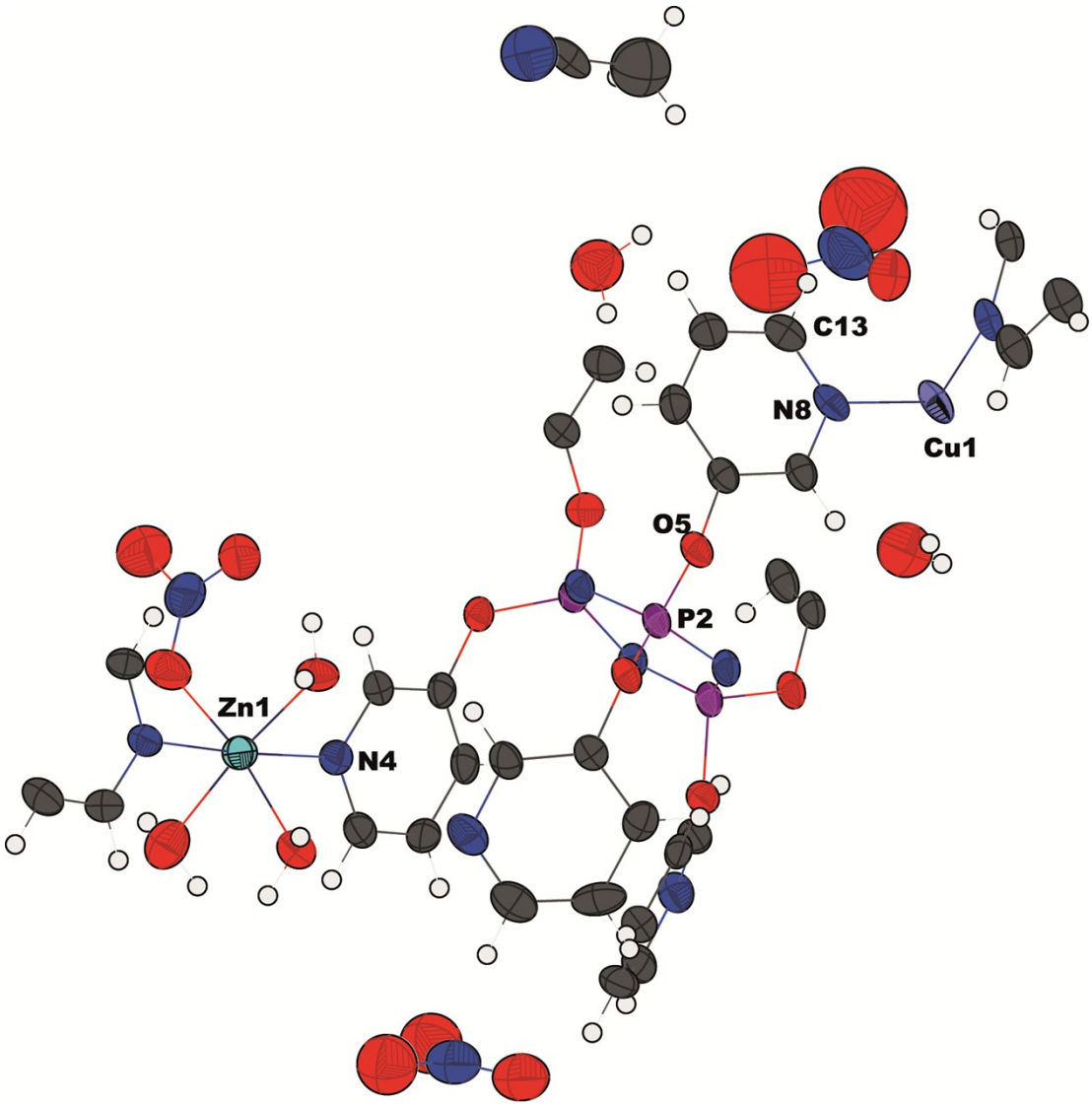


Figure S13. Thermal ellipsoid plot (50 % probability) of asymmetric unit of Compound **2** (other disordered part of the non-coordinating nitrate anions are omitted for clarity)

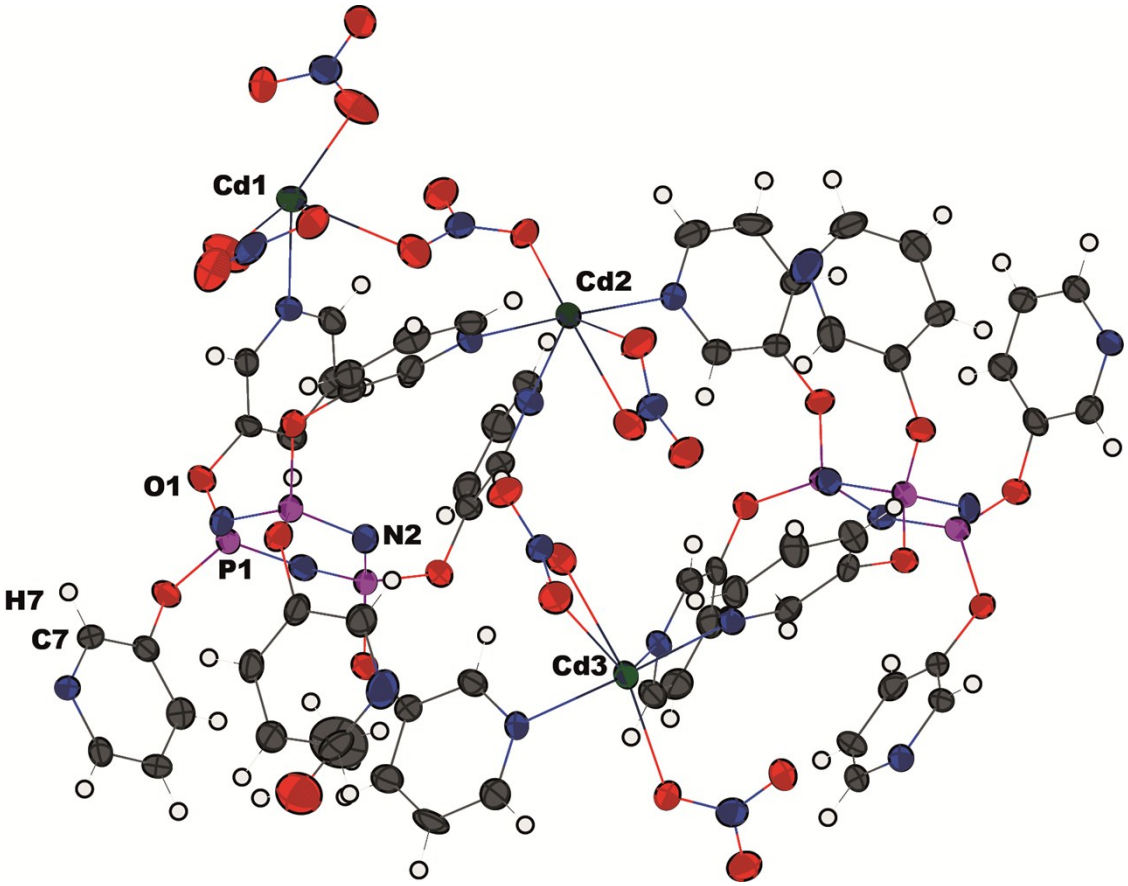


Figure S14. Thermal ellipsoid plot (50 % probability) of asymmetric unit of Compound **3**

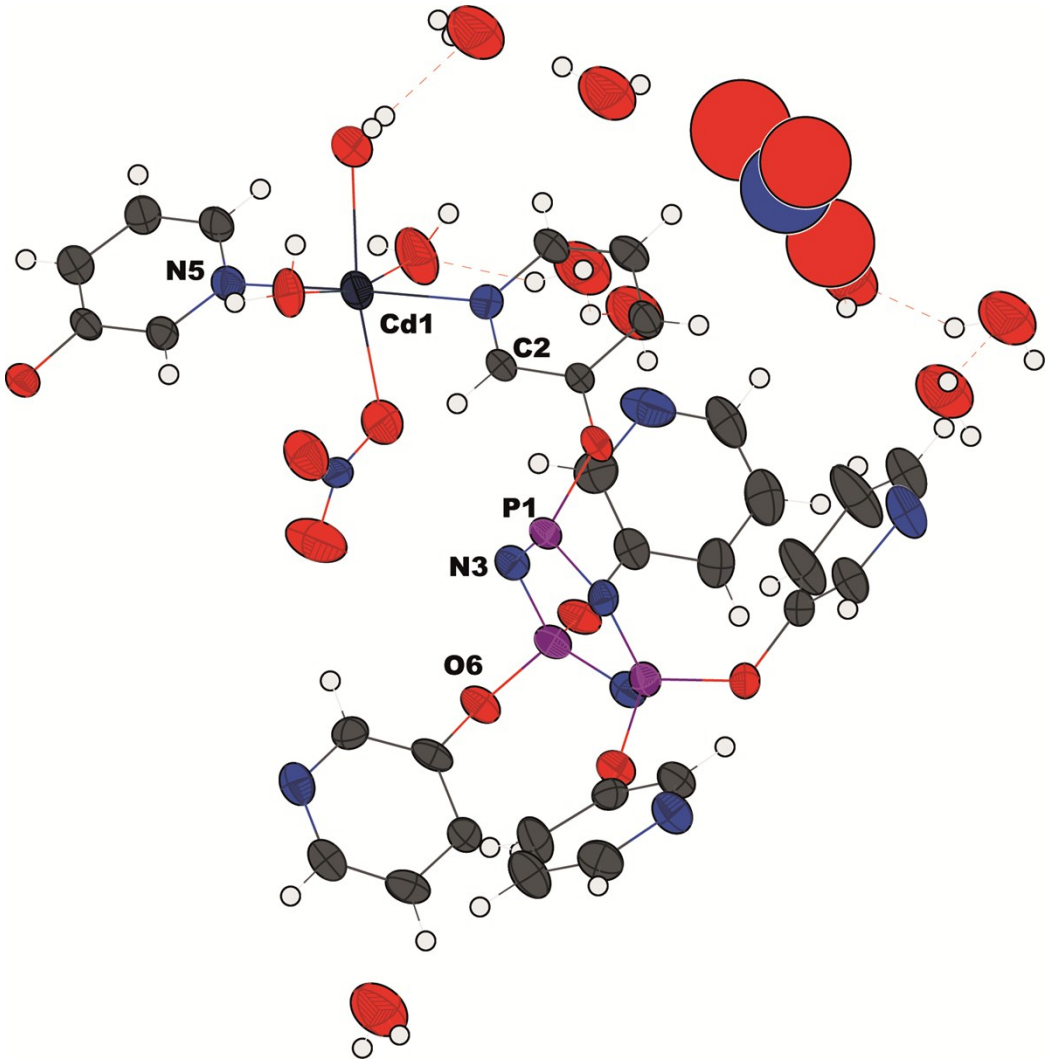


Figure S15. Thermal ellipsoid plot (50 % probability) of asymmetric unit of Compound **4**