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

Gulzar A. Bhat, Alok Ch. Kalita and Ramaswamy Murugavel*

Figure S1. FT-IR spectra of compounds 1-4.

Figure S2. 1H NMR spectrum of compound 1 (D2O 500 MHz).

Figure S3. 1H NMR spectrum of compound 2 (D2O 500 MHz).

Figure S4. 1H NMR spectrum of compound 3 (D2O 500 MHz).

Figure S5. 1H NMR spectrum of compound 4 (D2O 500 MHz).

Figure S6: 13C NMR spectrum of compound 1 (D2O).

Figure S7: 13C NMR spectrum of compound 2 (D2O).

Figure S8: 13C NMR spectrum of compound 3 (DMSO-d6).

Figure S9: 13C NMR spectrum of compound 4 (D2O).

Figure S10: 31P NMR spectra of compounds 1-4 in (D2O).

Figure S11. FT-IR spectra of compounds 5-7 (in KBr diluted discs).

Figure S12. 1H NMR spectrum of compound 5 (D2O 500 MHz).

Figure S13. 1H NMR spectrum of compound 6 (D2O 500 MHz).

Figure S14. 1H NMR spectrum of compound 7 (DMSO-d6 500 MHz).

Figure S15. 1H NMR spectrum of compound 8 (DMSO-d6 500 MHz).

Figure S16: 13C NMR spectrum of compound 5 (DMSO-d6).

Figure S17: 13C NMR spectrum of compound 6 (CD3CN-d3).

Figure S18: 13C NMR spectrum of compound 7 (CD3CN-d3).

Figure S19: ESI-MS spectrum of compound 5 (reported in CH3CN).

Figure S20: ESI-MS spectrum of compound 7 (reported in CH3CN).

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

Figure S22: Molecular structure of 3 showing immediate hydrogen bonding 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 and –OPO$_{3}$H units, lattice H$_2$O molecules and OPO$_{3}$H 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$_{3}$H 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$_{3}$H units of tertiary 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$_{3}$H units of tertiary butyl phosphate and OPO$_{3}$H$_2$ 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$_2$O 500 MHz).

Figure S3. $^1$H NMR spectrum of compound 2 (D$_2$O 500 MHz).
Figure S4. $^1$H NMR spectrum of compound 3 (D$_2$O 500 MHz).

Figure S5. $^1$H NMR spectrum of compound 4 (D$_2$O 500 MHz).

Figure S6: $^{13}$C NMR spectrum of compound 1 (D$_2$O)
Figure S7: $^{13}$C NMR spectrum of compound 2 (D$_2$O)

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

Figure S9: $^{13}$C NMR spectrum of compound 4 (D$_2$O)
Figure S10: $^{31}$P NMR spectra of compounds 1-4 in (D$_2$O).

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$_2$O 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$_3$CN-d$_3$)

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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$_2$O molecules and OPO$_3$H 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$_3$H 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$_3$H units of tertiary 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$_3$H units of tertiary butyl phosphate and OPO$_3$H$_2$ 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, metal monoorganophosphates are often isolated as well-defined clusters. 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 °].

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

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 °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-H(1A)...O(4)#1</td>
<td>0.91</td>
<td>1.91</td>
<td>2.822(2)</td>
<td>177.0</td>
</tr>
<tr>
<td>N(1)-H(1B)...O(2)#2</td>
<td>0.91</td>
<td>1.88</td>
<td>2.786(2)</td>
<td>175.9</td>
</tr>
<tr>
<td>N(1)-H(1C)...O(2)</td>
<td>0.91</td>
<td>1.83</td>
<td>2.741(2)</td>
<td>173.9</td>
</tr>
<tr>
<td>O(3)-H(3)...O(4)#3</td>
<td>0.84</td>
<td>1.75</td>
<td>2.577(2)</td>
<td>168.0</td>
</tr>
</tbody>
</table>

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 °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(2)-H(2)...O(4)#1</td>
<td>0.84</td>
<td>1.72</td>
<td>2.544(6)</td>
<td>166.6</td>
</tr>
<tr>
<td>N(1)-H(1A)...O(3)</td>
<td>0.91</td>
<td>1.86</td>
<td>2.761(7)</td>
<td>170.1</td>
</tr>
<tr>
<td>N(1)-H(1B)...O(3)#2</td>
<td>0.91</td>
<td>1.82</td>
<td>2.720(7)</td>
<td>168.5</td>
</tr>
<tr>
<td>N(1)-H(1C)...O(4)#3</td>
<td>0.91</td>
<td>1.89</td>
<td>2.797(7)</td>
<td>176.6</td>
</tr>
</tbody>
</table>

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 °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2)-H(2A)...O(3)#1</td>
<td>0.96</td>
<td>2.62</td>
<td>3.551(5)</td>
<td>163.1</td>
</tr>
<tr>
<td>N(1)-H(1A)...O(4)#2</td>
<td>0.89</td>
<td>1.91</td>
<td>2.778(3)</td>
<td>171.5</td>
</tr>
<tr>
<td>N(1)-H(1B)...O(2)</td>
<td>0.89</td>
<td>1.94</td>
<td>2.822(3)</td>
<td>174.8</td>
</tr>
<tr>
<td>N(1)-H(1C)...O(2)#3</td>
<td>0.89</td>
<td>1.86</td>
<td>2.744(3)</td>
<td>174.8</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(4)-H(4)...O(2)#1</td>
<td>0.82(2)</td>
<td>1.77(2)</td>
<td>2.5387(15)</td>
<td>172(2)</td>
</tr>
<tr>
<td>O(3)-H(3)...O(2)#1</td>
<td>0.82(2)</td>
<td>1.77(2)</td>
<td>2.5854(14)</td>
<td>176(2)</td>
</tr>
</tbody>
</table>

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 °].

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>d(D-H)</th>
<th>d(H...A)</th>
<th>d(D...A)</th>
<th>&lt;(DHA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(3)-H(3)...O(2)#1</td>
<td>0.84</td>
<td>1.75</td>
<td>2.591(3)</td>
<td>174.1</td>
</tr>
<tr>
<td>O(7)-H(7)...O(4)#2</td>
<td>0.84</td>
<td>1.75</td>
<td>2.531(3)</td>
<td>154.5</td>
</tr>
<tr>
<td>O(8)-H(8)...O(2)#3</td>
<td>0.84</td>
<td>1.95</td>
<td>2.532(3)</td>
<td>125.8</td>
</tr>
<tr>
<td>N(1)-H(1A)...O(4)#2</td>
<td>0.91</td>
<td>1.90</td>
<td>2.805(3)</td>
<td>173.2</td>
</tr>
<tr>
<td>N(1)-H(1B)...O(6)#2</td>
<td>0.91</td>
<td>1.99</td>
<td>2.868(3)</td>
<td>161.5</td>
</tr>
<tr>
<td>N(1)-H(1C)...O(6)#4</td>
<td>0.91</td>
<td>1.89</td>
<td>2.779(3)</td>
<td>166.3</td>
</tr>
</tbody>
</table>

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