Electronic Supplementary Material (ESI) for Dalton Transactions

Tri-, hepta- and octa-nuclear Ag(I) complexes derived from 2-pyridyl functionalized tris(amido)phosphate ligand

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Supporting Information

Table S1: Selected bond-lengths and angles for **1**.C_7H_8, **2**.$3H_2O$, **3**.$5CH_3OH.3H_2O$ and **4**.H_2O

Compound	**Bond lengths**	**Bond Angles**
1.C_7H_8	P(1)-O(1): 1.476(2) P(1)-N(3): 1.649(3) P(1)-N(1): 1.650(2) P(1)-N(2): 1.655(3) P(2)-O(2): 1.476(2) P(2)-N(6): 1.644(2) P(2)-N(4): 1.646(3) P(2)-N(5): 1.654(2) P(3)-O(3): 1.474(2) P(3)-N(7): 1.642(3) P(3)-N(8): 1.647(3) P(3)-N(9): 1.655(3) P(4)-O(4): 1.477(2) P(4)-N(12): 1.640(3) P(4)-N(10): 1.640(3) P(4)-N(11): 1.655(3)	O(1)-P(1)-N(3): 109.92(13) O(1)-P(1)-N(1): 115.51(13) N(3)-P(1)-N(1): 109.67(13) O(1)-P(1)-N(2): 114.24(13) N(3)-P(1)-N(2): 104.78(13) N(1)-P(1)-N(2): 101.97(13) O(2)-P(2)-N(6): 112.54(13) O(2)-P(2)-N(4): 109.62(12) N(6)-P(2)-N(4): 110.81(13) O(2)-P(2)-N(5): 114.73(12) N(6)-P(2)-N(5): 103.39(13) N(4)-P(2)-N(5): 105.41(13) O(3)-P(3)-N(7): 115.70(13) O(3)-P(3)-N(8): 109.74(12) N(7)-P(3)-N(8): 109.64(13) O(3)-P(3)-N(9): 114.15(13) N(7)-P(3)-N(9): 101.62(13) N(8)-P(3)-N(9): 105.27(13) O(4)-P(4)-N(12): 109.58(13) O(4)-P(4)-N(10): 112.87(13) N(12)-P(4)-N(10): 111.51(13) O(4)-P(4)-N(11): 114.21(13) N(12)-P(4)-N(11): 105.05(13) N(10)-P(4)-N(11): 103.26(13)

2.3H_2O	Ag(1)-N(12A): 2.197(16) Ag(1)-N(42): 2.203(17) Ag(2)-N(52): 2.165(17) Ag(2)-N(32): 2.187(16) Ag(3)-N(62): 2.19(2) Ag(3)-N(22): 2.19(2) Ag(4)-N(82): 2.172(18) Ag(4)-N(122): 2.185(18) Ag(5)-N(72): 2.173(18) Ag(5)-N(112): 2.177(19) Ag(6)-N(102): 2.14(2) Ag(6)-N(92): 2.192(19) P(1)-O(1): 1.465(19) P(1)-N(1): 1.649(18) P(1)-N(3): 1.666(18) P(1)-N(2): 1.68(2) P(2)-O(2): 1.443(17) P(2)-N(6): 1.653(19) P(2)-N(4): 1.664(18) P(2)-N(5): 1.668(19) P(3)-O(3): 1.473(16) P(3)-N(7): 1.595(19) P(3)-N(8): 1.620(18) P(3)-N(9): 1.684(17) P(4)-O(4): 1.499(16) P(4)-N(11): 1.627(18) P(4)-N(12): 1.645(18) P(4)-N(10): 1.682(19)	N(12A)-Ag(1)-N(42): 171.6(7) N(52)-Ag(2)-N(32): 168.0(6) N(62)-Ag(3)-N(22): 172.6(8) N(82)-Ag(4)-N(122): 171.3(7) N(72)-Ag(5)-N(112): 177.4(8) N(102)-Ag(6)-N(92): 169.0(8) O(1)-P(1)-N(1): 116.3(10) O(1)-P(1)-N(3): 115.3(11) N(1)-P(1)-N(3): 103.8(10) O(1)-P(1)-N(2): 113.0(11) N(1)-P(1)-N(2): 100.9(10) N(3)-P(1)-N(2): 105.9(10) O(2)-P(2)-N(6): 116.3(10) O(2)-P(2)-N(4): 112.6(10) N(6)-P(2)-N(4): 102.4(10) O(2)-P(2)-N(5): 115.9(9) N(6)-P(2)-N(5): 104.7(10) N(4)-P(2)-N(5): 103.3(10) O(3)-P(3)-N(7): 115.6(10) O(3)-P(3)-N(8): 113.9(9) N(7)-P(3)-N(8): 104.9(10) O(3)-P(3)-N(9): 113.7(10) N(7)-P(3)-N(9): 103.3(10) N(8)-P(3)-N(9): 104.1(9) O(4)-P(4)-N(11): 117.7(10) O(4)-P(4)-N(12): 111.5(9) N(11)-P(4)-N(12): 107.3(9) O(4)-P(4)-N(10): 114.0(9) N(11)-P(4)-N(10): 101.0(9) N(12)-P(4)-N(10): 104.0(10)
3.5CH_3OH.3H_2O	Ag(1)-N(9): 2.104(4) Ag(1)-N(3): 2.124(4) Ag(1)-Ag(5): 2.7522(6) Ag(1)-Ag(2): 2.9083(6) Ag(2)-N(6): 2.106(4) Ag(2)-N(12): 2.123(4) Ag(2)-Ag(3): 2.7641(6) Ag(3)-N(66): 2.152(5) Ag(3)-N(126): 2.169(5)	N(9)-Ag(1)-N(3): 164.00(16) N(9)-Ag(1)-Ag(5): 80.25(11) N(3)-Ag(1)-Ag(5): 84.28(11) N(9)-Ag(1)-Ag(2): 99.90(11) N(3)-Ag(1)-Ag(2): 94.89(11) Ag(5)-Ag(1)-Ag(2): 172.37(2) N(6)-Ag(2)-N(12): 163.44(16) N(6)-Ag(2)-Ag(3): 82.13(11) N(12)-Ag(2)-Ag(3): 81.40(11)

	Ag(4)-N(76): 2.182(5) Ag(4)-N(116): 2.215(5) Ag(4)-O(4): 2.549(3) Ag(5)-N(36): 2.185(5) Ag(5)-N(96): 2.193(5) Ag(6)-N(106): 2.181(5) Ag(6)-N(26): 2.220(5) Ag(6)-O(1): 2.549(3) Ag(7)-N(86): 2.160(5) Ag(7)-N(56): 2.177(5) Ag(7)-O(3): 2.517(3) Ag(8)-N(16): 2.174(5) Ag(8)-N(46): 2.220(5) Ag(8)-O(2): 2.581(4) P(1)-O(1): 1.471(4) P(1)-N(3): 1.604(4) P(1)-N(1): 1.649(4) P(1)-N(2): 1.686(4) P(2)-O(2): 1.469(4) P(2)-N(6): 1.605(4) P(2)-N(5): 1.649(4) P(2)-N(4): 1.682(4) P(3)-O(3): 1.479(3) P(3)-N(9): 1.606(4) P(3)-N(7): 1.660(4) P(3)-N(8): 1.688(4) P(4)-O(4): 1.494(4) P(4)-N(12): 1.603(4) P(4)-N(10): 1.649(4) P(4)-N(11): 1.673(4)	N(6)-Ag(2)-Ag(1): 101.05(11) N(12)-Ag(2)-Ag(1): 95.36(11) Ag(3)-Ag(2)-Ag(1): 166.29(2) N(66)-Ag(3)-N(126): 162.44(19) N(66)-Ag(3)-Ag(2): 80.91(13) N(126)-Ag(3)-Ag(2): 81.56(13) N(76)-Ag(4)-N(116): 168.58(19) N(76)-Ag(4)-O(4): 99.69(15) N(116)-Ag(4)-O(4): 89.83(15) N(36)-Ag(5)-N(96): 161.18(19) N(36)-Ag(5)-Ag(1): 78.83(13) N(96)-Ag(5)-Ag(1): 82.89(14) N(106)-Ag(6)-N(26): 168.8(2) N(106)-Ag(6)-O(1): 99.20(16) N(26)-Ag(6)-O(1): 88.55(16) N(86)-Ag(7)-N(56): 159.37(19) N(86)-Ag(7)-O(3): 91.99(17) N(56)-Ag(7)-O(3): 102.05(15) N(16)-Ag(8)-N(46): 162.52(18) N(16)-Ag(8)-O(2): 100.82(15) N(46)-Ag(8)-O(2): 88.08(15) O(1)-P(1)-N(3): 113.3(2) O(1)-P(1)-N(1): 110.5(2) N(3)-P(1)-N(1): 109.0(2) O(1)-P(1)-N(2): 111.9(2) N(3)-P(1)-N(2): 109.1(2) N(1)-P(1)-N(2): 102.5(2) O(2)-P(2)-N(6): 112.3(2) O(2)-P(2)-N(5): 112.2(2) N(6)-P(2)-N(5): 106.4(2) O(2)-P(2)-N(4): 112.2(2) N(6)-P(2)-N(4): 109.9(2) N(5)-P(2)-N(4): 103.3(2) O(3)-P(3)-N(9): 113.2(2) O(3)-P(3)-N(7): 110.9(2) N(9)-P(3)-N(7): 107.5(2) O(3)-P(3)-N(8): 111.5(2) N(9)-P(3)-N(8): 109.8(2) N(7)-P(3)-N(8): 103.3(2)

		O(4)-P(4)-N(12): 115.1(2) O(4)-P(4)-N(10): 109.6(2) N(12)-P(4)-N(10): 107.9(2) O(4)-P(4)-N(11): 110.8(2) N(12)-P(4)-N(11): 109.4(2) N(10)-P(4)-N(11): 103.3(2) P(1)-O(1)-Ag(6): 96.08(17) P(2)-O(2)-Ag(8): 93.68(17) P(3)-O(3)-Ag(7): 96.95(17) P(4)-O(4)-Ag(4): 97.92(17)
4.H_2O	Ag(1)-N(12)#1: 2.139(8) Ag(1)-N(1): 2.140(7) Ag(1)-Ag(2): 2.9477(10) Ag(1)-Ag(1)#1: 3.2192(13) Ag(1)-Ag(1)#2: 3.2192(14) Ag(2)-N(2): 2.286(7) Ag(2)-N(32)#1: 2.331(16) Ag(2)-N(32')#1: 2.343(15) Ag(2)-N(2)#1: 2.393(7) Ag(2)-Ag(3): 2.8990(12) Ag(2)-Ag(2)#2: 2.9018(11) Ag(2)-Ag(2)#1: 2.9019(11) Ag(2)-P(1)#1: 3.033(2) Ag(3)-N(22): 2.238(9) Ag(3)-N(22)#2: 2.238(9) Ag(3)-N(22)#1: 2.238(9) Ag(3)-Ag(2)#1: 2.8990(12) Ag(3)-Ag(2)#2: 2.8990(12) N(1)-P(1): 1.649(7) N(2)-C(21): 1.389(12) N(2)-P(1): 1.641(9) N(2)-Ag(2)#2: 2.393(7) O(1)-P(1): 1.480(7) P(1)-N(3): 1.668(8) P(1)-Ag(2)#2: 3.033(2) B(1)-F(4): 1.345(17) B(1)-F(1): 1.346(17) B(1)-F(2): 1.347(17) B(1)-F(3): 1.348(17)	N(12)#1-Ag(1)-N(1):168.3(3) N(12)#1-Ag(1)-Ag(2): 94.8(2) N(1)-Ag(1)-Ag(2): 84.8(2) N(12)#1-Ag(1)-Ag(1)#1: 71.7(2) N(1)-Ag(1)-Ag(1)#1: 119.13(19) Ag(2)-Ag(1)-Ag(1)#1: 73.70(2) N(12)#1-Ag(1)-Ag(1)#2: 127.2(2) N(1)-Ag(1)-Ag(1)#2: 64.48(19) Ag(2)-Ag(1)-Ag(1)#2: 91.256(18) Ag(1)#1-Ag(1)-Ag(1)#2: 60.0 N(2)-Ag(2)-N(32)#1: 104.4(4) N(2)-Ag(2)-N(32')#1: 106.0(4) N(32)#1-Ag(2)-N(32')#1: 8.5(7) N(2)-Ag(2)-N(2)#1: 151.1(4) N(32)#1-Ag(2)-N(2)#1: 93.0(4) N(32')#1-Ag(2)-N(2)#1: 94.6(4) N(2)-Ag(2)-Ag(3): 76.35(19) N(32)#1-Ag(2)-Ag(3): 123.5(6) N(32')#1-Ag(2)-Ag(3): 132.0(5) N(2)#1-Ag(2)-Ag(3): 74.8(2) N(2)-Ag(2)-Ag(2)#2: 53.35(18) N(32)#1-Ag(2)-Ag(2)#2: 157.5(3) N(32')#1-Ag(2)-Ag(2)#2: 156.4(3) N(2)#1-Ag(2)-Ag(2)#2: 108.77(19) Ag(3)-Ag(2)-Ag(2)#2: 59.967(15) N(2)-Ag(2)-Ag(2)#1: 112.01(18) N(32)#1-Ag(2)-Ag(2)#1: 142.4(3) N(32')#1-Ag(2)-Ag(2)#1: 142.0(3) N(2)#1-Ag(2)-Ag(2)#1: 50.02(18)

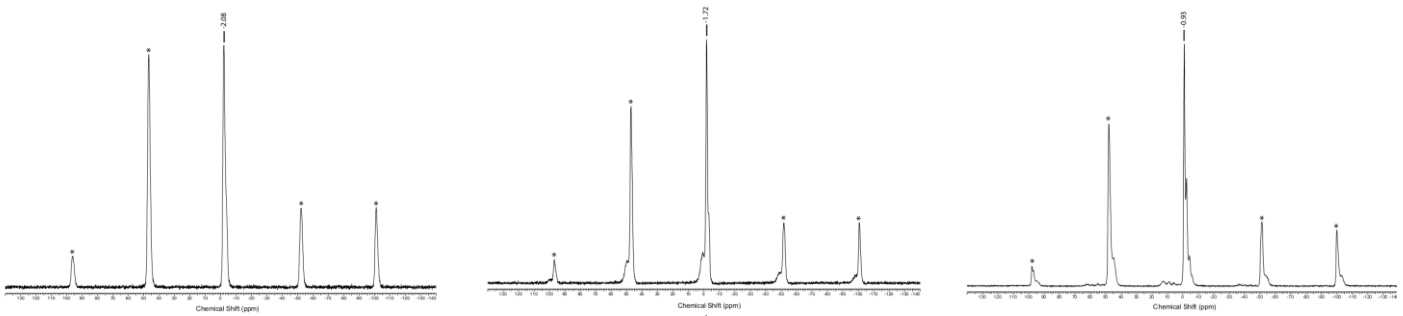
		Ag(3)-Ag(2)-Ag(2)#1: 59.967(15) Ag(2)#2-Ag(2)-Ag(2)#1: 60.0 N(2)-Ag(2)-Ag(1): 81.7(2) N(32)#1-Ag(2)-Ag(1): 95.9(6) N(32')#1-Ag(2)-Ag(1): 87.8(5) N(2)#1-Ag(2)-Ag(1): 119.71(18) Ag(3)-Ag(2)-Ag(1): 138.44(3) Ag(2)#2-Ag(2)-Ag(1): 78.59(2) Ag(2)#1-Ag(2)-Ag(1): 97.925(19) N(2)-Ag(2)-P(1)#1: 175.76(19) N(32)#1-Ag(2)-P(1)#1: 71.7(4) N(32')#1-Ag(2)-P(1)#1: 69.9(3) N(2)#1-Ag(2)-P(1)#1: 32.6(2) Ag(3)-Ag(2)-P(1)#1: 107.13(5) Ag(2)#2-Ag(2)-P(1)#1: 130.37(5) Ag(2)#1-Ag(2)-P(1)#1: 72.09(5) Ag(1)-Ag(2)-P(1)#1: 96.81(5) N(22)-Ag(3)-N(22)#2: 117.89(12) N(22)-Ag(3)-N(22)#1: 117.89(12) N(22)#2-Ag(3)-N(22)#1: 117.89(12) N(22)-Ag(3)-Ag(2)#1: 132.3(2) N(22)#2-Ag(3)-Ag(2)#1: 88.2(2) N(22)#1-Ag(3)-Ag(2)#1: 73.6(2) N(22)-Ag(3)-Ag(2)#2: 88.2(2) N(22)#2-Ag(3)-Ag(2)#2: 73.6(2) N(22)#1-Ag(3)-Ag(2)#2: 132.3(2) Ag(2)#1-Ag(3)-Ag(2)#2: 60.07(3) N(22)-Ag(3)-Ag(2): 73.6(2) N(22)#2-Ag(3)-Ag(2): 132.3(2) N(22)#1-Ag(3)-Ag(2): 88.2(2) Ag(2)#1-Ag(3)-Ag(2): 60.06(3) Ag(2)#2-Ag(3)-Ag(2): 60.06(3) C(11)-N(1)-P(1): 120.1(6) C(11)-N(1)-Ag(1): 113.6(5) P(1)-N(1)-Ag(1): 115.6(4) C(21)-N(2)-P(1): 121.0(7) C(21)-N(2)-Ag(2): 106.3(6) P(1)-N(2)-Ag(2): 124.9(4) C(21)-N(2)-Ag(2)#2: 125.1(6)

		P(1)-N(2)-Ag(2)#2: 95.7(3) Ag(2)-N(2)-Ag(2)#2: 76.6(2) O(1)-P(1)-N(2): 116.8(4) O(1)-P(1)-N(1): 118.0(4) N(2)-P(1)-N(1): 101.7(4) O(1)-P(1)-N(3): 105.3(4) N(2)-P(1)-N(3): 107.1(4) N(1)-P(1)-N(3): 107.2(4) O(1)-P(1)-Ag(2)#2: 165.7(3) N(2)-P(1)-Ag(2)#2: 51.7(3) N(1)-P(1)-Ag(2)#2: 62.3(3) N(3)-P(1)-Ag(2)#2: 87.5(3) F(4)-B(1)-F(1): 108.7(10) F(4)-B(1)-F(2): 110.2(10) F(1)-B(1)-F(2): 110.3(11) F(4)-B(1)-F(3): 109.5(10) F(1)-B(1)-F(3): 109.5(11) F(2)-B(1)-F(3): 108.5(10)

Table S2: Table of hydrogen bonding parameters for **1**.C_7H_8, **2**.$3H_2O$, **3**.$5CH_3OH.3H_2O$ and **4**.H_2O

Compound	D-H...A	d(H...A)Å	d(D...A)Å	<(DHA)°
1.C_7H_8	N(1)-H(1)...N(52P)	1.99	2.853(4)	167.8
	N(2)-H(2)...N(42P)	2.16	3.035(4)	172.9
	N(3)-H(3)...O(2)#1	2.00	2.797(3)	149.5
	N(4)-H(4)...O(1)#2	2.00	2.845(3)	159.7
	N(5)-H(5)...N(32P)	2.10	2.977(3)	175.4
	N(6)-H(6)...N(22P)	1.98	2.853(4)	173.0
	N(7)-H(7)...N(112)	1.96	2.829(4)	168.5
	N(8)-H(8)...O(4)#3	2.02	2.776(3)	143.1
	N(9)-H(9)...N(122)	2.19	3.058(4)	171.5
	N(10)-H(10)...N(92P)	1.99	2.867(4)	174.4
	N(11)-H(11)...N(82P)	2.10	2.981(4)	176.1
	N(12)-H(12)...O(3)#4	2.00	2.863(3)	166.1
	Symmetry transformations used to generate equivalent atoms:			
	#1 -x+1,y-1/2,-z+1/2 #2 -x+1,y+1/2,-z+1/2 #3 -x,y+1/2,-z+1/2 #4 -x,y-1/2,-z+1/2			
2.$3H_2O$	N(1)-H(1)...O(10)	2.37	3.09(3)	141.5
	N(1)-H(1)...O(9)	2.63	3.47(3)	166.7
	N(2)-H(2)...O(13)	2.25	3.05(2)	155.9
	N(3)-H(3)...O(5)	2.38	3.21(2)	162.7
	N(4)-H(4)...O(13)	2.34	3.14(2)	155.0
	N(5)-H(5)...O(10)	2.37	3.10(2)	142.7
	N(5)-H(5)...O(8)	2.42	3.24(3)	161.1
	N(6)-H(6)...O(7)	2.23	3.00(3)	147.7
	N(7)-H(7)...O(19)	2.29	3.05(3)	146.4
	N(8)-H(8)...O(22)	2.36	3.15(2)	153.9
	N(9)-H(9)...O(16)	2.48	3.24(2)	148.5
	N(9)-H(9)...O(15)	2.54	3.34(3)	154.9
	N(10)-H(10)...O(17)	2.18	3.01(2)	161.5
	N(10)-H(10)...O(19)	2.37	3.11(2)	144.1
	N(11)-H(11)...O(22)	2.24	3.05(2)	156.1
	N(12)-H(12)...O(16)	2.30	3.03(3)	143.7
3.$5CH_3OH.3H_2O$	N(1)-H(1A)...O(2)	1.98	2.821(6)	163.9
	N(5)-H(5)...O(3)	1.95	2.804(5)	172.0
	N(7)-H(7)...O(4)	1.96	2.811(5)	171.1
	N(10)-H(10)...O(1)	1.97	2.827(5)	171.7

4.H_2O	N(3)-H(3)...F(3) #1	2.03	2.886(6)	175.6
	N(3)-H(3)...F(1) #2	2.55	3.312(5)	147.4
	N(3)-H(3)...F(2) #3	2.35	3.166(2)	159.3
	Symmetry transformations used to generate equivalent atoms:			
	#1 1-y,x-y,z #2 x, y, z #3 1-x+y, 1-x, z			



a b c

Figure S1: Solid state ^{31}P-CP-MAS NMR spectra of **2** (a), **3** (b) and **4** (c) recorded at a spinning rate of 10 KHz. The peaks denoted with asterisks are spinning side bands

The solid-state NMR spectra were measured on a Bruker Avance DSX 500 spectrometer operating at 202.40 MHz for ^{31}P. All spectra were collected using a 4 mm triple resonance probe and zirconia rotors. The ^{31}P{^{1}H} MAS NMR spectra were measured at a MAS rate of 10 kHz with ^{1}H TPPM decoupling during acquisition at an *rf* field of *ca.* 83 kHz. A ^{31}P $\pi/3$ pulse length of 2.1 μs with a recycle delay of 120.0 s was used.

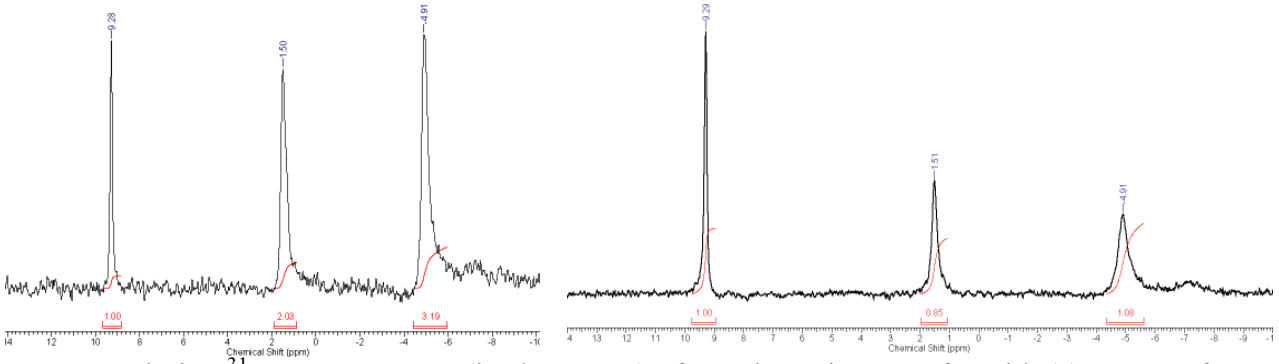


Figure S2: Solution ^{31}P- NMR spectra (in d_6-DMSO) of reaction mixtures of **1** with (a) excess of $AgClO_4$ and (b) excess of $AgBF_4$ indicating the formation of **3** and **4** at different ratios after three days.

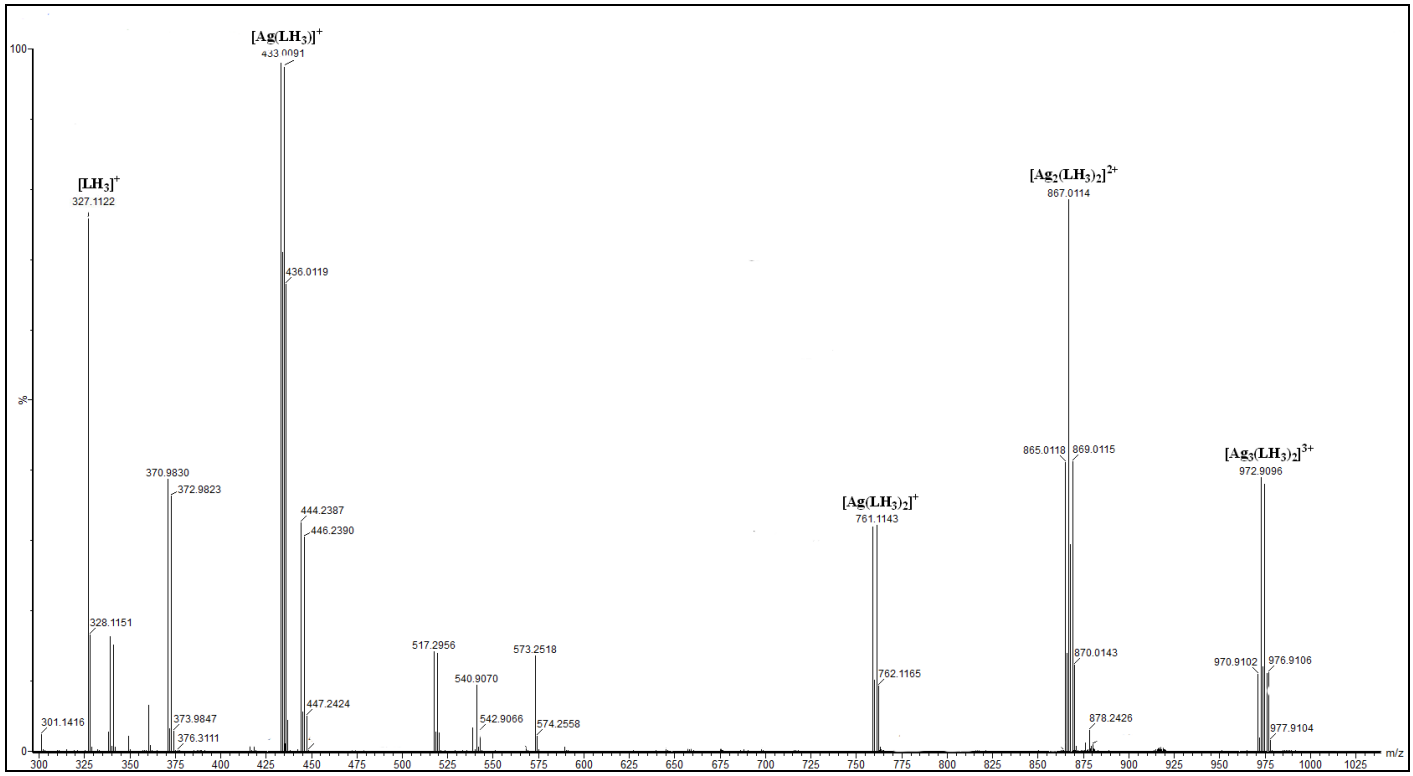


Figure S3: ESI(+) Mass spectra of **2**.

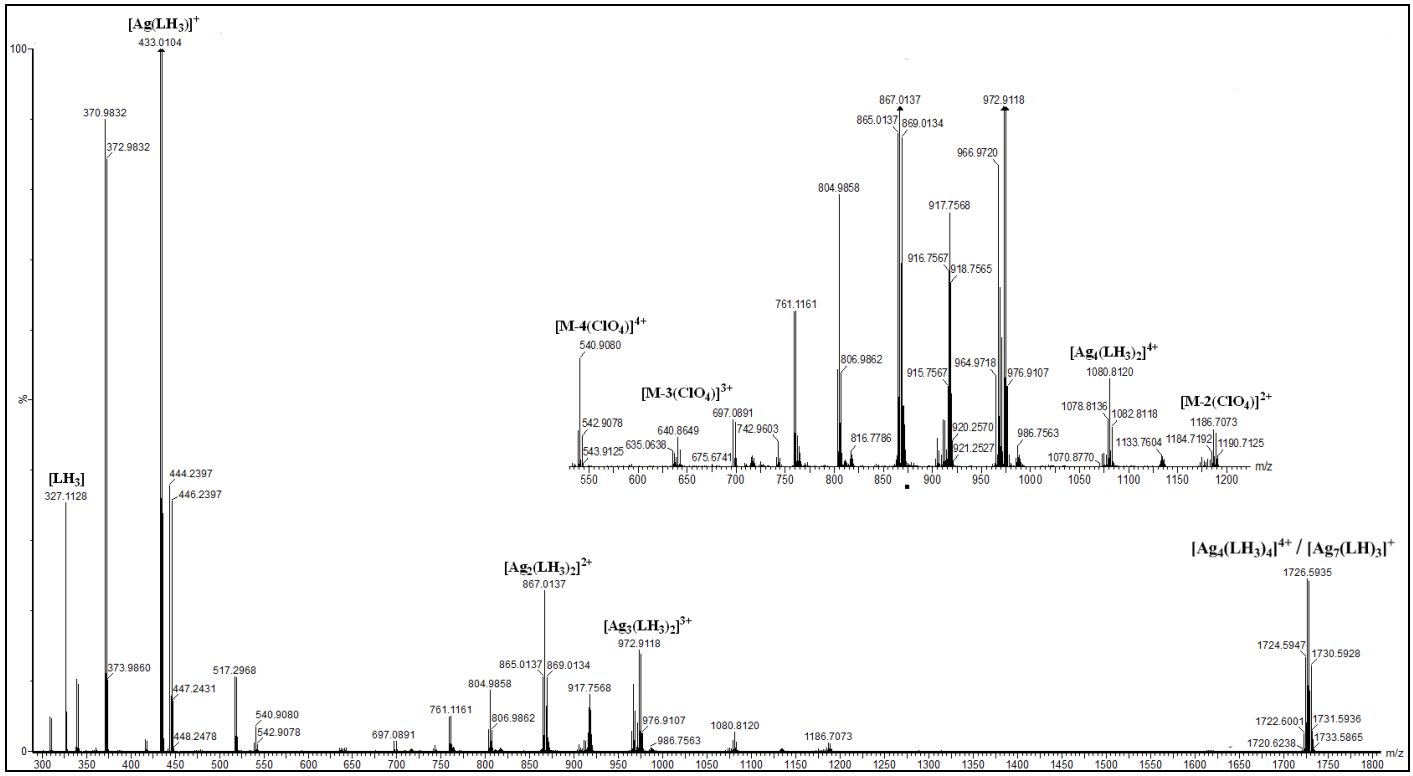


Figure S4: ESI(+) mass spectra of **3**; M = $\{[Ag_8(LH_2)_4](ClO_4)_4\}$

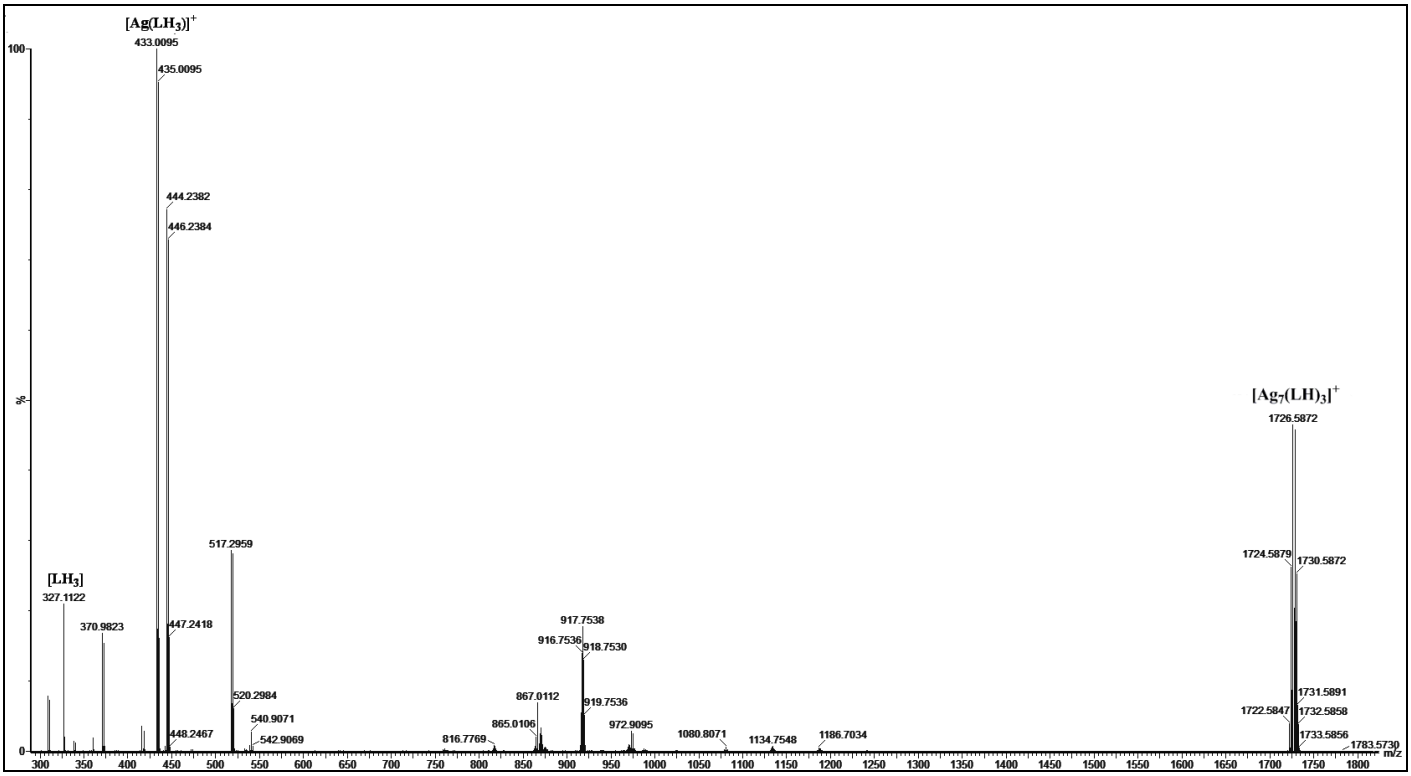


Figure S5: ESI(+) mass Spectra of **4**.

As the set of ligands and metal ions used are same, many of the peaks were found to be common in all of them. The peak at *m/z* 433.0 corresponds to smallest fragment $[Ag(LH_3)]^+$ and was observed in all the spectra. While the peak at *m/z* 1726.5 corresponds to the cationic core of **4**, a similar peak was found in the spectra of **3** as well. Although the exact reason for this is unclear, we attribute this to the presence of both mono- and di-anionic imido P(V) species in dilute solutions. Concurrently, the peak at *m/z* 540.9, corresponding to the tetra-cationic core in **3**, was also found in the spectra of **4**.

Additional Figures

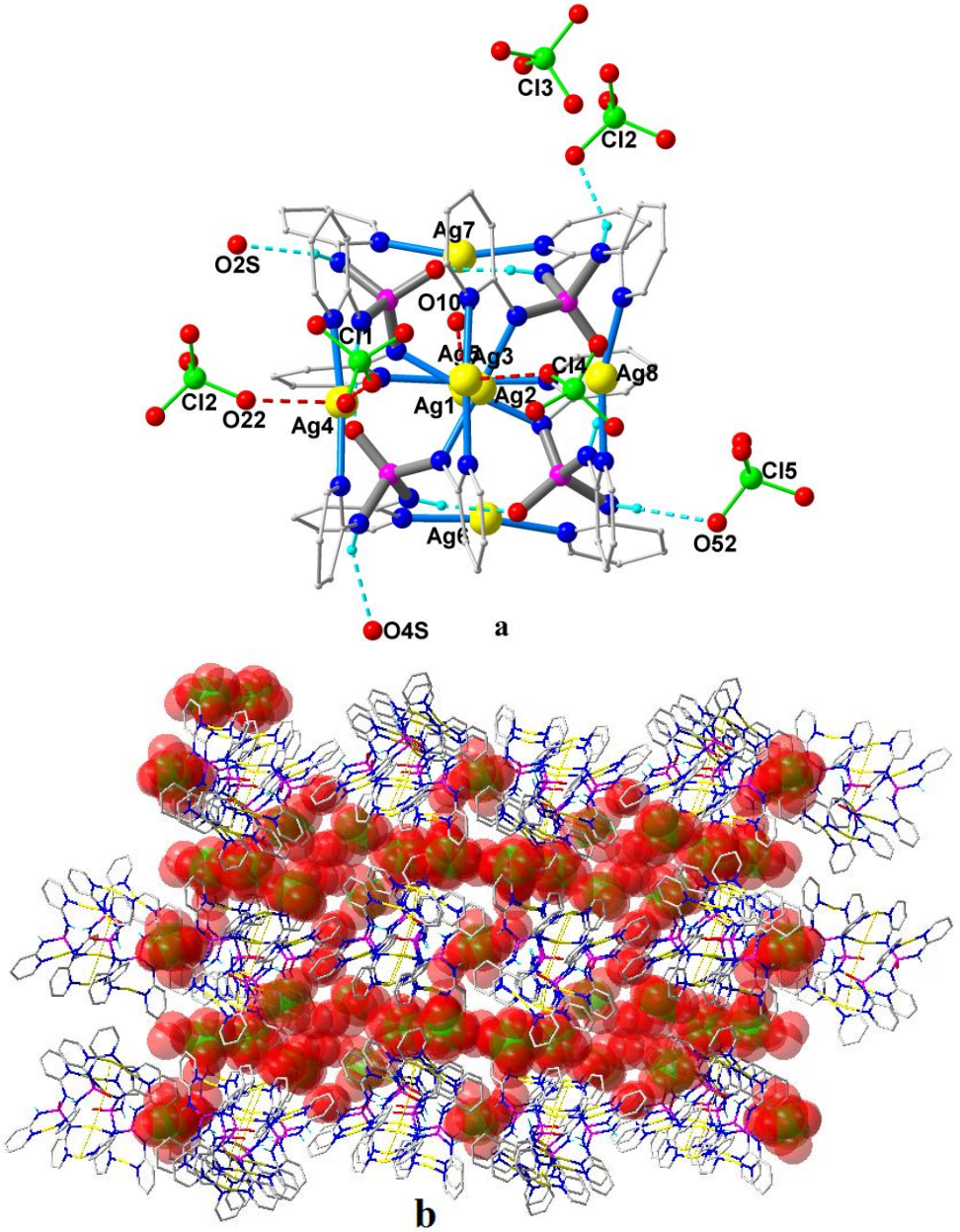


Figure S6: (a) View of the octa-nuclear cluster in **3**.5CH_3OH.3H_2O along with coordinated and H-bonded perchlorates. The disordered perchlorate groups are omitted; (c) packing diagram of **3**.5CH_3OH.3H_2O showing 1D-solvent channel

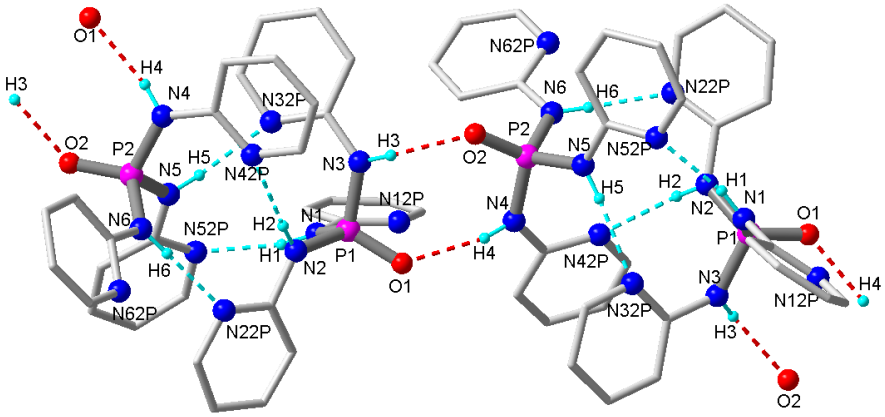


Figure S7: Crystal Structure of **1**.C_7H_8

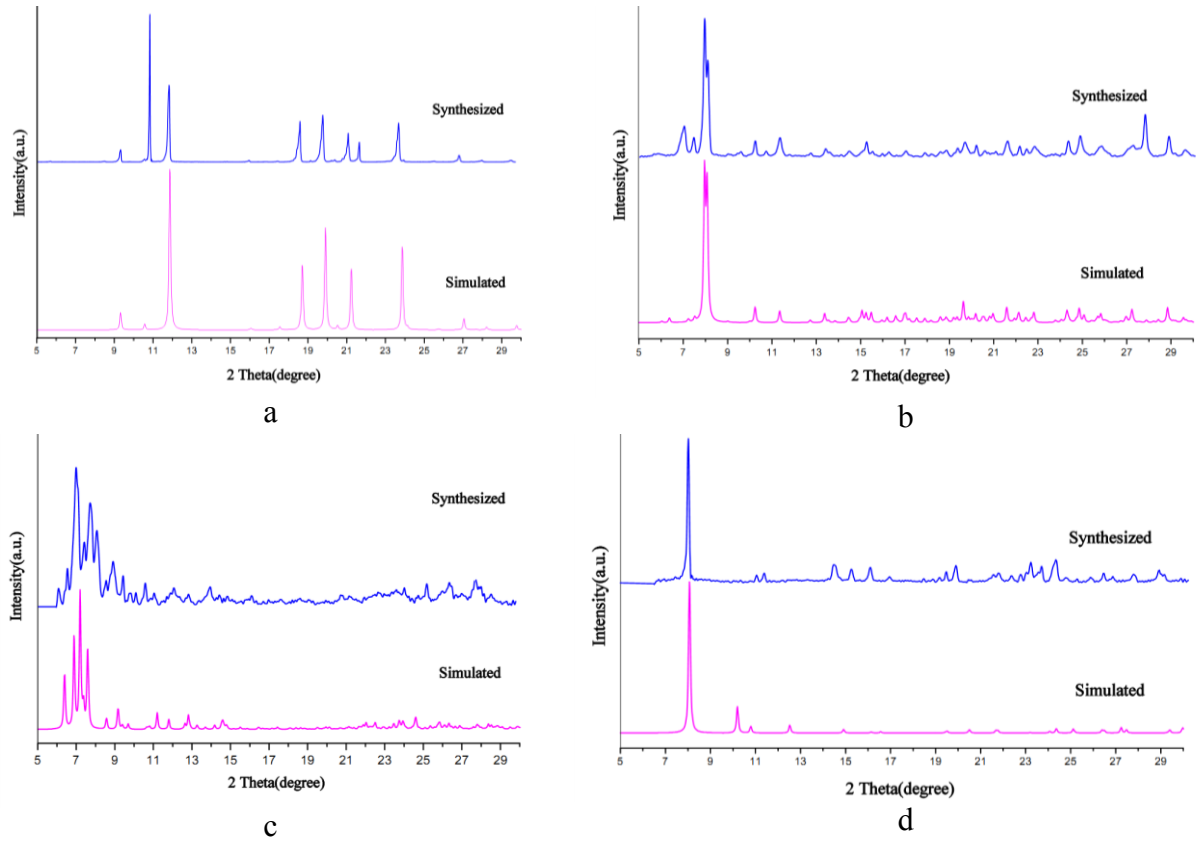


Figure S8: PXRD patterns for **1**.C_7H_8 (a), **2** (b), **3** (c) and **4** (d). A slight mismatch of the synthesized and simulated patterns for **1**, **2** and **3** is due to the presence of solvated molecules in their single crystal X-ray data

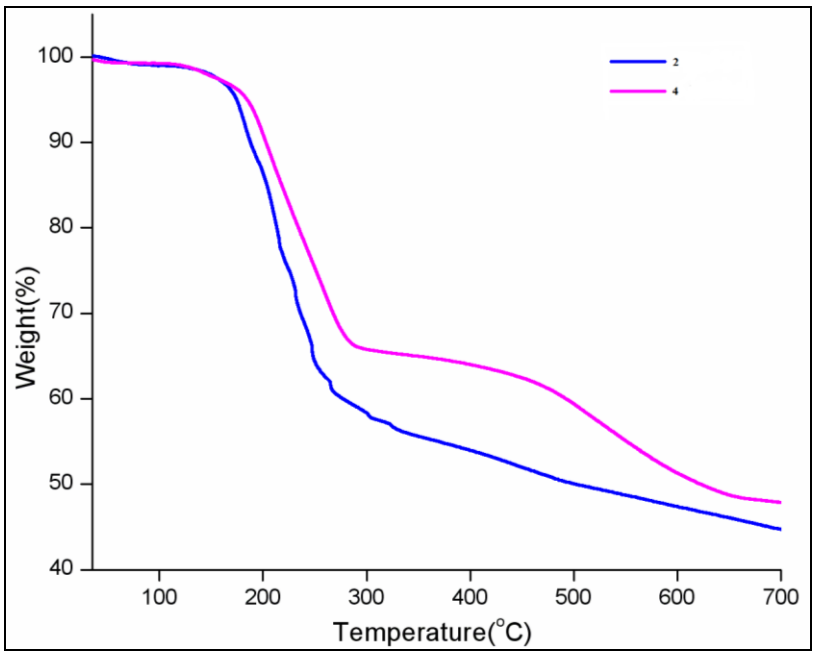


Figure S9: TGA traces of the compounds **2** and **4**