Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information for

Intriguing Structural Chemistry of Neutral and Anionic Layered Monoalkylphosphates: Single-Source Precursors for High-Yield Ceramic Phosphates

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Figure S24: Hydrogen bonding interactions in **1** (a) represents the sheet formation due to extensive hydrogen bonding between the hydrogen atoms of cyclohexyl ammonium and $–OPO_3H$ units, lattice H_2O molecules and OPO_3H units of methyl phosphate; (b) represents the layered structure of **1.**

Figure S25: Hydrogen bonding interactions in **3** (a) represents the sheet formation due to extensive hydrogen bonding between the hydrogen atoms of cyclohexyl ammonium and $–OPO_3H$ units of isopropyl phosphate; (b) represents the layered structure of **3**.

Figure S26: Hydrogen bonding interactions in **4** (a) represents the sheet formation due to extensive hydrogen bonding between the hydrogen atoms of cyclohexyl ammonium and $–OPO_3H$ units of teritiary butyl phosphate; (b) represents one dimensional chain formation in **4.**

Figure S27: Hydrogen bonding interactions in **9** (a) represents the sheet formation due to extensive hydrogen bonding between the hydrogen atoms of cyclohexyl ammonium and $–OPO_3H$ units of teritiary butyl phosphate and OPO_3H_2 units of free isopropyl phosphate.

Figure S28. FT-IR spectrum of compound **3.**

Figure S29. DSC trace of compound **3.**

Figure S30. SEM characterisation of compound **10** with EDX and element mapping.

Table S1: Hydrogen bond table for **1** [Å and °].

Table S2: Hydrogen bond table for **2** [Å and °].

Table S3: Hydrogen bond table for **3** [Å and °].

Table S4: Hydrogen bond table for **4** [Å and °].

Table S5: Hydrogen bond table for **7** [Å and °].

Table S6: Hydrogen bond table for **9** [Å and °].

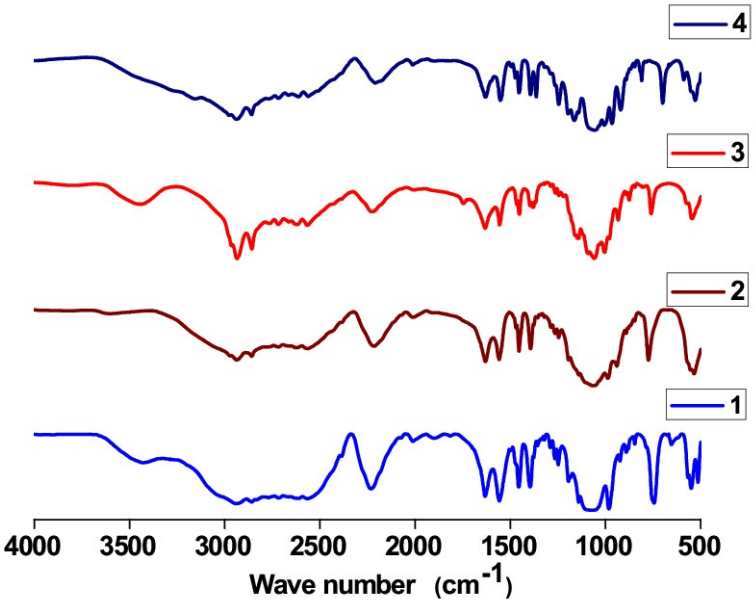

Figure S1. FT-IR spectra of compounds **1-4** (as KBr diluted discs).

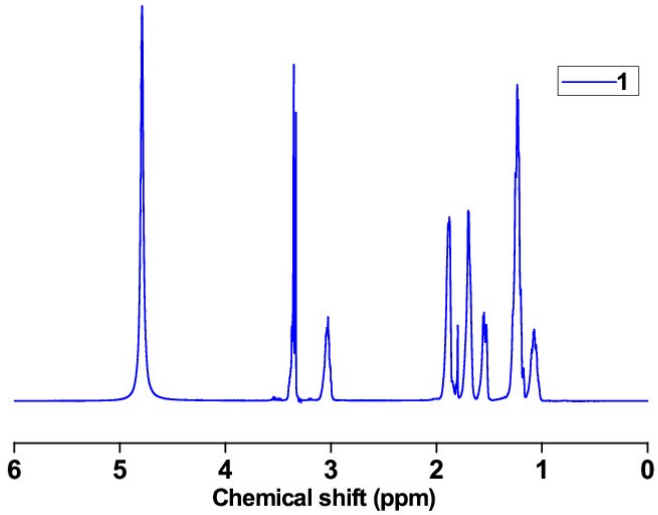

Figure S2. ^{1}H NMR spectrum of compound **1** (D_2O 500 MHz).

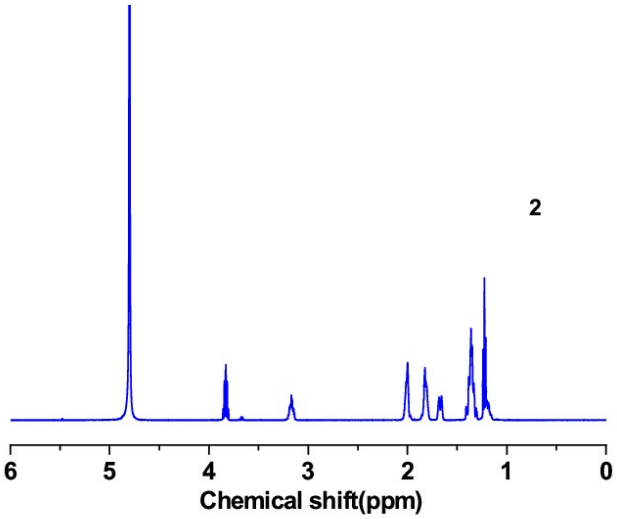

Figure S3. ^{1}H NMR spectrum of compound **2** (D_2O 500 MHz).

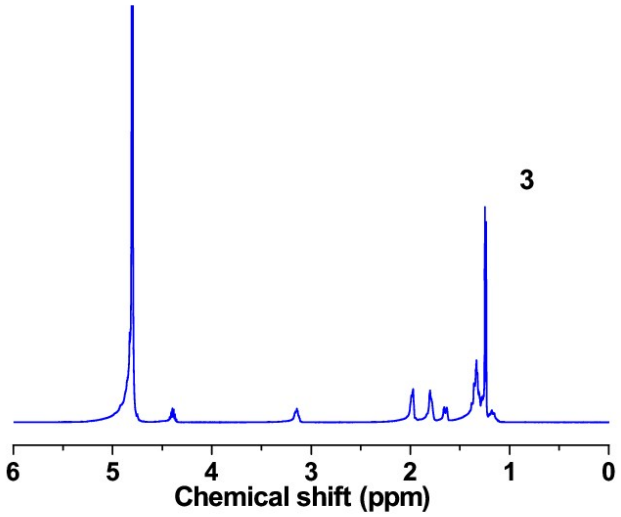

Figure S4. ^{1}H NMR spectrum of compound **3** (D_2O 500 MHz).

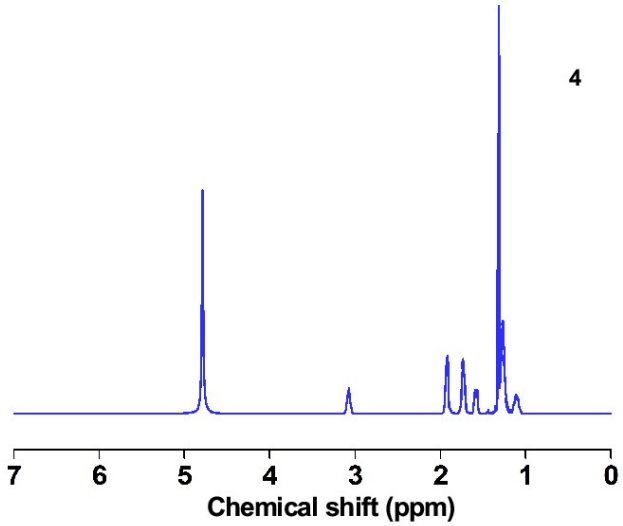

Figure S5. ^{1}H NMR spectrum of compound **4** (D_2O 500 MHz).

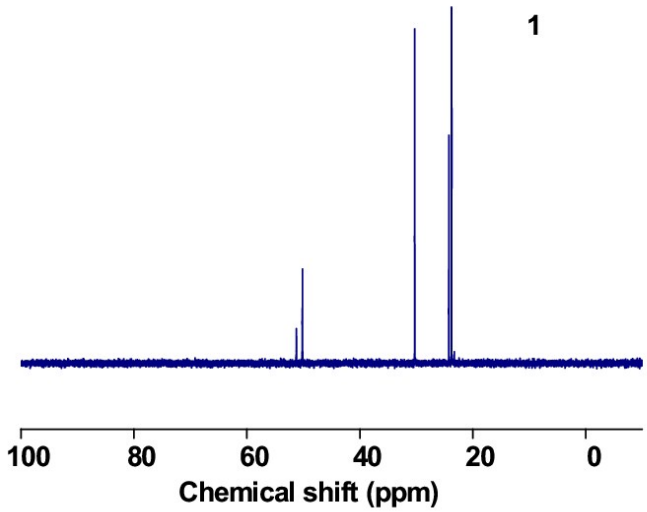

Figure S6: ^{13}C NMR spectrum of compound **1** (D_2O)

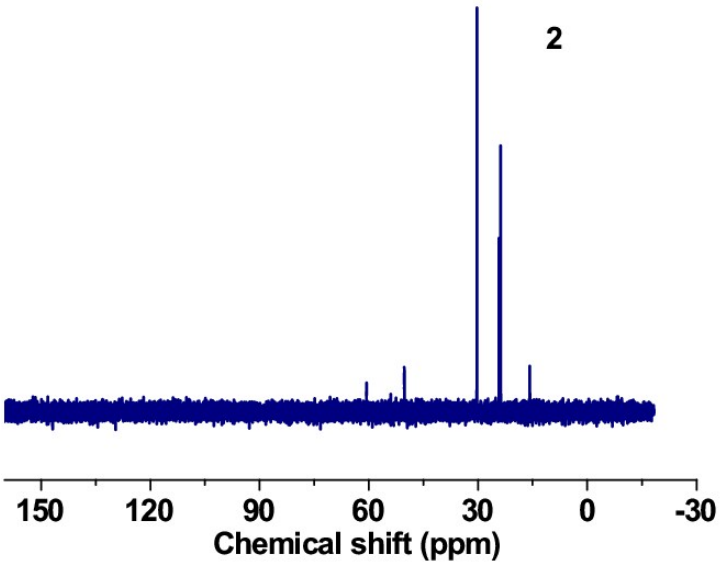

Figure S7: ^{13}C NMR spectrum of compound **2** (D_2O)

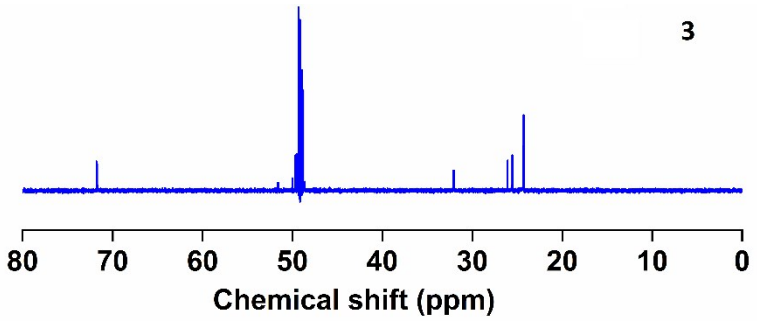

Figure S8: ^{13}C NMR spectrum of compound **3** (DMSO-d6)

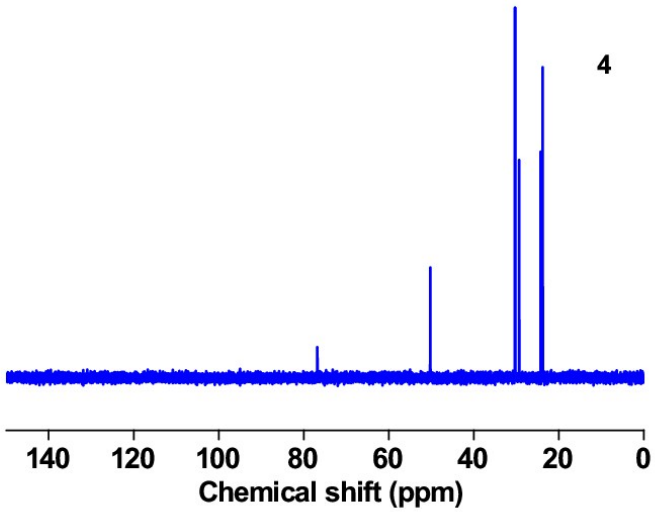

Figure S9: ^{13}C NMR spectrum of compound **4** (D_2O)

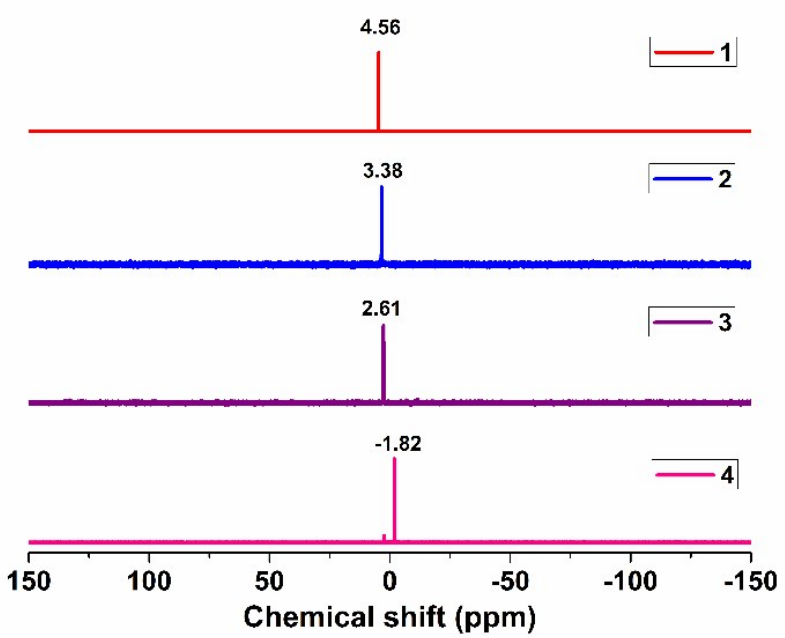

Figure S10: ^{31}P NMR spectra of compounds **1-4** in (D_2O).

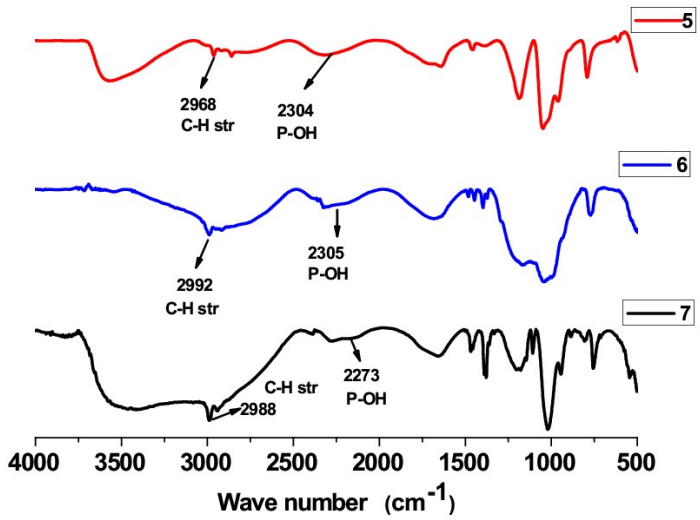

Figure S11. FT-IR spectra of compound **5-7.**

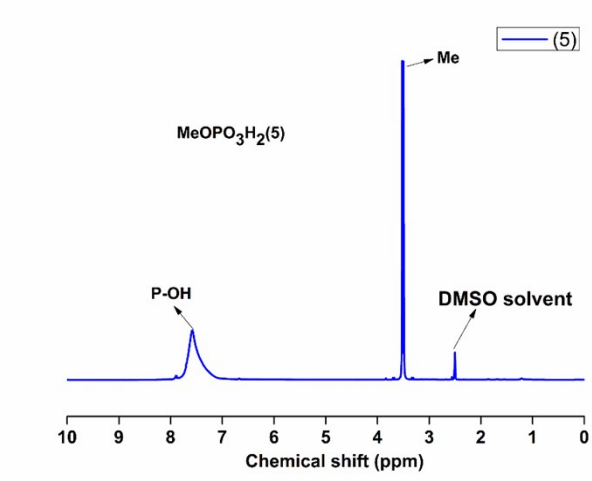

Figure S12. ^{1}H NMR spectrum of compound **5** (DMSO-d6 500 MHz).

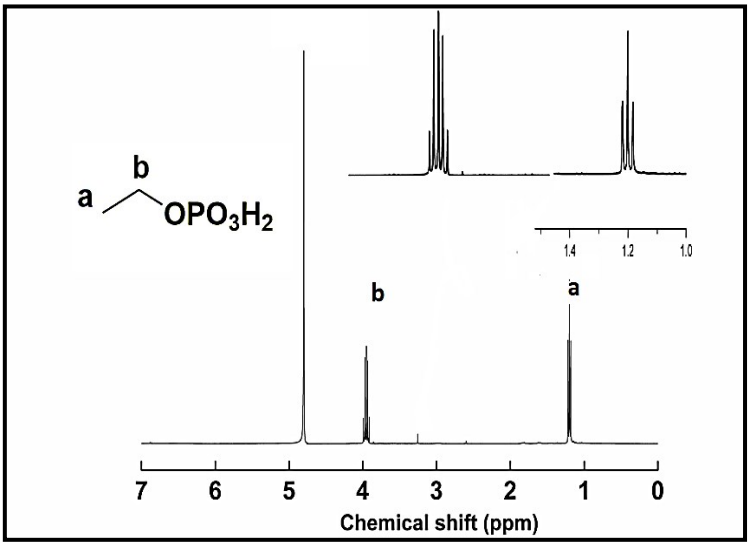

Figure S13. ^{1}H NMR spectrum of compound **6** (D_2O 500 MHz).

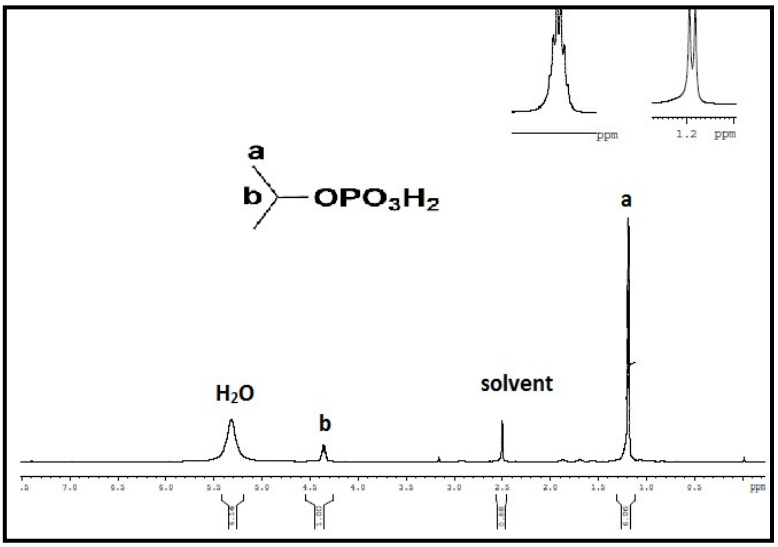

Figure S14. ^{1}H NMR spectrum of compound **7** (DMSO-d_6 500 MHz).

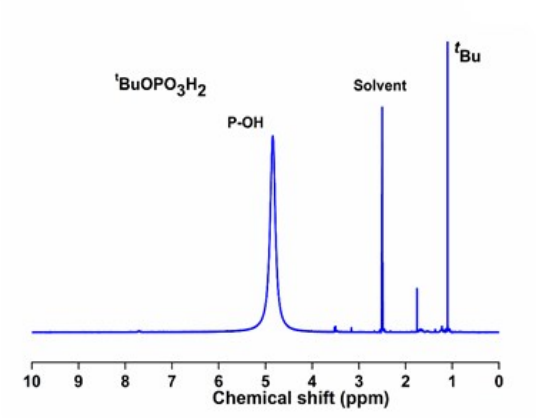

Figure S15. ^{1}H NMR spectrum of compound **8** (DMSO-d_6 500 MHz).

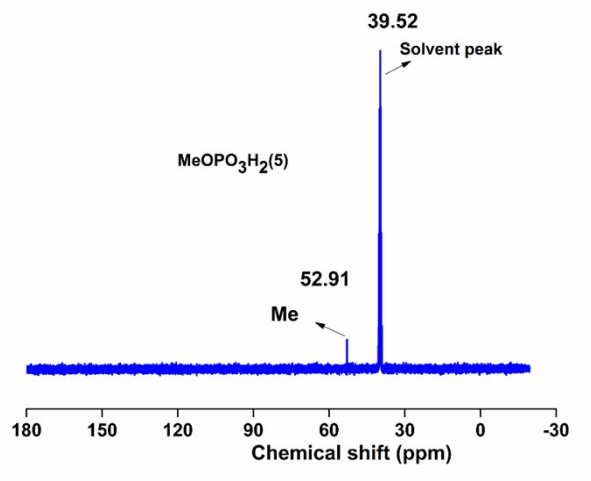

Figure S16: ^{13}C NMR spectrum of compound **5** (DMSO-d_6)

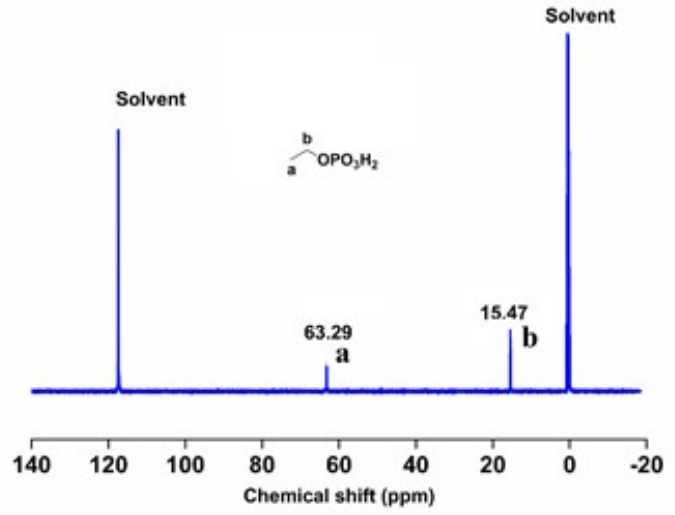

Figure S17: ^{13}C NMR spectrum of compound **6** (CD_3CN-d_3)

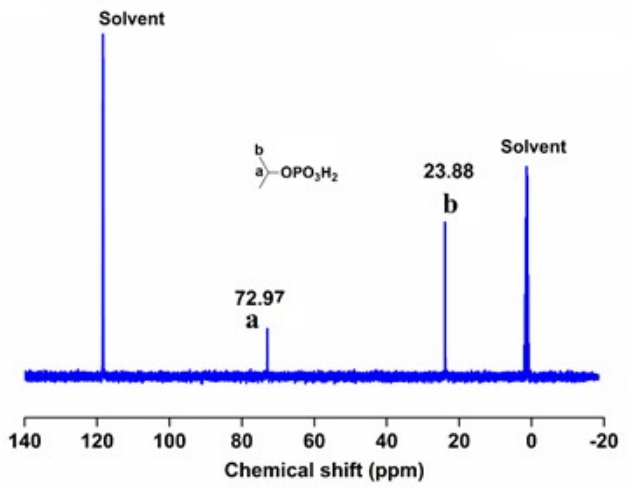

Figure S18: ^{13}C NMR spectrum of compound **7** (CD_3CN-d_3)

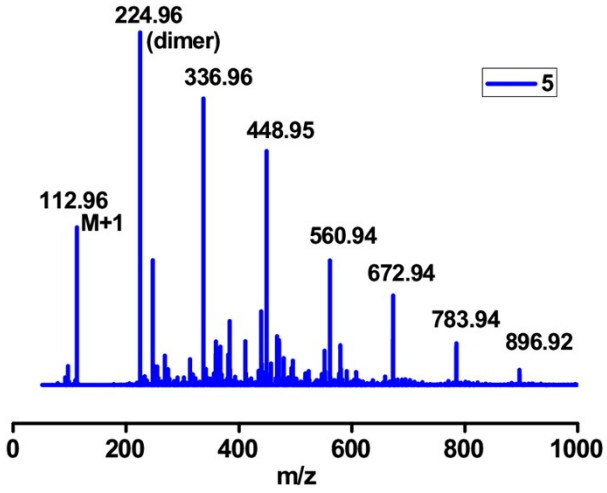

Figure S19: ESI-MS spectrum of compound **5** (reported in CH_3CN)

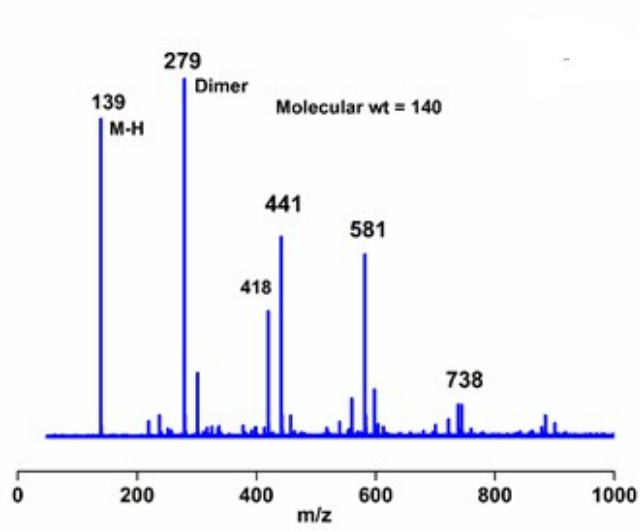

Figure S20: ESI-MS spectrum of compound **7** (reported in CH_3CN)

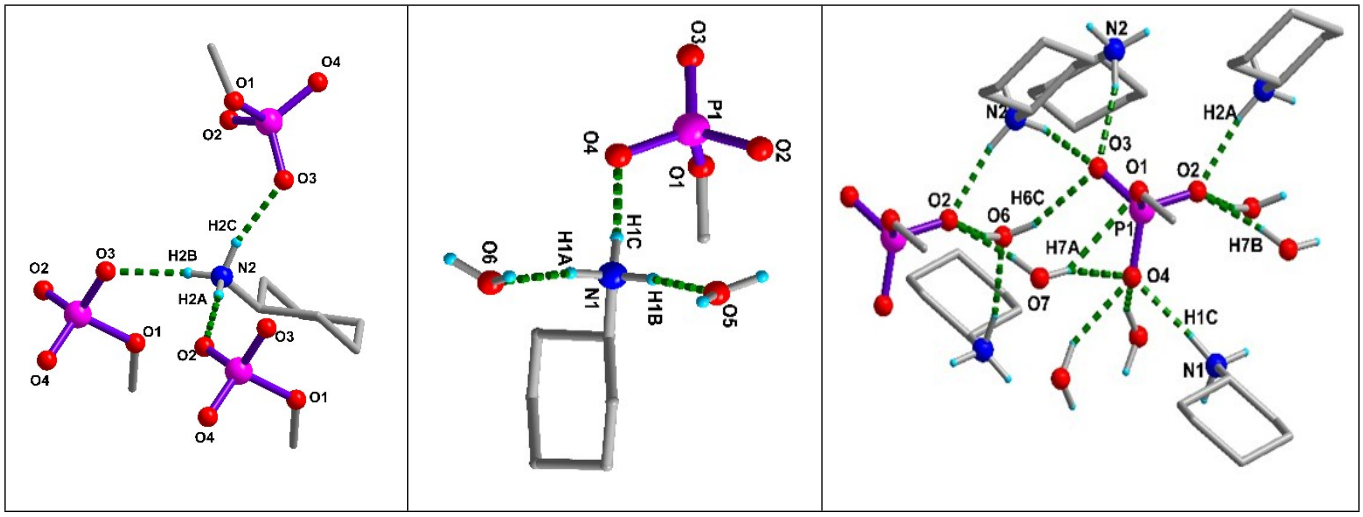

Figure S21: Molecular structure of **1** showing immediate hydrogen bonding interactions between hydrogen atoms of quaternised cyclohexyl amine and the oxygen and hydrogen atoms of methyl phosphate ligand.

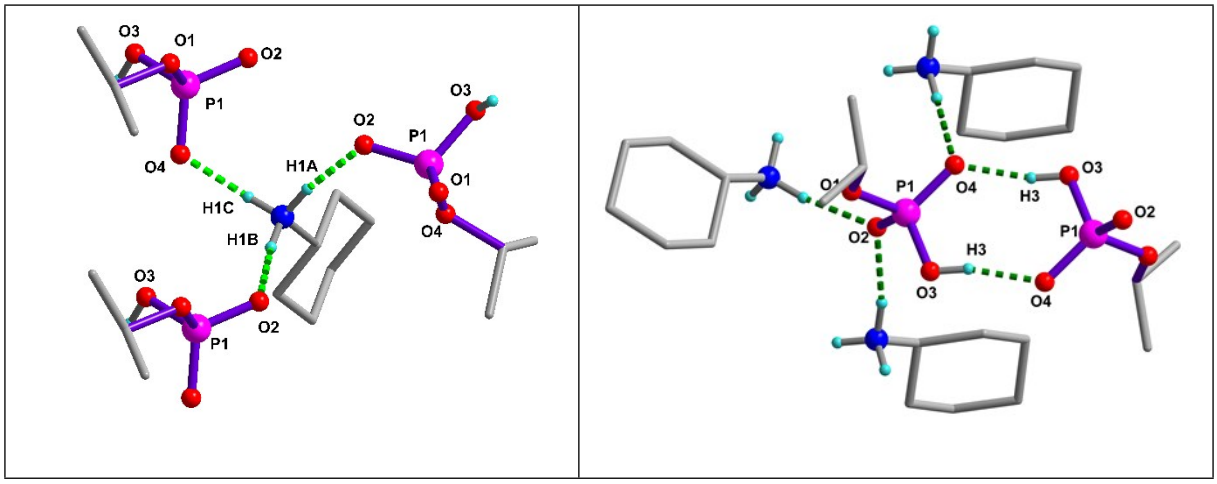

Figure S22: Molecular structure of **3** showing immediate hydrogen bonding interactions between hydrogen atoms of quaternised cyclohexyl amine and the oxygen and hydrogen atoms of isopropyl phosphate ligand.

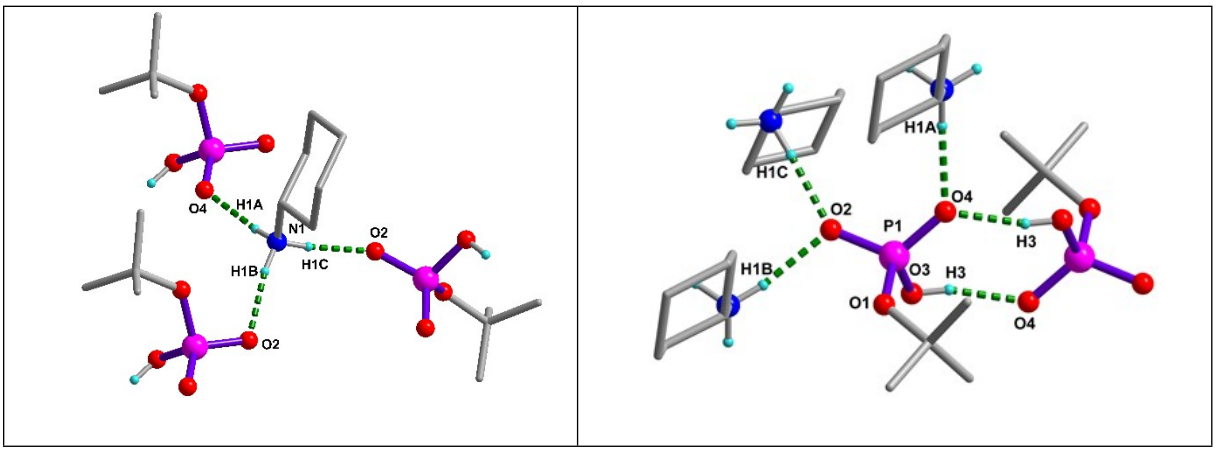

Figure S23: Molecular structure of **4** showing immediate hydrogen bonding between hydrogen atoms of quaternised cyclohexyl amine and the oxygen and hydrogen atoms of tertiary butyl phosphate ligand.

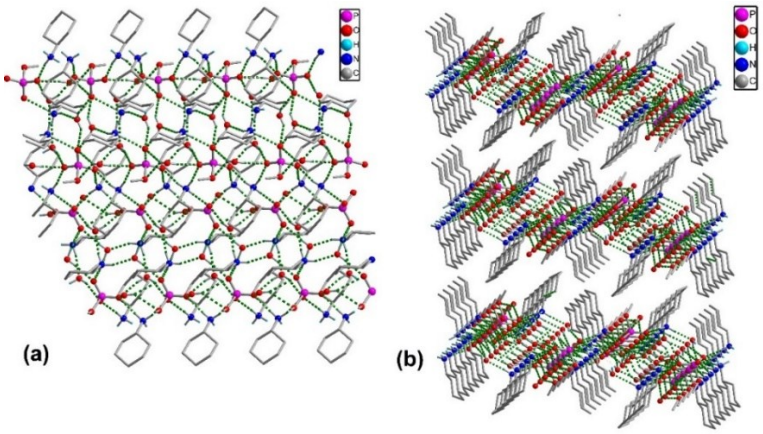

Figure S24: Hydrogen bonding interactions in **1** (a) represents the sheet formation due to extensive hydrogen bonding between the hydrogen atoms of cyclohexyl ammonium, lattice H_2O molecules and OPO_3H units of methyl phosphate; (b) represents the layered structure of **1.**

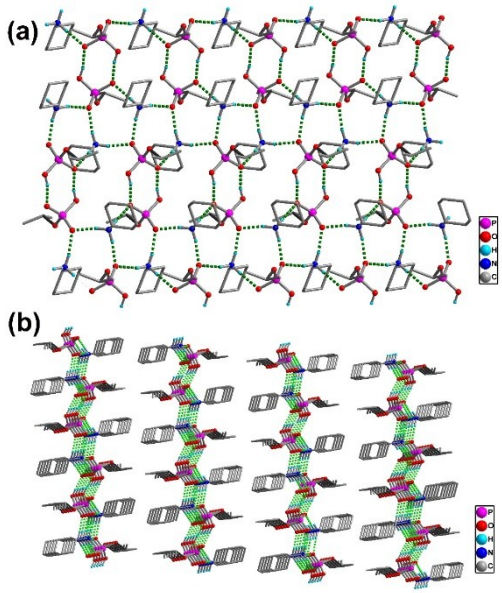

Figure S25: Hydrogen bonding interactions in **3** (a) represents the sheet formation due to extensive hydrogen bonding between the hydrogen atoms of cyclohexyl ammonium and $–OPO_3H$ units of isopropyl phosphate; (b) represents the layered structure of **3.**

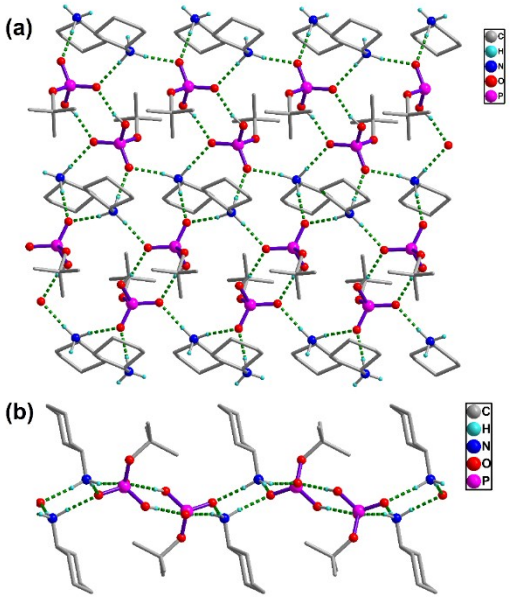

Figure S26: Hydrogen bonding interactions in **4** (a) represents the sheet formation due to extensive hydrogen bonding between the hydrogen atoms of cyclohexyl ammonium and $–OPO_3H$ units of teritiary butyl phosphate; (b) represents one dimensional chain formation in **4.**

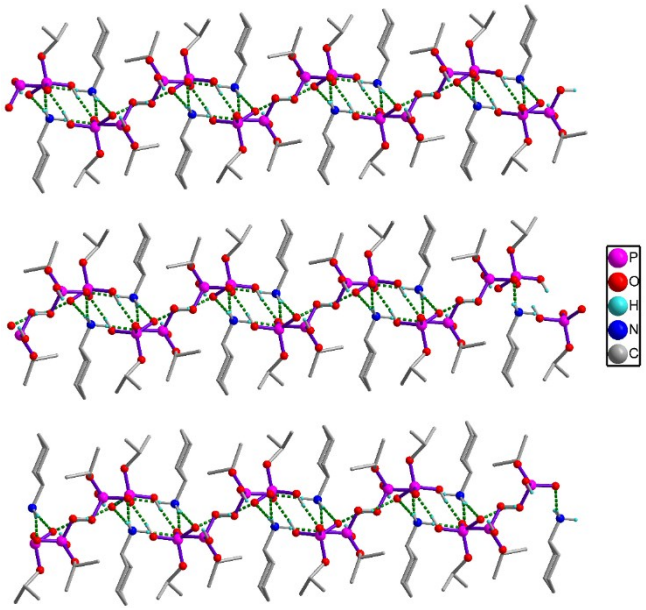

Figure S27: Hydrogen bonding interactions in **9**; represents the sheet formation due to extensive hydrogen bonding between the hydrogen atoms of cyclohexyl ammonium and $–OPO_3H$ units of teritiary butyl phosphate and OPO_3H_2 units of free isopropyl phosphate.

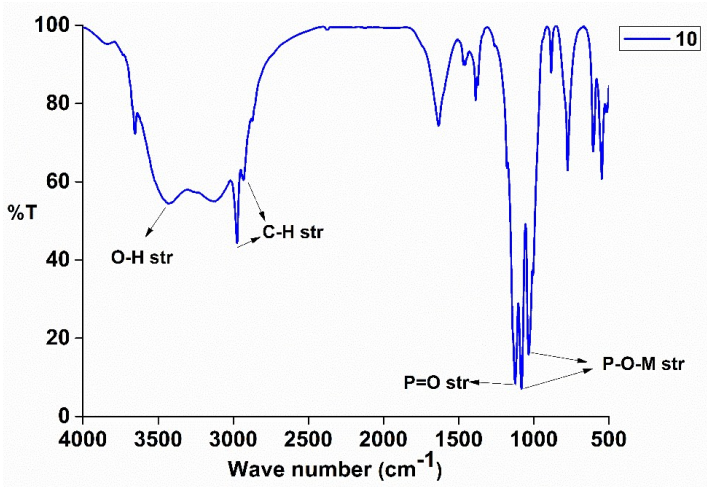

Figure S28. FT-IR spectrum of compound **10**

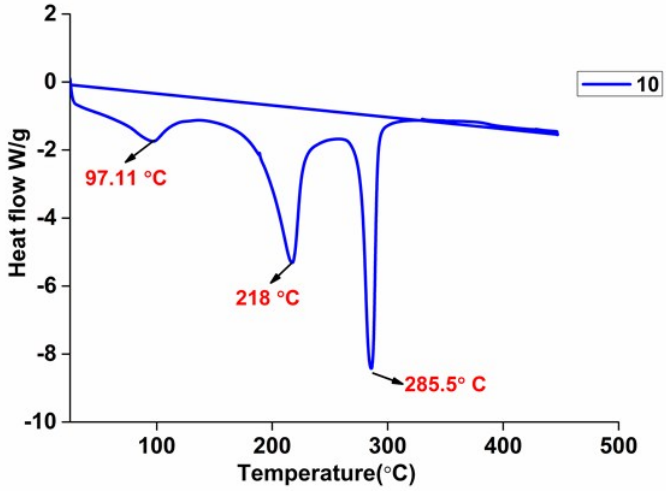

Figure S29. DSC trace of **10**

Morphological characterisation of 10

The SEM micrographs (Figure 14) viewed down two perpendicular directions underline the presence of large plates that are stacked over one another to form a lamellar structure (micrographs in Figure 14(a) - (d)). An EDX analysis of a section of this lamellar structure revealed uniform distribution of various elements with high homogeneity. While the formation of layered structures among metal phosphonates is very common,[44] metal mono organophosphates are often isolated as well-defined clusters.[47-49] Thus, compounds such as **10** can be exploited for the applications generally exhibited by layered phosphonates apart from them being also utilized for low-temperature synthesis of ceramic phosphates.

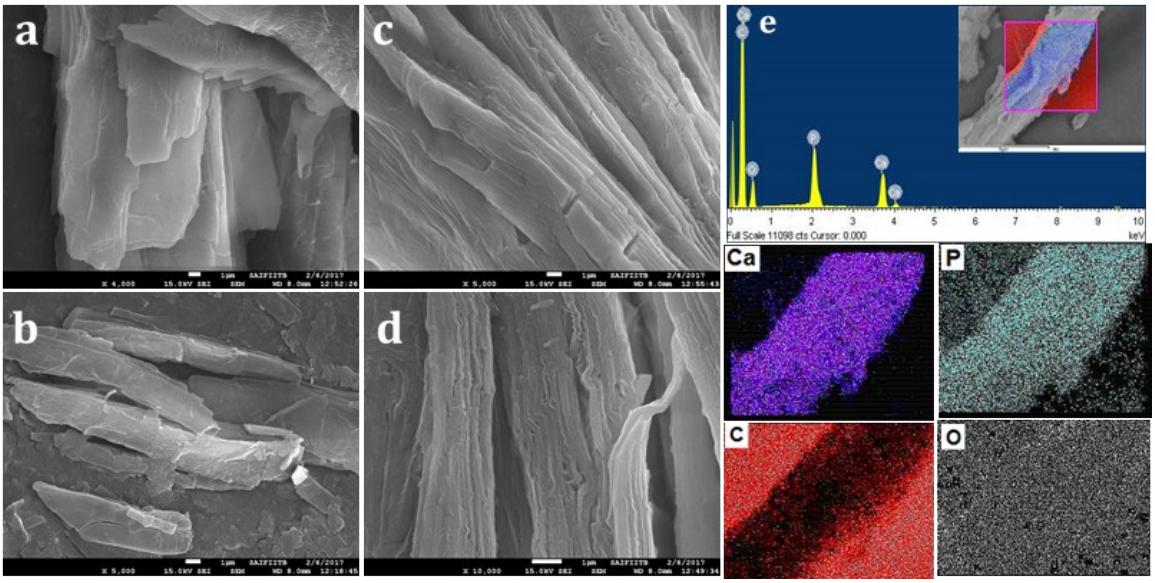

Figure S30. The SEM micrographs of **10** showing plate like crystals (at (a) 4000x and (b) 5000x magnification) that are stacked one over other to form lamellar structure (at (c) 5000x and (d) 10000x magnification); (e) EDX spectrum of **10** with elemental mapping.

Table S1: Hydrogen bond table for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(6)-H(6C)...O(3)#1	0.85	2.12	2.934(4)	161.2
O(6)-H(6D)...O(2)#2	0.85	2.01	2.850(4)	167.9
N(2)-H(2A)...O(2)	0.89	1.89	2.766(4)	167.8
N(2)-H(2B)...O(3)#3	0.89	2.01	2.884(4)	167.6
N(2)-H(2C)...O(3)#4	0.89	1.93	2.798(4)	165.2
N(1)-H(1A)...O(6)	0.89	1.94	2.814(4)	166.6
N(1)-H(1B)...O(5)#2	0.89	1.98	2.839(5)	161.6
N(1)-H(1C)...O(4)	0.89	1.96	2.850(4)	175.7
O(5)-H(5C)...O(4)	0.85	2.15	2.872(5)	143.0
O(5)-H(5D)...O(4)#1	0.85	2.06	2.835(5)	150.4
O(7)-H(7A)...O(4)#3	0.85	2.52	3.317(5)	155.9
O(7)-H(7A)...O(1)#3	0.85	2.46	3.173(5)	141.5
O(7)-H(7B)...O(2)	0.85	1.99	2.840(5)	174.3
C(8)-H(8A)...O(1)	0.97	2.64	3.603(5)	170.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z+1 #2 -x+1,-y+1,-z+1 #3 x,y-1,z
#4 -x+1,y-1/2,-z+3/2

Table S2: Hydrogen bond table for **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(4)#1	0.91	1.91	2.822(2)	177.0
N(1)-H(1B)...O(2)#2	0.91	1.88	2.786(2)	175.9
N(1)-H(1C)...O(2)	0.91	1.83	2.741(2)	173.9
O(3)-H(3)...O(4)#3	0.84	1.75	2.577(2)	168.0

Symmetry transformations used to generate equivalent atoms:
#1 x,y-1,z #2 -x+3/2,y-1/2,-z+3/2 #3 -x+3/2,-y+3/2,-z+1

Table S3: Hydrogen bond table for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(4)#1	0.84	1.72	2.544(6)	166.6
N(1)-H(1A)...O(3)	0.91	1.86	2.761(7)	170.1
N(1)-H(1B)...O(3)#2	0.91	1.82	2.720(7)	168.5
N(1)-H(1C)...O(4)#3	0.91	1.89	2.797(7)	176.6

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z #2 -x+1/2,y-1/2,-z+1/2 #3 -x+1/2,y+1/2,-z+1/2

Table S4: Hydrogen bond table for **4** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2A)...O(3)#1	0.96	2.62	3.551(5)	163.1
N(1)-H(1A)...O(4)#2	0.89	1.91	2.778(3)	165.4
N(1)-H(1B)...O(2)	0.89	1.94	2.822(3)	171.5
N(1)-H(1C)...O(2)#3	0.89	1.86	2.744(3)	174.8

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,-y+3/2,-z+1/2 #2 x,y+1,z #3 -x+1,y+1/2,-z+1/2
#4 -x+3/2,-y+1/2,-z+1/2

Table S5: Hydrogen bond table for **7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4)...O(2)#1	0.82(2)	1.77(2)	2.5837(15)	172(2)
O(3)-H(3)...O(2)#1	0.82(2)	1.77(2)	2.5854(14)	176(2)

Symmetry transformations used to generate equivalent atoms:
#1 y,-x+1/2,-z+5/2 #2 y,-x+1/2,-z+3/2

Table S6: Hydrogen bond table for **9** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(2)#1	0.84	1.75	2.591(3)	174.1
O(7)-H(7)...O(4)#2	0.84	1.75	2.531(3)	154.5
O(8)-H(8)...O(2)#3	0.84	1.95	2.532(3)	125.8
N(1)-H(1A)...O(4)#2	0.91	1.90	2.805(3)	173.2
N(1)-H(1B)...O(6)#2	0.91	1.99	2.868(3)	161.5
N(1)-H(1C)...O(6)#4	0.91	1.89	2.779(3)	166.3

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1 #2 -x+1/2,y+1/2,-z+1/2 #3 x,y+1,z
#4 x-1/2,-y+3/2,z-1/2