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Electronic Supplementary Information

Amine templated open-framework vanadium(III) phosphites with catalytic properties

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(S1) Structure refinement

During the structural resolution of the compound **4**, 3 and 4 eÅ^3 peaks around some vanadium atoms appeared in the difference electron-density map and it was not possible to find the carbon and nitrogen atoms of the organic cation. Moreover, the values of the residual w$R2 \approx 0.6$ and the parameter $y \approx 1000$ of the weight factor, were unusually big for this step of the structural resolution. So, the PLATON program[1] was used in order to analyze the possible errors in the structural resolution. In this way, the TWINROTMAT option suggested the existence of a merohedric twin by 180° rotation around the [110] reciprocal lattice direction, in agreement with the twin's law expressed by the [010, 100, 00-1] matrix. The use of this matrix in the refinement procedure, allowed us to locate the positions of the carbon and nitrogen atoms of the cycloheptylamine molecule. After the refinement, the masses of the two components of the twin were found to have percentages of 53.8(2) and 46.2(2).

For compound **1**, the hydrogen positions of the phosphite groups and those related to the coordinated water molecule could be identified from the difference Fourier maps. For the final refinement, the hydrogen atom of the P(2)-H(2) bond were restrained to 1.35(1) Å and those related to the coordinated water molecule were placed in geometrically ideal positions (O(6W)-H(6A,B): 0.85(1) Å; H(6A)-H(6B): 1.35(2) Å) and refined using the riding mode. Hydrogen atoms of amine molecules were fixed geometrically and allowed to ride on their parent C and N atoms (C(1)–H: 0.98 Å, C(2)–H: 0.97 Å, C(3)–H: 0.96 Å, N–H: 0.90 Å, $U_{iso}(H) = 1.2U_{eq}(C(1,2), N)$ Å^2; $1.5U_{eq}(C(3)$ Å^2). Anisotropic thermal parameters were used for all non-hydrogen atoms.

For compound **2**, phosphite-hydrogenphosphate, $(HPO_3)^{2-}$-$(HPO_4)^{2-}$ substitutions were deduced from subsequent Fourier-difference map calculations as well as from the electroneutrality considerations. To that effect too big values of the electron-densities and of the P-Q distances for apical hydrogen and too small values for oxygen were observed. After the final refinement of the occupation factors, the following disordered systems $(HP(1)O_3)_{0.78(2)}(HP(1)O_4)_{0.22(2)}$, $(HP(2)O_3)_{0.72(2)}(HP(2)O_4)_{0.28(2)}$, $(HP(3)O_3)_{0.25(4)}(HP(3)O_4)_{0.08(4)}$ were calculated. In addition for this compound, due to the high rotational freedom presented by the tetrahedra in the P(4) site, the P(4) phosphorous atom was disordered in two positions with occupation factors of 0.72(2) and 0.28(2). For compound **3**, using the same criteria of electron-densities, P-Q

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[1] A. L. Spek, *PLATON94: Program for the Automated Analysis of Molecular Geometry*, University of Utrecth, The Netherlands, 1994.

distances and electroneutrality, the dihydrogenphosphate-dihydrogenphosphite replacement with $(H_2P(4)O_3)_{0.40(3)}(H_2P(4)O_4)_{0.10(3)}$ formula was calculated. For compound **4**, no disorders were observed.

The protons corresponding to the OH- groups of the different tetrahedra were geometrically placed. H- and OH- groups implicated in the different anionic phosphorous groups replacements were treated as disordered ones with complementary occupation factors. In order to model correctly the disorder systems, P-H and P-O bonds corresponding to H- and OH- disordered groups were restrained to the ideal values (1.30(1) Å and 1.50(1) Å, respectively). Moreover, in order to maintain the geometry of each $(HPO_3)^{2-}$ and $(H_2PO_3)^{1-}$ group, the three distances of the apical hydrogen atoms to their corresponding oxygen atoms forming the pseudotetrahedra base were refined as a variable.

For compound **2**, the carbon ring belonging to the cyclopentylamonium template is completely disordered in two positions, showing the existence of two different conformers at low temperature. After the refinement, the occupancy factors of the conformers were 0.40(2)/0.27(2). In order to maintain the pentagonal geometry of the two conformer rings, both C-N and C-C distances were restrained to 1.45(1) Å, and the distance between no consecutive carbon atoms to 2.24(3) Å. In addition, equal isotropic thermal displacements were used for the carbon atoms of each two conformer rings. For compounds **3** and **4**, in order to maintain the geometry of the rings of cyclohexylamonium and cycloheptylamonium molecules, the C-N and C-C bonds were restrained to 1.50(1) Å and 1.51(2) Å, respectively.

For compounds **3** and **4**, three electronic density peaks corresponding to oxygen atoms belonging to crystallization water molecules (Occ. O(W1) = 0.30; Occ. O(W2) = 0.20; Occ. O(W3) = 0.055) were located in the difference density map. Their occupancies were refined until their isotropic thermal parameters values were of a similar order. O(W1) and O(W2) water molecules and cyclohexylamonium and cycloheptylamonium molecules are too close, giving rise to disorder systems. The hydrogen atoms attached to the crystallization water molecules were not located. Although hydronium cations and water molecules cannot be distinguished in the X-ray refinement, for charge balance, an additional proton should be distributed over one crystallization water with site occupancy of 1/6.

For the final refinement of compounds **2**, **3** and **4** the hydrogen atoms related to the coordinated water molecules were first located and placed in geometrically ideal positions (O(6W)-H(6A,B): 0.85(1) Å; H(6A)-H(6B): 1.35(2) Å) and refined using the riding mode. Hydrogen atoms of amine molecules were fixed geometrically and allowed to ride on their parent C and N atoms (C–H: 0.98, 0.97 Å, N–H: 0.89 Å, $U_{iso}(H) = 1.2U_{eq}(C)$ Å^2; $1.5U_{eq}(N)$ Å^2). Isotropic thermal displacements were used for carbon and nitrogen atoms. Anisotropic thermal parameters were used for all the atoms belonging to the inorganic framework except for the hydrogen atoms and, the oxygen atoms implicated in the $(HPO_3)^{2-}$-$(HPO_4)^{2-}$ and $(H_2PO_3)^{1-}$-$(H_2PO_4)^{1-}$ disorder systems.

Table S1.1. Bond distances (Å) and angles (°) for **1**.

Octahedron [V(1)O$_6$]

V(1)	**O(3)^{iii}**	**O(3)**	**O(1)**	**O(1)^{iii}**	**O(2)**	**O(2)^{iii}**
O(2)^{iii}	93.39(7)	86.61(7)	92.47(7)	87.52(7)	180.00	***2.043(2)***
O(2)	86.61(7)	93.39(7)	87.52(7)	92.47(7)	***2.043(2)***	
O(1)^{iii}	90.56(7)	89.44(7)	180.00	***1.994(2)***		
O(1)	89.44(7)	90.56(7)	***1.994(2)***			
O(3)	180.00	***1.986(2)***				
O(3)^{iii}	***1.986(2)***					

Octahedron [V(2)O$_4$(H$_2$O)$_2$]

V(2)	**O(5)^{vi}**	**O(5)^{v}**	**O(4)^{iv}**	**O(4)**	**O(6W)**	**O(6W)^{iv}**
O(6W)^{iv}	90.56(7)	89.44(7)	91.68(7)	88.32(7)	180.00	***2.075(2)***
O(6W)	89.44(7)	90.56(7)	88.32(7)	91.68(7)	***2.074(2)***	
O(4)	90.02(7)	89.98(7)	180.00	***1.972(2)***		
O(4)^{iv}	89.98(7)	90.02(7)	***1.972(2)***			
O(5)^{v}	180.00	***1.965(2)***				
O(5)^{vi}	***1.965(2)***					

Piramid [HP(1)O$_3$]

P(1)	**O(7)**	**O(1)**	**O(3)^{ii}**	**H(1P)**
H(1P)	99(1)	112(1)	113(1)	***1.27(3)***
O(3)^{ii}	111.5(1)	111.6(1)	***1.526(2)***	
O(1)	109.8(1)	***1.525(2)***		
O(7)	***1.495(2)***			

Piramid [HP(2)O$_3$]

P(2)	**O(4)**	**O(5)**	**O(2)**	**H(2P)**
H(2P)	104(1)	105.5(1)	111(1)	***1.37(1)***
O(2)	113.3(1)	111.2(1)	***1.524(2)***	
O(5)	112.0(1)	***1.517(2)***		
O(4)	***1.514(2)***			

Simmetry codes: *i* = x+1, y, z; *ii* = -x+2, -y+1, -z+1; *iii* = -x+1, -y+1, -z+1; *iv* = -x, -y, -z+1; *v* = x-1, y, z; *vi* = -x+1, -y, -z+1; *vii* = -x+1, -y+1, -z+2.

Table S1.1. (Continuation).

2-methylpiperazonium cation

N(1)	**C(2)**	**C(1)**	**H(0A)**	**H(0B)**
H0B	108.91	108.91	107.74	0.90
H0A	108.91	108.91	0.90	
C(1)	113.3(3)	***1.484(6)***		
C(2)	***1.466(7)***			

C(1)	**C(3)**	**N(1)**	**C(2)^{vii}**	**H(1)**
H(1)	108.58	108.58	108.58	0.98
C(2)^{vii}	113.0(6)	110.1(4)	***1.515(5)***	
N(1)	108.0(5)	***1.484(6)***		
C(3)	***1.32(1)***			

C(2)	**N(1)**	**C(1)^{vii}**	**H(2A)**	**H(2B)**
H(2B)	109.94	109.94	108.33	0.97
H(2A)	109.94	109.94	0.97	
C(1)^{vii}	108.8(4)	***1.515(5)***		
N(1)	***1.466(7)***			

C(3)	**C(1)**	**H(3A)**	**H(3B)**	**H(3C)**
H(3C)	109.47	109.47	109.47	0.96
H(3B)	109.47	109.47	0.96	
H(3A)	109.47	0.96		
C(1)	***1.32(1)***			

Table S1.2. Bond distances (Å) and angles (°) for **2**.

Octahedron [V(1)O$_6$]

V(1)	**O(9)^{vi}**	**O(9)**	**O(9)^{vii}**	**O(9)^{iv}**	**O(9)^{viii}**	**O(9)^{ii}**
O(9)^{ii}	180.00	87.8(1)	180.00	92.2(1)	92.2(1)	***2.014(3)***
O(9)^{viii}	87.8(1)	180.00	87.8(1)	92.2(1)	***2.014(3)***	
O(9)^{iv}	87.8(1)	87.8(1)	180.00	***2.014(3)***		
O(9)^{vii}	92.2(1)	92.2(1)	***2.014(3)***			
O(9)	92.2(1)	***2.014(3)***				
O(9)^{vi}	***2.014(3)***					

Octahedron [V(2)O$_5$(H$_2$O)]

V(2)	**O(2)^{i}**	**O(5)**	**O(4)**	**O(3)^{iv}**	**O(1)**	**O(6)**
O(6)	85.1(1)	179.4(1)	85.7(1)	92.5(1)	86.0(1)	***2.088(3)***
O(1)	88.7(1)	93.5(1)	85.7(1)	177.9(1)	***2.001(3)***	
O(3)^{iv}	92.7(1)	88.0(1)	92.8(1)	***2.000(3)***		
O(4)	171.1(1)	92.5(1)	***1.985(3)***			
O(5)	94.7(1)	***1.975(3)***				
O(2)^{i}	***1.967(3)***					

Octahedron [V(3)O$_6$]

V(3)	**O(8)^{vii}**	**O(8)**	**O(8)^{vi}**	**O(7)**	**O(7)^{vi}**	**O(7)^{vii}**
O(7)^{vii}	89.8(1)	87.5(1)	177.5(1)	92.8(2)	92.8(2)	***1.999(4)***
O(7)^{vi}	87.5(1)	177.5(1)	89.8(1)	92.8(2)	***1.999(4)***	
O(7)	177.5(2)	89.8(1)	87.5(1)	***1.999(4)***		
O(8)^{vi}	89.9(1)	89.9(1)	***1.998(3)***			
O(8)	89.9(1)	***1.998(3)***				
O(8)^{vii}	***1.998(3)***					

Table S1.2. (Continuation).

Piramid HP(1)O$_3$ / Pseudotetrahedron HP(1)O$_4$

P(1)	**O(1')**	**O(8)**	**O(4)**	**O(9)**	**H(1)**
H(1)	3(2)	108(1)	107(1)	106(1)	***1.30(1)***
O(9)	106.6(7)	114.5(2)	112.1(2)	***1.534(3)***	
O(4)	109.7(7)	108.5(2)	***1.525(3)***		
O(8)	105.1(7)	***1.515(3)***			
O(1')	***1.509(9)***				

O(1´)-H(1´)	0.82 Å
O(1´)-P(1)-H(1´)	109.47°

Piramid HP(2)O$_3$ / Pseudotetrahedron HP(2)O$_4$

P(2)	**O(2')**	**O(2)**	**O(3)**	**O(1)**	**H(2)**
H(2)	2(1)	107(1)	107(1)	107(1)	***1.30(1)***
O(1)	108.9(5)	112.8(2)	110.4(2)	***1.521(3)***	
O(3)	106.8(5)	112.7(2)	***1.518(3)***		
O(2)	104.9(5)	***1.515(3)***			
O(2')	***1.528(8)***				

O(2´)-H(2´)	0.82 Å
O(2´)-P(2)-H(2´)	109.47°

Piramid HP(3)O$_3$ / Pseudotetrahedron HP(3)O$_4$

P(3)	**O(3')**	**O(5)**	**O(5)^{iii}**	**O(5)^{i}**	**H(3)**
H(3)	0(0)	104.8(1)	104.8(1)	104.8(1)	***1.30(1)***
O(5)^{i}	104.8(1)	113.7(1)	113.7(1)	***1.514(3)***	
O(5)^{iii}	104.8(1)	113.7(1)	***1.514(3)***		
O(5)	104.8(1)	***1.514(3)***			
O(3')	***1.50(1)***				

O(3´)-H(3´)	0.82 Å
O(3´)-P(3)-H(3´)	109.47°

Pseudotetrahedron H$_2$P(4A)O$_4$

P(4A)	**O(7)^{v}**	**O(7)**	**O(10)**	**O(11A)**
O(11A)	113.0(4)	113.0(4)	96(1)	***1.55(2)***
O(10)	108.7(4)	108.7(4)	***1.52(1)***	
O(7)	115.6(4)	***1.486(4)***		
O(7)^{v}	***1.486(4)***			

O(10)-H(10A)	0.82 Å
O(10)-P(4A)-H(10A)	109.47°
O(11A)-H(11A)	0.82 Å
O(11A)-P(4A)-H(11A)	109.47°

Pseudotetrahedron H$_2$P(4B)O$_4$

P(4B)	**O(7)**	**O(7)^{v}**	**O(10)**	**O(11B)**
O(11B)	107(1)	107(1)	101(2)	***1.65(4)***
O(10)	110.1(9)	110.1(9)	***1.52(2)***	
O(7)^{v}	119.6(8)	***1.455(7)***		
O(7)	***1.455(7)***			

O(10)-H(10B)	0.82 Å
O(10)-P(4B)-H(10B)	109.47°
O(11B)-H(11B)	0.82 Å
O(11B)-P(4B)-H(11B)	109.47°

Table S1.2. (Continuation).

Cyclopentylammonium cation

N(1)	**C(1A)**	**C(1B)**	**H(1A)**	**H(1B)**	**H(1C)**
H(1C)	109.47	94.23	109.47	109.47	0.89
H(1B)	109.47	122.62	109.47	0.89	
H(1A)	109.47	110.21	0.89		
C(1B)	17(2)	***1.45(1)***			
C(1A)	***1.43(1)***				

C(1A)	**N(1)**	**C(2A)**	**C(3A)**	**H(1A1)**
H(1A1)	117.22	117.22	117.22	0.98
C(3A)	98(1)	105(1)	***1.46(1)***	
C(2A)	99(1)	***1.45(1)***		
N(1)	***1.43(1)***			

C(1B)	**N(1)**	**C(2B)**	**C(3B)**	**H(1B1)**
H(1B1)	114.32	114.32	114.32	0.98
C(3B)	102(2)	104(1)	***1.45(1)***	
C(2B)	107(2)	***1.45(1)***		
N(1)	***1.45(1)***			

C(2A)	**C(4A)**	**C(1A)**	**H(2A1)**	**H(2A2)**
H(2A2)	111.30	111.30	109.19	0.97
H(2A1)	111.30	111.30	0.97	
C(1A)	102(1)	***1.45(1)***		
C(4A)	***1.44(1)***			

C(2B)	**C(4B)**	**C(1B)**	**H(2B1)**	**H(2B2)**
H(2B2)	111.20	111.20	109.12	0.97
H(2B1)	111.20	111.20	0.97	
C(1B)	103(2)	***1.45(1)***		
C(4B)	***1.46(1)***			

C(3A)	**C(5A)**	**C(1A)**	**H(3A1)**	**H(3A2)**
H(3A2)	110.51	110.51	108.68	0.97
H(3A1)	110.51	110.51	0.97	
C(1A)	106(1)	***1.46(1)***		
C(5A)	***1.44(1)***			

C(3B)	**C(5B)**	**C(1B)**	**H(3B1)**	**H(3B2)**
H(3B2)	110.65	110.65	108.77	0.97
H(3B1)	110.65	110.65	0.97	
C(1B)	105(1)	***1.45(1)***		
C(5B)	***1.45(1)***			

C(4A)	**C(2A)**	**C(5A)**	**H(4A1)**	**H(4A2)**
H(4A2)	110.19	110.19	108.49	0.97
H(4A1)	110.19	110.19	0.97	
C(5A)	108(1)	***1.44(1)***		
C(2A)	***1.44(1)***			

C(4B)	**C(5B)**	**C(2B)**	**H(4B1)**	**H(4B2)**
H(4B2)	112.06	112.06	109.71	0.97
H(4B1)	112.06	112.06	0.97	
C(2B)	99(2)	***1.46(1)***		
C(5B)	***1.44(1)***			

C(5A)	**C(4A)**	**C(3A)**	**H(5A1)**	**H(5A2)**
H(5A2)	110.56	110.56	108.71	0.97
H(5A1)	110.56	110.56	0.97	
C(3A)	106(1)	***1.44(1)***		
C(4A)	***1.44(1)***			

C(5B)	**C(4B)**	**C(3B)**	**H(5B1)**	**H(5B2)**
H(5B2)	110.60	110.60	108.74	0.97
H(5B1)	110.60	110.60	0.97	
C(3B)	106(2)	***1.45(1)***		
C(4B)	***1.44(1)***			

Symmetry codes: *i* = -x+y, -x+1, z; *ii* = y-1, -x+y, -z+1; *iii* = -y+1, x-y+1, z; *iv* = x-y+1, x+1, -z+1; *v* = x, y, -z+3/2; *vi* = -y+1, x-y+2, z; *vii* = -x+y-1, -x+1, z; *viii* = -x, -y+2, -z+1.

Table S1.2. (Continuation).

Cyclopentylammonium cation

N(1)	**C(1A)**	**C(1B)**	**H(1A)**	**H(1B)**	**H(1C)**
H(1C)	109.47	94.23	109.47	109.47	0.89
H(1B)	109.47	122.62	109.47	0.89	
H(1A)	109.47	110.21	0.89		
C(1B)	17(2)	***1.45(1)***			
C(1A)	***1.43(1)***				

C(1A)	**N(1)**	**C(2A)**	**C(3A)**	**H(1A1)**
H(1A1)	117.22	117.22	117.22	0.98
C(3A)	98(1)	105(1)	***1.46(1)***	
C(2A)	99(1)	***1.45(1)***		
N(1)	***1.43(1)***			

C(1B)	**N(1)**	**C(2B)**	**C(3B)**	**H(1B1)**
H(1B1)	114.32	114.32	114.32	0.98
C(3B)	102(2)	104(1)	***1.45(1)***	
C(2B)	107(2)	***1.45(1)***		
N(1)	***1.45(1)***			

C(2A)	**C(4A)**	**C(1A)**	**H(2A1)**	**H(2A2)**
H(2A2)	111.30	111.30	109.19	0.97
H(2A1)	111.30	111.30	0.97	
C(1A)	102(1)	***1.45(1)***		
C(4A)	***1.44(1)***			

C(2B)	**C(4B)**	**C(1B)**	**H(2B1)**	**H(2B2)**
H(2B2)	111.20	111.20	109.12	0.97
H(2B1)	111.20	111.20	0.97	
C(1B)	103(2)	***1.45(1)***		
C(4B)	***1.46(1)***			

C(3A)	**C(5A)**	**C(1A)**	**H(3A1)**	**H(3A2)**
H(3A2)	110.51	110.51	108.68	0.97
H(3A1)	110.51	110.51	0.97	
C(1A)	106(1)	***1.46(1)***		
C(5A)	***1.44(1)***			

C(3B)	**C(5B)**	**C(1B)**	**H(3B1)**	**H(3B2)**
H(3B2)	110.65	110.65	108.77	0.97
H(3B1)	110.65	110.65	0.97	
C(1B)	105(1)	***1.45(1)***		
C(5B)	***1.45(1)***			

C(4A)	**C(2A)**	**C(5A)**	**H(4A1)**	**H(4A2)**
H(4A2)	110.19	110.19	108.49	0.97
H(4A1)	110.19	110.19	0.97	
C(5A)	108(1)	***1.44(1)***		
C(2A)	***1.44(1)***			

C(4B)	**C(5B)**	**C(2B)**	**H(4B1)**	**H(4B2)**
H(4B2)	112.06	112.06	109.71	0.97
H(4B1)	112.06	112.06	0.97	
C(2B)	99(2)	***1.46(1)***		
C(5B)	***1.44(1)***			

C(5A)	**C(4A)**	**C(3A)**	**H(5A1)**	**H(5A2)**
H(5A2)	110.56	110.56	108.71	0.97
H(5A1)	110.56	110.56	0.97	
C(3A)	106(1)	***1.44(1)***		
C(4A)	***1.44(1)***			

C(5B)	**C(4B)**	**C(3B)**	**H(5B1)**	**H(5B2)**
H(5B2)	110.60	110.60	108.74	0.97
H(5B1)	110.60	110.60	0.97	
C(3B)	106(2)	***1.45(1)***		
C(4B)	***1.44(1)***			

Symmetry codes: *i* = -x+y, -x+1, z; *ii* = y-1, -x+y, -z+1; *iii* = -y+1, x-y+1, z; *iv* = x-y+1, x+1, -z+1; *v* = x, y, -z+3/2; *vi* = -y+1, x-y+2, z; *vii* = -x+y-1, -x+1, z; *viii* = -x, -y+2, -z+1.

Table S1.3. Bond distances (Å) and angles (°) for **3**.

Octahedron [V(1)O$_6$]

V(1)	**O(9)^{vii}**	**O(9)**	**O(9)^{viii}**	**O(9)^{v}**	**O(9)^{ix}**	**O(9)^{ii}**
O(9)^{ii}	180.00	88.0(1)	88.0(1)	92.0(1)	92.0(1)	***2.023(3)***
O(9)^{ix}	88.0(1)	180.00	88.0(1)	92.0(1)	***2.023(3)***	
O(9)^{v}	88.0(1)	88.0(1)	180.00	***2.023(2)***		
O(9)^{viii}	92.0(1)	92.0(1)	***2.023(2)***			
O(9)	92.0(1)	***2.023(2)***				
O(9)^{vii}	***2.023(2)***					

Octahedron [V(2)O$_5$(H$_2$O)]

V(2)	**O(2)^{iv}**	**O(5)**	**O(4)**	**O(3)^{v}**	**O(1)**	**O(6)**
O(6)	85.4(1)	179.4(1)	88.0(1)	92.5(1)	86.1(1)	***2.101(3)***
O(1)	88.6(1)	93.5(1)	85.4(1)	177.7(1)	***2.001(3)***	
O(3)^{v}	93.2(1)	88.0(1)	92.7(1)	***1.997(3)***		
O(4)	171.3(1)	92.4(1)	***1.993(3)***			
O(5)	94.2(1)	***1.984(3)***				
O(2)^{iv}	***1.971(3)***					

Octahedron [V(3)O$_6$]

V(3)	**O(8)**	**O(8)^{vii}**	**O(8)^{viii}**	**O(7)**	**O(7)^{vii}**	**O(7)^{viii}**
O(7)^{vii}	86.9(1)	90.9(1)	177.1(1)	91.8(1)	91.8(1)	***2.006(3)***
O(7)^{viii}	90.9(1)	177.1(1)	86.9(1)	91.8(1)	***2.006(3)***	
O(7)	177.1(1)	86.9(1)	90.9(1)	***2.006(3)***		
O(8)	90.5(1)	90.5(1)	***2.006(3)***			
O(8)^{vii}	90.5(1)	***2.006(3)***				
O(8)^{viii}	***2.006(3)***					

Table S1.3. (Continuation).

Piramid [HP(1)O_3]

P(1)	**O(8)**	**O(4)**	**O(9)**	**H(1)**
H(1)	108(2)	107(2)	107(2)	***1.36(4)***
O(9)	114.6(2)	112.7(2)	***1.530(3)***	
O(4)	108.3(2)	***1.527(3)***		
O(8)	***1.514(3)***			

Piramid [HP(2)O_3]

P(2)	**O(2)**	**O(1)**	**O(3)**	**H(2)**
H(2)	102(2)	110(2)	108(2)	***1.31(4)***
O(3)	112.5(2)	109.7(2)	***1.523(3)***	
O(1)	113.6(2)	***1.521(3)***		
O(2)	***1.507(3)***			

Piramid [HP(3)O_3]

P(3)	**O(5)**	**O(5)^{i}**	**O(5)^{iv}**	**H(3)**
H(3)	103.8(2)	103.8(2)	103.8(2)	***1.30(1)***
O(5)^{iv}	114.5(1)	114.5(1)	***1.528(3)***	
O(5)^{i}	114.5(1)	***1.528(3)***		
O(5)	***1.528(3)***			

Piramid $H_2P(4)O_3$ / Pseudotetrahedron $H_2P(4)O_4$

P(4)	**O(4')**	**O(7)**	**O(7)^{vi}**	**O(10)**	**H(4)**
H(4)	**11(2)**	108.0(6)	108.0(6)	106(1)	***1.30(1)***
O(10)	95(2)	108.9(2)	108.9(2)	***1.513(7)***	
O(7)^{vi}	112.6(6)	116.5(3)	***1.482(3)***		
O(7)	112.6(6)	***1.482(3)***			
O(4')	***1.51(1)***				

O(4')-H(4')	0.82 Å
O(4')-P(4)-H(4')	109.47º
O(10)-H(10)	0.82 Å
O(10)-P(4)-H(10)	109.47º

Table S1.3. (Continuation).

Cyclohexylammonium cation

N(1)	**C(1)**	**H(1A)**	**H(1B)**	**H(1C)**
H(1C)	109.47	109.47	109.47	0.89
H(1B)	109.47	109.47	0.89	
H(1A)	109.47	0.89		
C(1)	***1.485(9)***			

C(1)	**N(1)**	**C(2)**	**C(3)**	**H(11)**
H(11)	108.04	108.04	108.04	0.98
C(3)	110(1)	115(1)	***1.54(1)***	
C(2)	109(1)	***1.53(2)***		
N(1)	***1.485(9)***			

C(2)	**C(1)**	**C(4)**	**H(2A)**	**H(2B)**
H(2B)	109.84	109.84	108.27	0.97
H(2A)	109.84	109.84	0.97	
C(4)	109(2)	***1.55(2)***		
C(1)	***1.53(2)***			

C(3)	**C(5)**	**C(1)**	**H(3A)**	**H(3B)**
H(3B)	108.31	108.31	107.41	0.97
H(3A)	108.31	108.31	0.97	
C(1)	116(1)	***1.54(1)***		
C(5)	***1.51(2)***			

C(4)	**C(6)**	**C(2)**	**H(4A)**	**H(4B)**
H(4B)	109.53	109.53	108.09	0.97
H(4A)	109.53	109.53	0.97	
C(2)	111(2)	***1.55(2)***		
C(6)	***1.54(2)***			

C(5)	**C(3)**	**C(6)**	**H(5A)**	**H(5B)**
H(5B)	109.43	109.43	107.98	0.97
H(5A)	109.43	109.43	0.97	
C(6)	111(2)	***1.54(2)***		
C(3)	***1.51(2)***			

C(6)	**C(4)**	**C(5)**	**H(6A)**	**H(6B)**
H(6B)	108.84	108.84	107.70	0.97
H(6A)	108.84	108.84	0.97	
C(5)	114(2)	***1.54(2)***		
C(4)	***1.54(2)***			

Simmetry codes: *i* = -y+1, x-y+1, z; *ii* = y-1, -x+y, -z+1; *iii* = x, y, -z+1/2; *iv* = -x+y, -x+1, z;
v = x-y+1, x+1, -z+1; *vi* = x, y, -z+3/2; *vii* = -y+1, x-y+2, z; *viii* = -x+y-1, -x+1, z;
ix = -x, -y+2, -z+1.

Table S1.4. Bond distances (Å) and angles (°) for **4**.

Octahedron [V(1)O$_6$]

V(1)	**O(9)^{viii}**	**O(9)**	**O(9)^{vi}**	**O(9)^{iv}**	**O(9)^{ii}**	**O(9)^{vii}**
O(9)^{vii}	88.2(1)	91.8(1)	91.8(1)	180.00	88.2(1)	***2.016(3)***
O(9)^{ii}	91.8(1)	88.2(1)	180.00	91.8(1)	***2.016(3)***	
O(9)^{iv}	91.8(1)	88.2(1)	88.2(1)	***2.016(3)***		
O(9)^{vi}	88.2(1)	91.8(1)	***2.016(3)***			
O(9)	180.00	***2.016(3)***				
O(9)^{viii}	***2.016(3)***					

Octahedron [V(2)O$_5$(H$_2$O)]

V(2)	**O(5)**	**O(2)^{iii}**	**O(4)**	**O(3)^{iv}**	**O(1)**	**O(6)**
O(6)	179.5(1)	84.9(1)	87.2(1)	91.9(1)	86.2(1)	***2.102(3)***
O(1)	94.0(2)	88.6(1)	85.2(1)	177.4(1)	***1.998(3)***	
O(3)^{iv}	87.9(2)	93.1(1)	92.8(1)	***1.997(3)***		
O(4)	93.3(1)	170.3(1)	***1.993(3)***			
O(2)^{iii}	94.6(2)	***1.968(3)***				
O(5)	***1.961(4)***					

Octahedron [V(3)O$_6$]

V(3)	**O(7)**	**O(7)^{vi}**	**O(7)^{vii}**	**O(8)^{vii}**	**O(8)^{vi}**	**O(8)**
O(8)	91.9(2)	176.1(2)	86.6(1)	90.1(1)	90.1(1)	***2.015(3)***
O(8)^{vi}	86.6(2)	91.9(2)	176.1(2)	90.1(1)	***2.015(3)***	
O(8)^{vii}	176.1(2)	86.6(2)	91.9(2)	***2.015(3)***		
O(7)^{vii}	91.5(2)	91.5(2)	***1.989(4)***			
O(7)^{vi}	91.5(2)	***1.989(4)***				
O(7)	***1.989(4)***					

Table S1.4. (Continuation).

Piramid [HP(1)O$_3$]

P(1)	**O(8)**	**O(4)**	**O(9)**	**H(1)**
H(1)	107(1)	107(1)	106(1)	***1.34(4)***
O(9)	114.8(2)	112.4(2)	***1.534(3)***	
O(4)	108.2(2)	***1.522(3)***		
O(8)	***1.508(3)***			

Piramid [HP(2)O$_3$]

P(2)	**O(2)**	**O(3)**	**O(1)**	**H(2)**
H(2)	109(2)	95(2)	116(2)	***1.34(4)***
O(1)	113.3(2)	109.9(2)	***1.523(4)***	
O(3)	112.6(2)	***1.518(3)***		
O(2)	***1.508(3)***			

Piramid [HP(3)O$_3$]

P(3)	**O(5)**	**O(5)^{i}**	**O(5)^{iii}**	**H(3)**
H(3)	104.5(2)	104.5(2)	104.5(2)	***1.36(5)***
O(5)^{iii}	114.0(1)	114.0(1)	***1.521(3)***	
O(5)^{i}	114.0(1)	***1.521(3)***		
O(5)	***1.521(3)***			

Piramid H$_2$P(4)O$_3$

P(4)	**O(7)^{v}**	**O(7)**	**O(10)**	**H(4)**
H(4)	111(1)	111(1)	99(3)	***1.39(4)***
O(10)	108.8(3)	108.8(3)	***1.530(8)***	
O(7)	116.1(3)	***1.492(4)***		
O(7)^{v}	***1.492(4)***			

O(10)-H(10)	0.82 Å
O(10)-P(4)-H(10)	109.47°

Table S1.4. (Continuation).

Cycloheptylammonium cation

N(1)	**C(1)**	**H(1A)**	**H(1B)**	**H(1C)**
H(1C)	109.47	109.47	109.47	0.89
H(1B)	109.47	109.47	0.89	
H(1A)	109.47	0.89		
C(1)	***1.481(9)***			

C(1)	**N(1)**	**C(2)**	**C(7)**	**H(11)**
H(11)	109.10	109.10	109.10	0.98
C(7)	101(1)	111(1)	***1.56(2)***	
C(2)	117(1)	***1.53(1)***		
N(1)	***1.481(9)***			

C(2)	**C(1)**	**C(3)**	**H(2A)**	**H(2B)**
H(2B)	104.54	104.54	105.66	0.97
H(2A)	104.54	104.54	0.97	
C(3)	131(2)	***1.56(1)***		
C(1)	***1.53(1)***			

C(3)	**C(4)**	**C(2)**	**H(3A)**	**H(3B)**
H(3B)	111.89	111.89	109.59	0.97
H(3A)	111.89	111.89	0.97	
C(2)	99(1)	***1.56(1)***		
C(4)	***1.52(2)***			

C(4)	**C(5)**	**C(3)**	**H(4A)**	**H(4B)**
H(4B)	108.39	108.39	107.45	0.97
H(4A)	108.39	108.39	0.97	
C(3)	116(2)	***1.52(1)***		
C(5)	***1.51(1)***			

C(5)	**C(4)**	**C(6)**	**H(5A)**	**H(5B)**
H(5B)	105.76	105.76	106.17	0.97
H(5A)	105.76	105.76	0.97	
C(6)	126(2)	***1.53(1)***		
C(4)	***1.51(1)***			

C(6)	**C(7)**	**C(5)**	**H(6A)**	**H(6B)**
H(6B)	109.93	109.93	108.33	0.97
H(6A)	109.93	109.93	0.97	
C(5)	109(2)	***1.53(1)***		
C(7)	***1.52(1)***			

C(7)	**C(6)**	**C(1)**	**H(7A)**	**H(7B)**
H(7B)	107.96	107.96	107.22	0.97
H(7A)	107.96	107.96	0.97	
C(1)	117(2)	***1.56(2)***		
C(6)	***1.52(1)***			

Simmetry codes: *i* = -y+1, x-y+1, z; *ii* = y-1, -x+y, -z+1; *iii* = -x+y, -x+1, z; *iv* = x-y+1, x+1, -z+1;
v = x, y, -z+3/2; *vi* = -y+1, x-y+2, z; *vii* = -x+y-1, -x+1, z; *viii* = -x, -y+2, -z+1;
ix = x, y, -z+1/2.

(S2) Structure Description

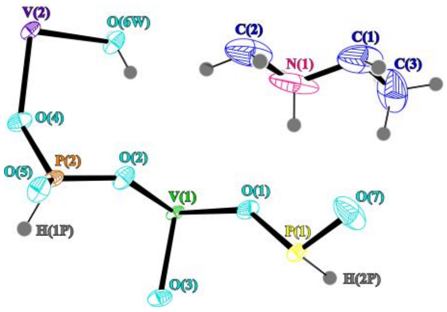


Figure S2.1. Thermal ellipsoid plots (50% probability) and atomic labelling schemes of compound **1**.

Table S2.1. Interlayer and intralayer hydrogen bonds systems in phase **1**.

Donor-H-Acceptor	***D-H (Å)***	***H...A (Å)***	***D...A (Å)***	***D-H...A (º)***
Interlayer				
N(1)-H0A-O3^{ii}	0.90	2.70	3.280(4)	123
N(1)-H0A-O7^{i}	0.90	1.80	2.697(5)	173
N(1)-H0B-O1	0.90	2.12	2.920(5)	148
N(1)-H0B-O7	0.90	2.32	3.105(4)	145
Intralayer				
O6W-H6A-O1^{i}	0.84(2)	2.49(3)	3.099(3)	131(2)
O6W-H6A-O2^{i}	0.84(2)	2.00(2)	2.767(2)	151(3)
O6W-H6B-O2	0.85(3)	2.53(3)	3.252(2)	143(3)
O6W-H6B-O3^{ii}	0.85(3)	2.07(3)	2.796(3)	143(2)

Simmetry codes: *i* = -1+x, y, z; *ii* = 1-x, 1-y, 1-z;

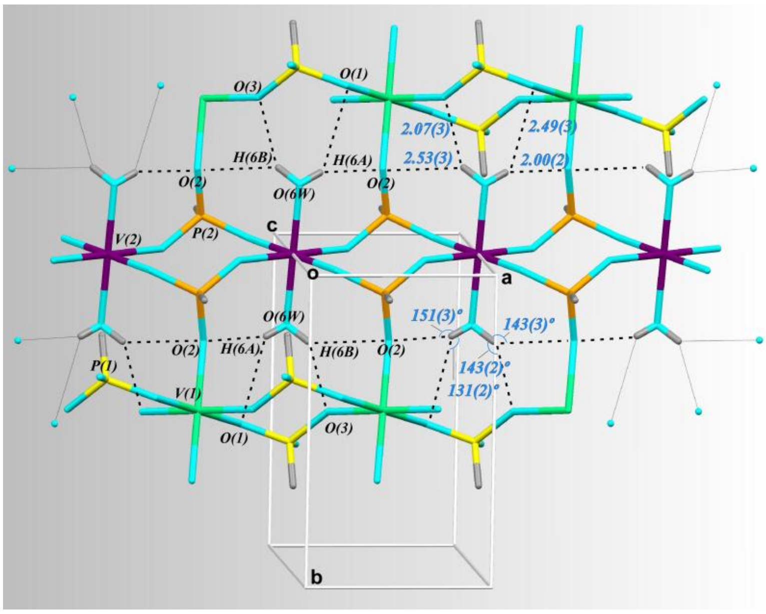


Figure S2.2. Intralayer hydrogen bonds scheme of compound **1**.

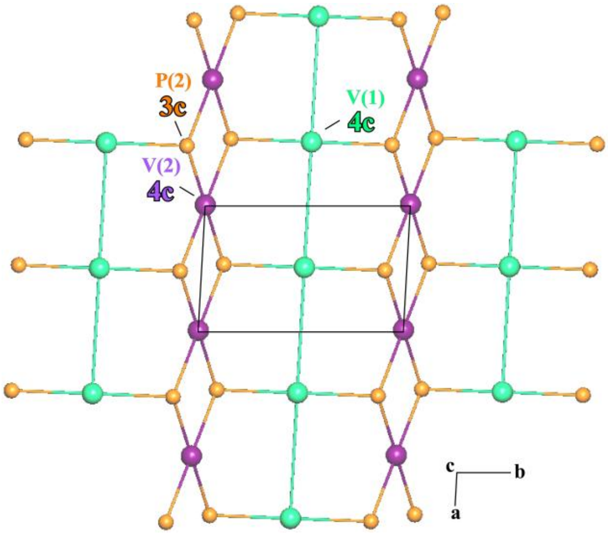


Figure S2.3. Topological simplification of the inorganic sheets of compound **1** removing the 2-connected nodes.

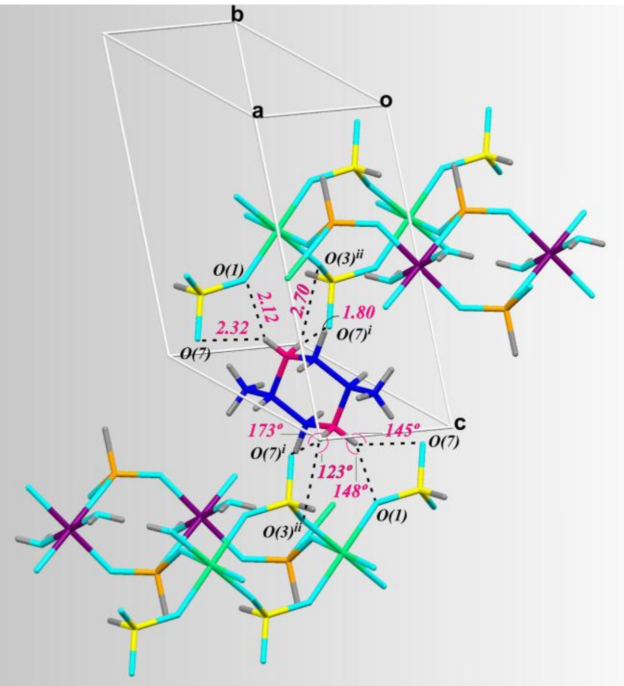


Figure S2.4. Interlayer hydrogen bonds scheme of compound **1**.

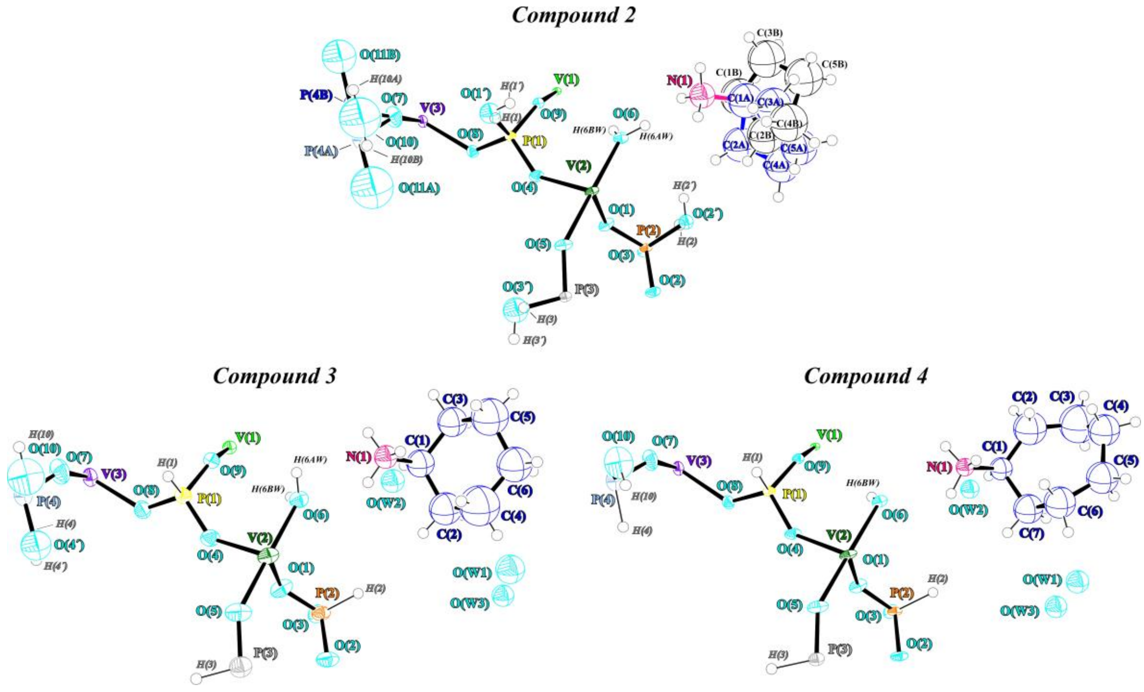
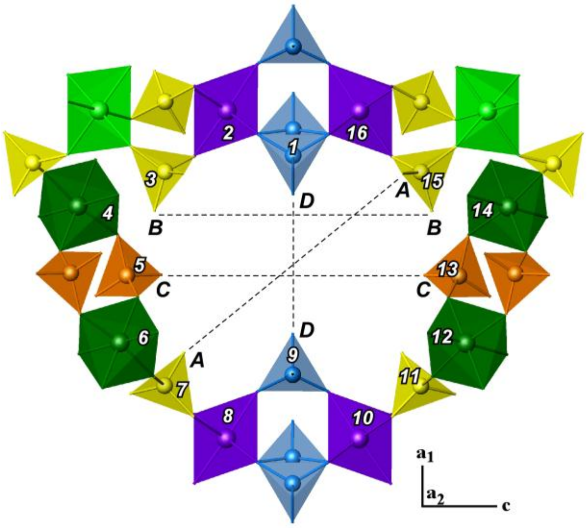


Figure S2.5. Thermal ellipsoid plots (50% probability) and atomic labelling schemes of compounds **2**, **3** and **4**.



Distances (Å)		2	3	4
A-A	O(1´)-O(1´)	12.85	-------	-------
	H(1)-H(1)	12.88	12.94	12.97
B-B	O(4)-O(4)	9.86	9.97	10.02
C-C	O(2´)-O(2´)	9.31	-------	-------
	H(2)-H(2)	9.71	9.69	9.44
D-D	O(10)-O(10)	6.93	7.02	6.96
	O(11A)-O(11A)	8.41	-------	-------
	O(4´)-O(4´)	-------	8.70	-------
	H(4)-H(4)	-------	9.18	8.97

Figure S2.6. Representation and dimensions of the 16-ring windows of the compounds **2**, **3** and **4**.

Layers consisting of the [V(1)O_6] and [V(2)O_5(H_2O)] octahedra connected to the HP(1)O_3, HP(2)O_3 and HP(3)O_3 units through oxygen vertices. [V(1)O_6] polyhedra are located over de 6_3 axes, exclusively bridging the [HP(1)O_3] units. Each [V(2)O_5(H_2O)] octahedron is linked to three [HP(2)O_3] units, one [HP(1)O_3] and one [HP(3)O_3] groups. For compound **2**, these phosphite groups are partially substituted by hydrogenphosphate groups as it is shown in Figure S2.7.

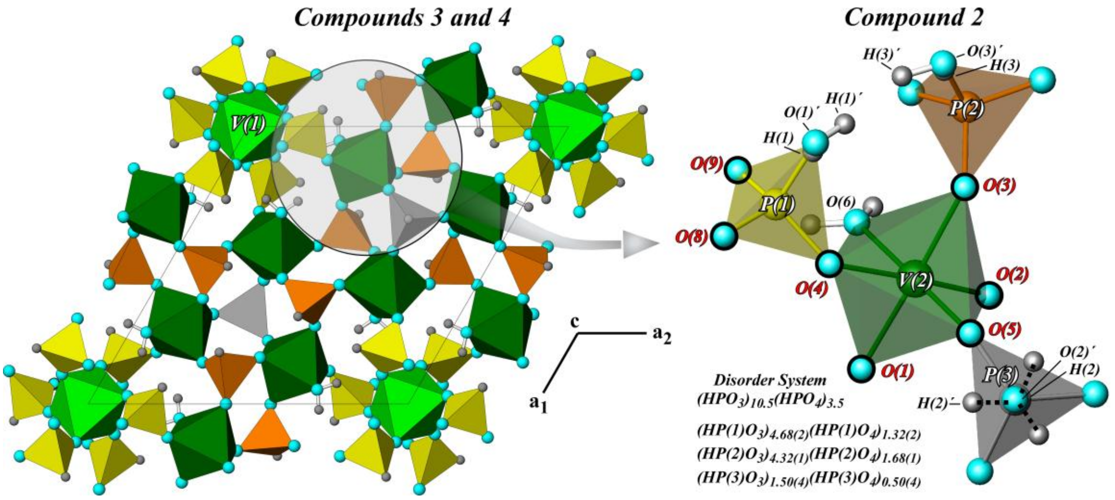


Figure S2.7. Polyhedral view of the layer A connectivity.

The layers packing has an ABAB sequence along the *c* axis, where B represents the location of the pillars formed by two [V(3)O_6] units and three [H_2P(4)O_4]/[H_2P(4)O_3] units, which link the A layers to build the 3D open framework. These pseudotetrahedral pyramids formed by the P(4) atoms correspond to [H_2PO_4] units in compound **2** and [H_2PO_3] ones in compound **4**. For compound **3**, a chemical disorder of the two types of anionic groups exists as it is shown in Figure S2.8.

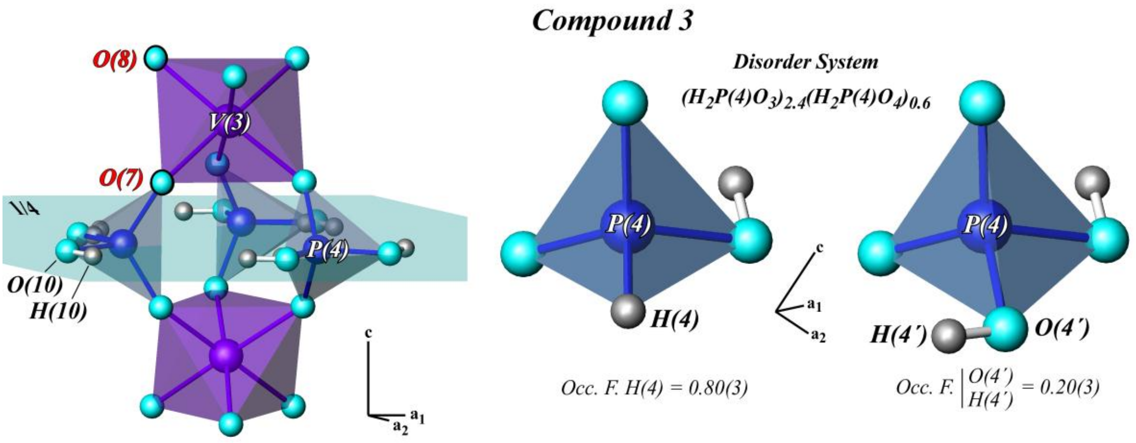


Figure S2.8. Pillar structure of compound **3**.

The terminal oxygen atoms of the P(4) polyhedra have U_{iso} quite high values. Their crystallographic position gives them a strong rotational freedom on the symmetry plane *m* on which they are located. This fact is particularly relevant in compound **2**, showing that the $H_2P(4)O_4$ groups are disordered in two positions, estimating an occupancy factor of 0.72(2) to position A and 0.28(2) to position B (Figure S2.9).

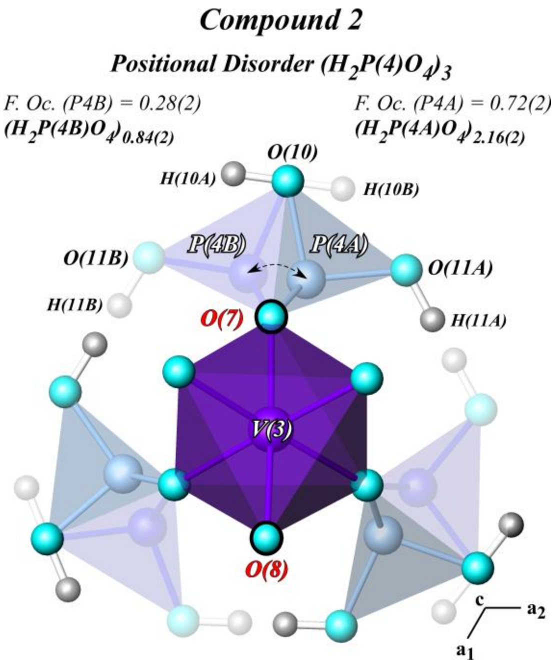


Figure S2.9. Positional disorder of the $H_2P(4)O_4$ groups in compound **2**.

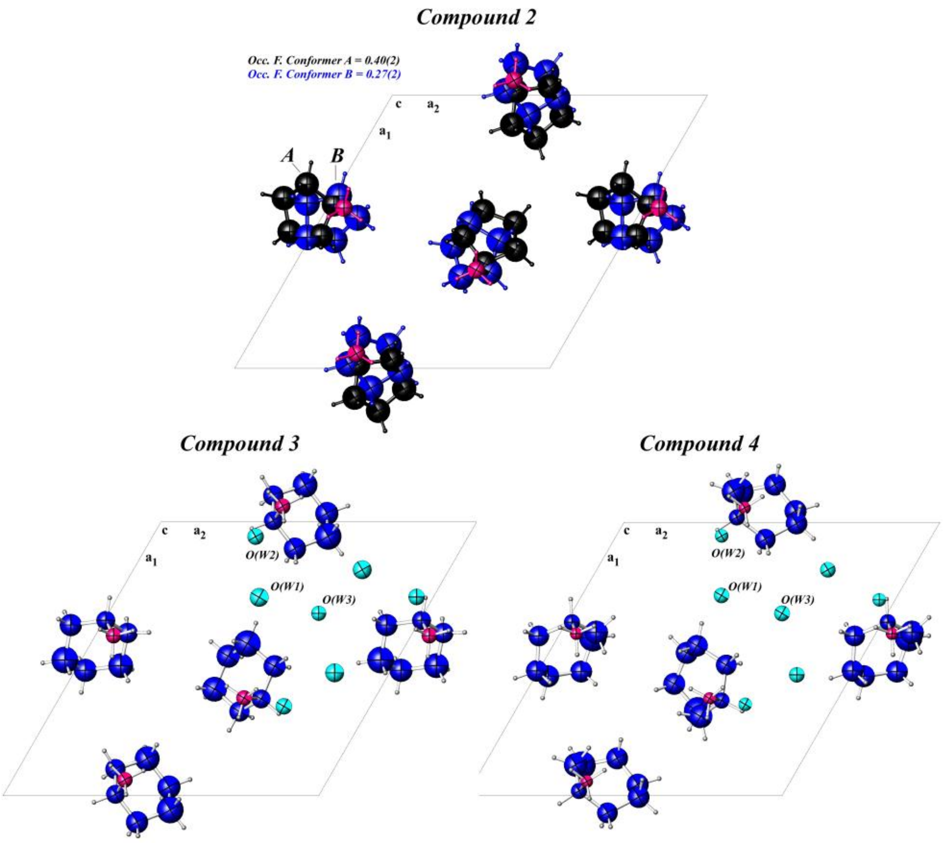


Figure S2.10. View of the interlayer spaces along *c*.

Hydrogen bonding plays an important role linking the amine cations to the framework (Table S2.2). The NH_3- group in phase **2** is rotated about 60° with respect to the same groups in phases **3** and **4**, possibly caused by a disorder of the hydrogen atoms (Figure S2.11). In this way, it generates an interlayer hydrogen bonding system with slightly different distances and angles for phase **2**. Regarding the intralayer bonds, the O(6W) oxygen of the water molecule coordinated to the $V(2)O_5(H_2O)$ octahedron, establishes interactions with the O(9) atom, from hydrogen H(6BW) and, with the O(1) and O(4) atoms, from hydrogen H(6AW). For phases **2** and **3** the H(6AW) hydrogen atom was located with different coordinates. Therefore, it is possible this hydrogen atom is disordered in two positions, resulting in differences in the intralayer hydrogen bonding system (Table S2.2). For phase **4**, it was not possible to locate the H(6AW) hydrogen atom.

Table S2.2. Interlayer and intralayer hydrogen bonds systems in phases **2**, **3** and **4**

Compound 2

Donor-H-Acceptor	*D-H (Å)*	*H...A (Å)*	*D...A (Å)*	*D-H...A (º)*
Interlayer				
N(1)-H(1A)-O(5)^{ii}	0.89	2.40	3.252(10)	161
N(1)-H(1B)-O(3)^{iii}	0.89	2.11	2.964(12)	161
N(1)-H(1C)-O(6)^{i}	0.89	2.22	2.901(10)	133
N(1)-H(1C)-O(4)^{ii}	0.89	2.43	2.954(12)	118
Intralayer				
O(6)-H(6AW)-N(1)^{i}	0.84(6)	2.07(6)	2.901(10)	170(5)
O(6)-H(6BW)-O(9)^{i}	0.84(6)	2.52(6)	2.989(4)	116(5)
O(6)-H(6BW)-O(9)^{iv}	0.84(6)	2.00(6)	2.821(4)	164(8)

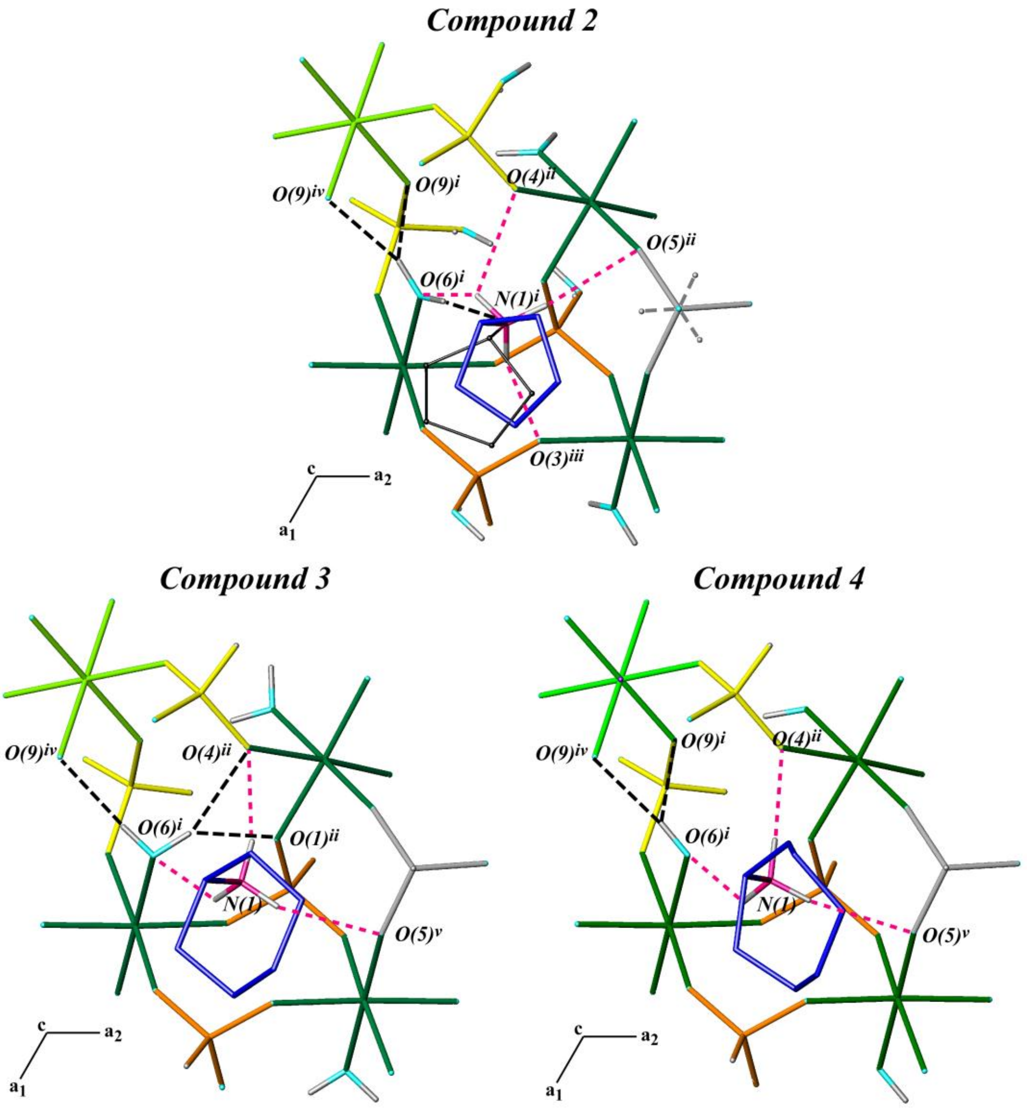
Compound 3

Donor-H-Acceptor	*D-H (Å)*	*H...A (Å)*	*D...A (Å)*	*D-H...A (º)*
Interlayer				
N(1)-H(1A)-O(5)^{v}	0.89	2.44	3.206(10)	145
N(1)-H(1B)-O(6)^{i}	0.89	2.25	2.932(9)	133
N(1)-H(1C)-O(4)^{ii}	0.89	2.11	2.966(10)	162
Intralayer				
O(6)-H(6AW)-O(1)^{ii}	0.851(11)	1.93(3)	2.648(4)	141(5)
O(6)-H(6AW)-O(4)^{ii}	0.851(11)	2.47(4)	3.181(4)	142(5)
O(6)-H(6BW)-O(9)^{iv}	0.86(3)	1.97(3)	2.821(4)	174(5)

Compound 4

Donor-H-Acceptor	*D-H (Å)*	*H...A (Å)*	*D...A (Å)*	*D-H...A (º)*
Interlayer				
N(1)-H(1A)-O(6)^{i}	0.89	2.31	2.876(10)	122
N(1)-H(1B)-O(4)^{ii}	0.89	2.04	2.931(12)	177
N(1)-H(1C)-O(5)^{v}	0.89	2.43	3.264(12)	156
Intralayer				
O(6)-H(6BW)-O(9)^{i}	0.84(4)	2.55(5)	3.008(5)	115(4)
O(6)-H(6BW)-O(9)^{iv}	0.84(4)	1.98(5)	2.810(6)	170(6)

Symmetry codes: *i* = x, y, z; *ii* = 1+x-y, 1+x, 1-z; *iii* = -x+y, 1-x, z; *iv* = -1+y, -x+y, 1-z; *v* = 1-x, 2-y, 1-z.



Compound 2

Compound 3

Compound 4

Symmetry codes: *i* = x, y, z; *ii* = 1+x-y, 1+x, 1-z; *iii* = -x+y, 1-x, z; *iv* = -1+y, -x+y, 1-z; *v* = 1-x, 2-y, 1-z

Figure S2.11. Inter- (pink) and Intra- (black) layer hydrogen bonding interactions of phases **2**, **3** and **4**.

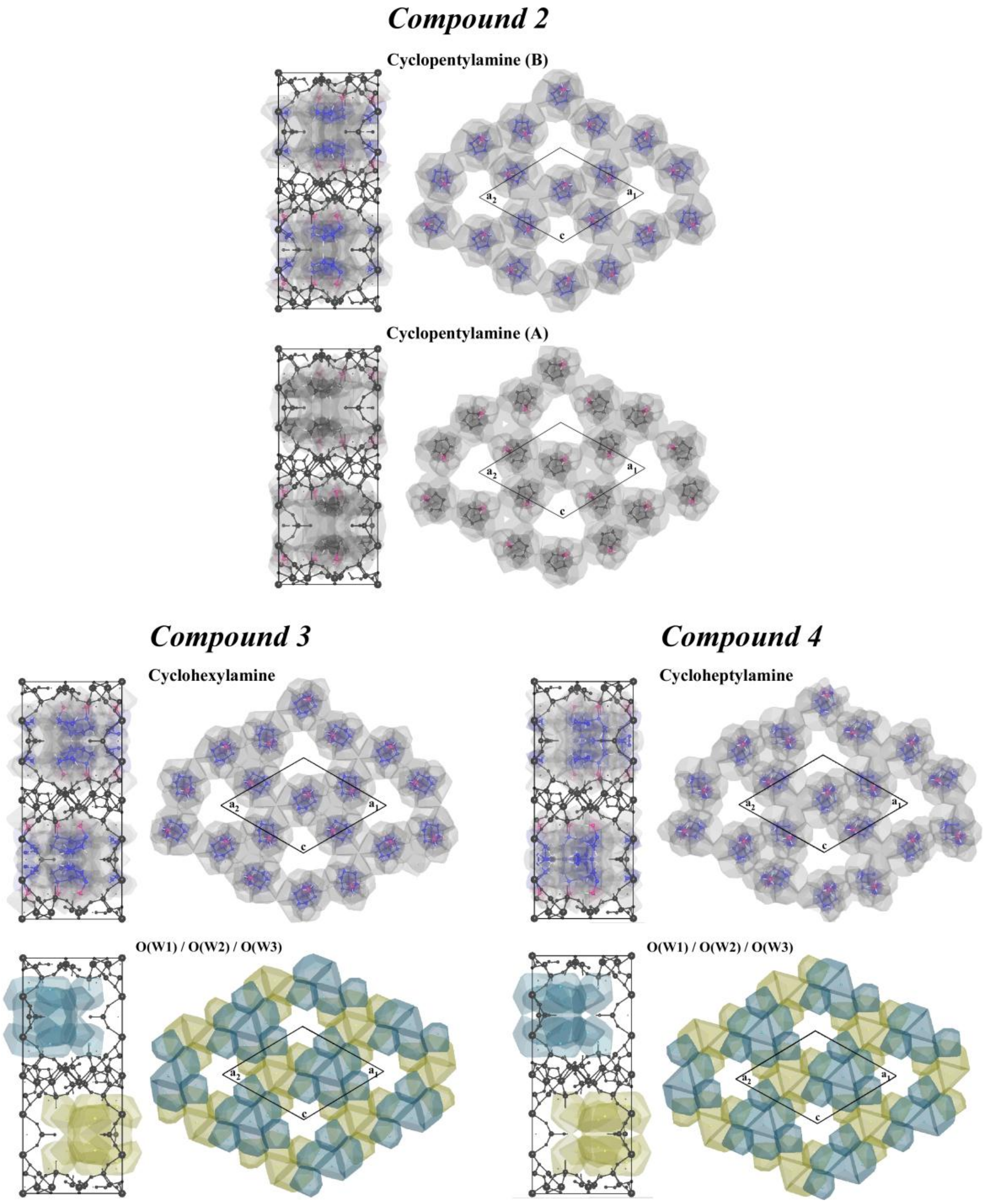


Figure S2.12. *VDP* representation of the solvent species located in the voids of the phases **2**, **3** and **4**.

S2(a). Discussion about the bond distances and angles and polyhedral distortion study.

Compound 1

The V-O distances range from 1.965(2) Å to 2.074(2) Å, in good agreement with 3+ oxidation state for the V atoms[2], based on the bond valence sums (BVS) calculations[3],. While the O-V-O *cis* angles range from 86.61(7)° to 93.39(7)°, the O-V-O *trans* ones are equal to the ideal values, 180°, because the metallic atoms are over inversion centres. The distortion of the octahedra, calculated by the Alvarez *et al.* method[4] using the SHAPE v1.1a program,[5] are S(O_h) = 0.104 and 0.077 for [V(1)O_6] and [V(2)O_4(H_2O)$_2$], respectively, near the value for the octahedral ideal symmetry (S(Oh) = 0.00) (Figure S2.13). The P-O bonds are in the range 1.495(2)-1.526(2) Å. The different P-H distances (P(1)-H = 1.27(3) Å, P(2)-H = 1.37(1) Å) corresponding to the two crystallographycally independent phosphorous atoms involves different geometries for the corresponding pseudotetrahedron. While the O-P-O angles vary from 109.8(1)° to 113.3(1)°, the H-P-O angles are in the range 99(1)°-113(1)° for [HP(1)O_3] and in the range 104(1)-110.8(1)° for [HP(2)O_3]. Anyway, these values are in the usual range for phosphite based compounds[6]. The distortion values of the [HPO_3] tetrahedra indicate a symmetry near to the ideal one (S(T_d) = 0.00)),[7] being the [HP(1)O_3] pyramid the most deviated from the *Spread* distortion mechanism to the *off-axis* distortion (S(T_d) = 0.954, S(D_{4h}) = 31.080) (Figure S2.13).

Compounds 2, 3 and 4

The V-O distances range from 1.961(4) Å to 2.102(3) Å, in good agreement with 3+ oxidation state for the V atoms,[2] based on the bond valence sums (BVS) calculations.[3] While the O-V-O *cis* angles range from 84.9(1)° to 94.7(1)°, the O-V-O *trans* ones reach minimum values of 170.3(1)°. The S(O_h) values for phases **2**, **3** and **4**, calculed by Continuous Simmetry Measure,[4,5] do not exceed the value of 0.20, which represent very slight distortions with regard to the ideal octahedron.[4] In Figure S2.9 (Supplementary Material) it can be observed that the progressive increase of the S(itp) values of the V(2) and V(3) octahedra is related to the increase of the size of the organic molecules enclosed into the channels. This relationship is not observed for the V(3) octahedra.

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[2] M. Schindler, F. C. Hawthorne, W. H. Baur, *Chem. Mater.*, 2000, **12**, 1248.

[3] I. D. Brown, D. Altermatt, *Acta Crystallogr.*, 1985, **B41(4)**, 244.

[4] S. Álvarez, D. Avnir, M. Llunel, M. Pinsky, *New. J. Chem.*, 2002, **26**, 996.

[5] M. Llunel, D. Casanova, J. Cirera, J.M. Bofill, P. Alemany, S. Álvarez, M. Pinski, D. Yatumir, *SHAPE v1.1a: Program for Continuous Shape Measure Calculations of Polyhedral Xn and MLn Fragments*, 2003.

[6] J. Loub, *Acta Crystallogr.*, 1991, **B47(4)**, 468.

[7] J. Cirera, P. Alemany, S. Álvarez, *Chem. Eur. J.*, 2004, **10**, 190.

The P-O bonds are in the 1.507(3)-1.534(3) Å range for the P(1), P(2) and P(3) tetrahedral phosphorus sites. It is noteworthy that the P(4)-O(7) bond, which link the V(3)O_6 octahedra forming the pillars that stack the inorganic layers, have the shortest distances in compounds **2**, **3** and **4** ((P(4A)-O(7) = 1.486(4) Å and P(4B)-O(7) = 1.455(7) Å in compound **2**). The longest distances are the P(4A)-O(11A) (1.55(2) Å) and P(4B)-O(11B) (1.65(4) Å) ones in compound **2**, as is expected for terminal P-OH groups. The O-P-O and H-P-O angles reach minimum and maximum values of 95(2)º and 119.6(8)º. The $S(T_d)$ values calculated for the phosphorous tetrahedra in compounds **2**, **3** and **4** indicate regular environments for the central atoms.[7] The [HP(3)O_3] units are the most deviated from de *Spread* curve to the *umbrella* distorion ($S(D_{4h})$ = 33.669, $S(T_d)$ = 1.100 for phase **3**) (Figure S2.13).

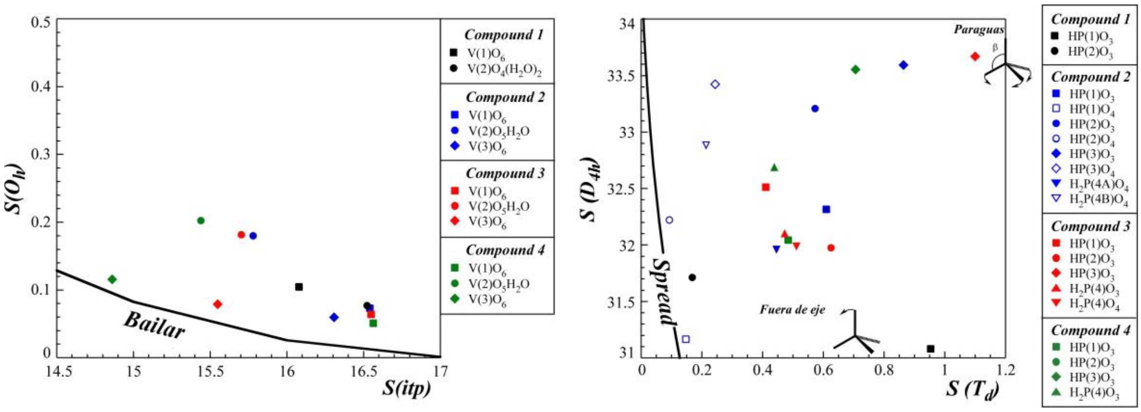

Figure S2.13. Distortion of the octahedra and pseudotetrahedra of the phases **1**, **2**, **3** and **4**.

(S3) Thermal study

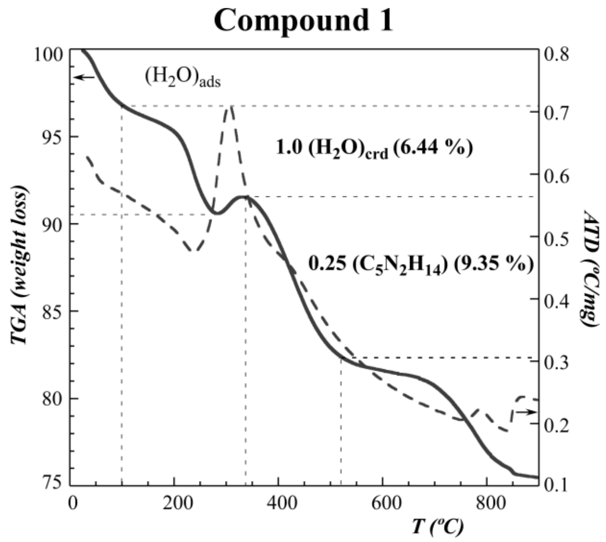

Figure S3.1. Thermal analysis (TGA, DTA) of phase **1**.

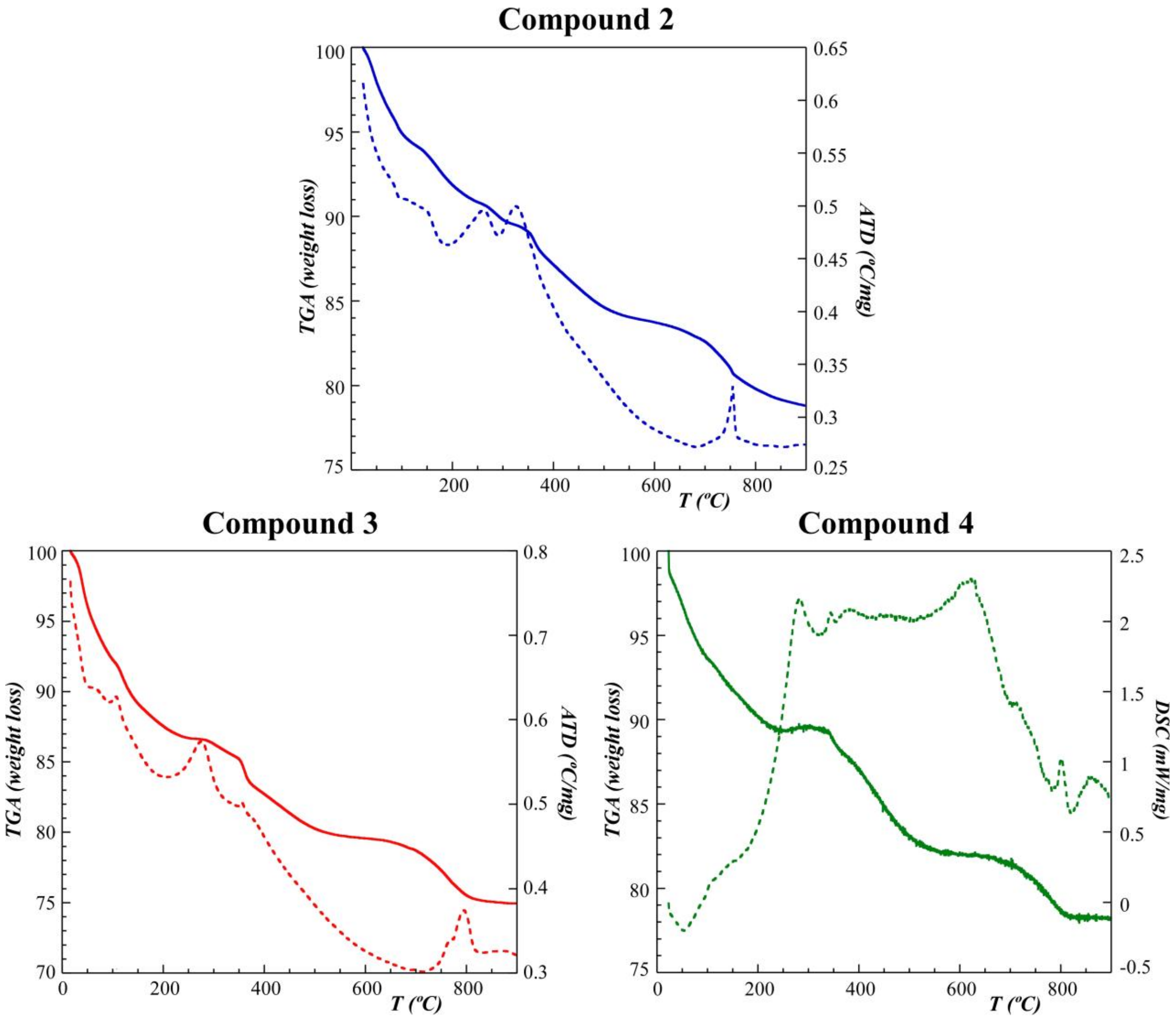

Figure S3.2. Thermal analysis (TGA, DTA or DSC) of phases **2**, **3** and **4**.

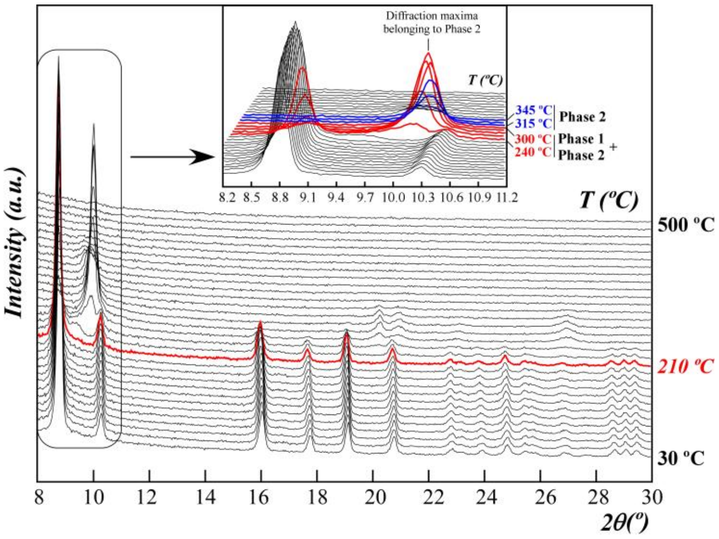

Figure S3.3. Thermodiffractogram of phase **1**.

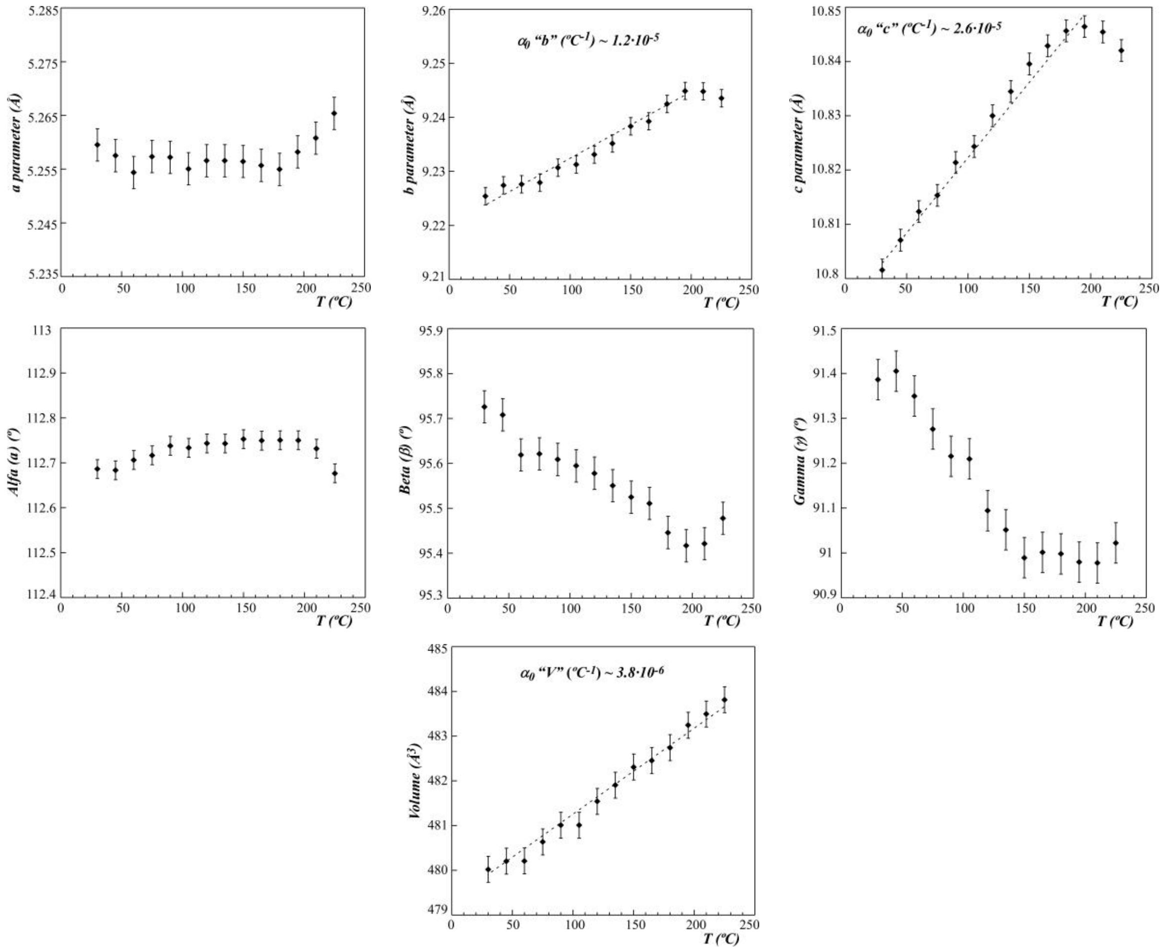

Figure S3.4. Thermal evolution of the parameters and volume of the unit cell for phase **1** in the 30 to 225 ºC temperature range.

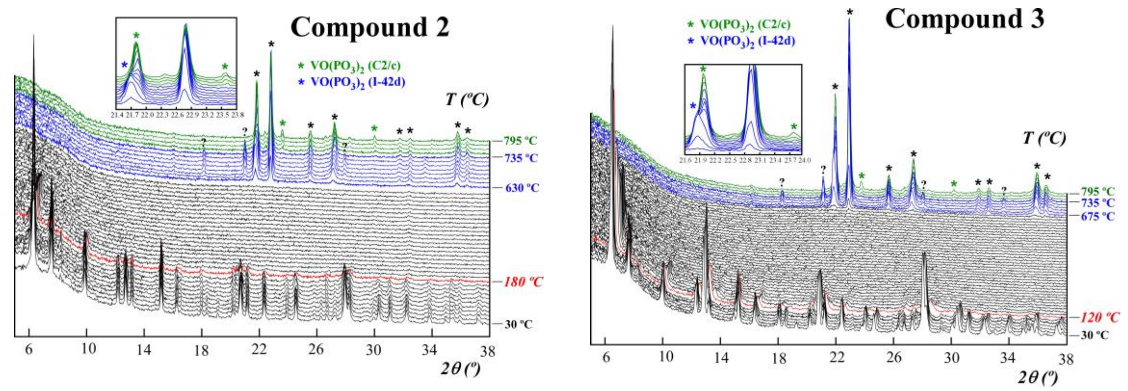

Figure S3.5. Thermodiffractograms of phases **2** and **3**.

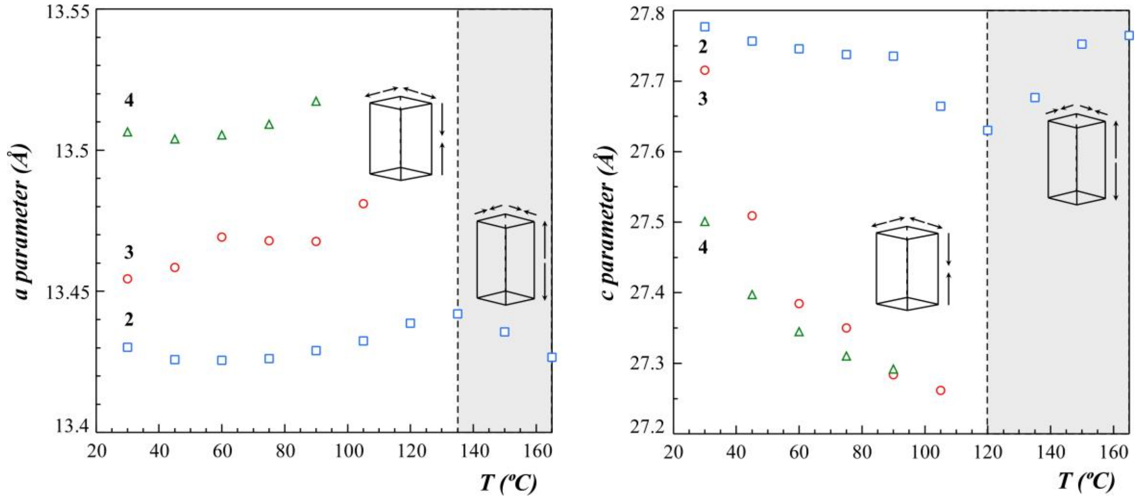

Figure S3.6. Thermal evolution of the *a* and *c* parameters of the unit cell for phases **2**, **3** and **4**.

(S4) Spectroscopic study

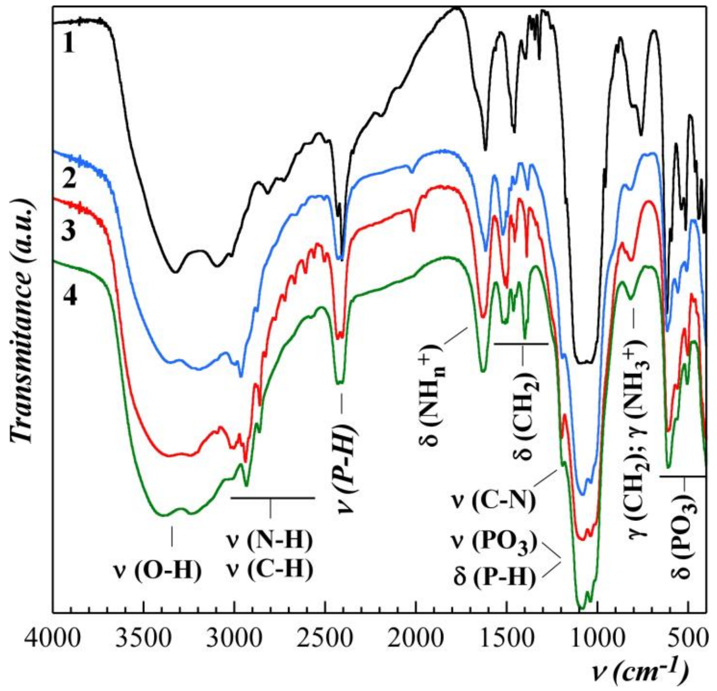

Figure S4.1. IR spectra of phases **1**, **2**, **3** and **4**.

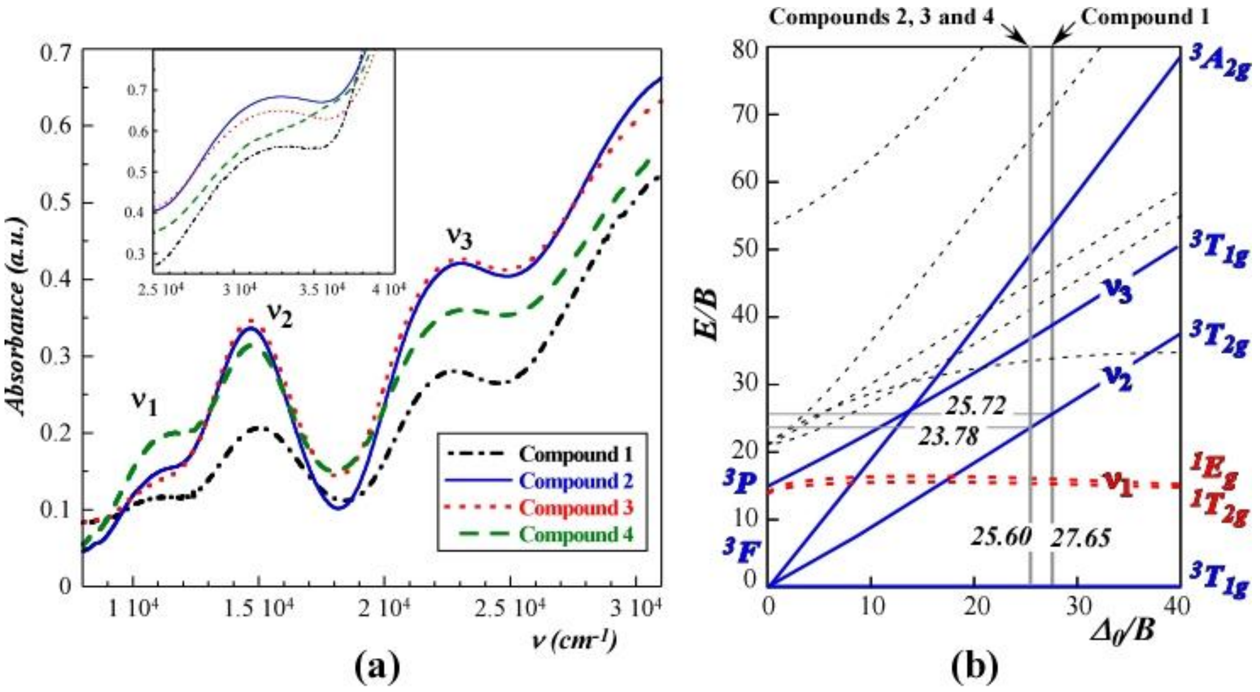

Figure S4.2. (a) UV-visible spectra of the four phases and **(b)** Tanabe-Sugano diagram for a d^2 system.

The ratio between the first two spin-allowed transitions is calculated as ν_3/ν_2. Based on these relations, the values of ν/B and □Δ_0/B can be obtained geometrically from the

Tanabe-Sugano diagram for a d^2 system (Figure S4.2(b)). Then, it is possible to calculate the values of Δ_0, which are 16135 cm^{-1} for **1** and 15825 cm^{-1} for **2**, **3** and **4**, in agreement with the values calculated by the energy level equations for *Dq*.

(S5) Catalytic Behaviour

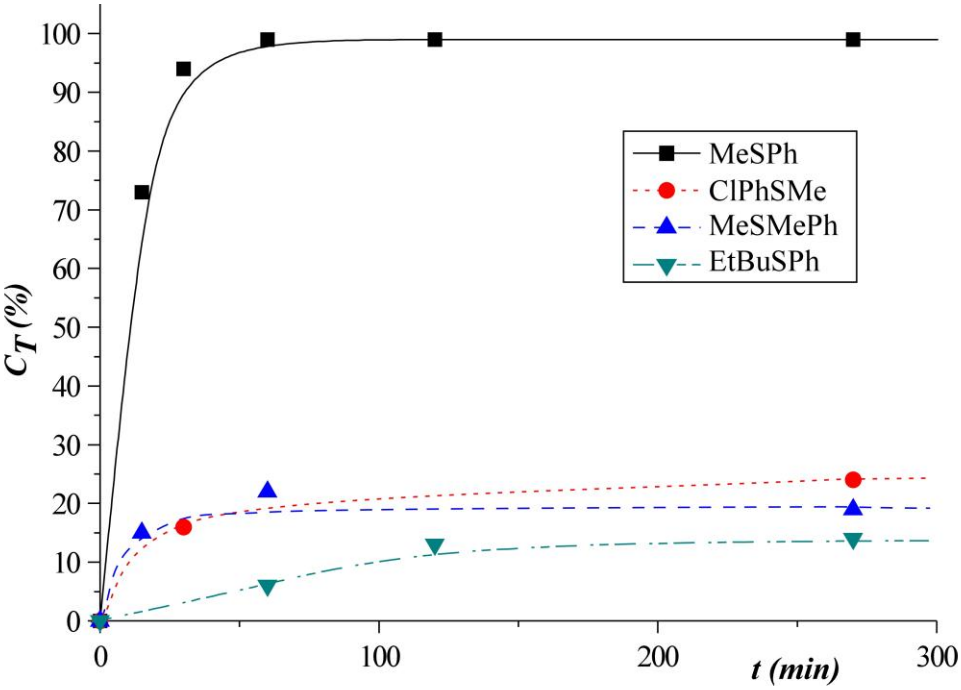

Figure S5.1. Kinetic profiles of the oxidation reaction of various sulfides over catalyst **1** with H_2O_2 as oxidizing agent.

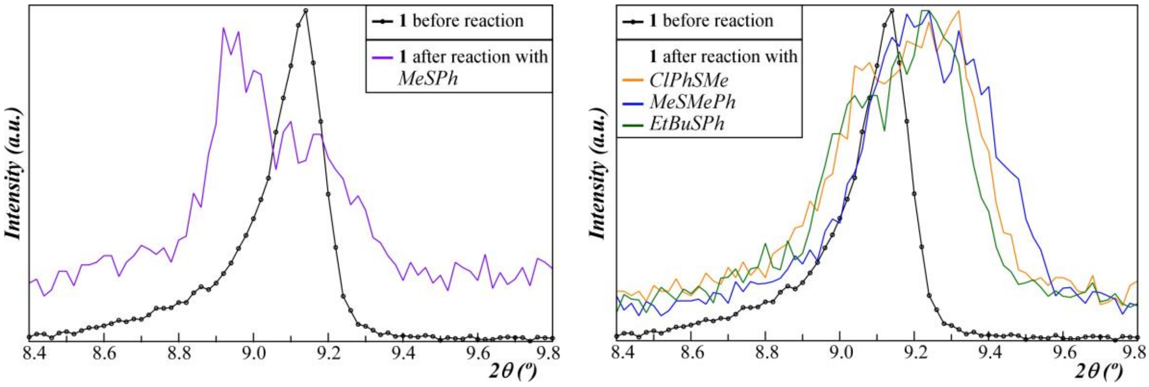

Figure S5.2 Detail of the powder X-ray diffraction patterns of catalyst **1** before and after the reactions with various alkyl aryl sulfides with H_2O_2 as oxidizing agent.

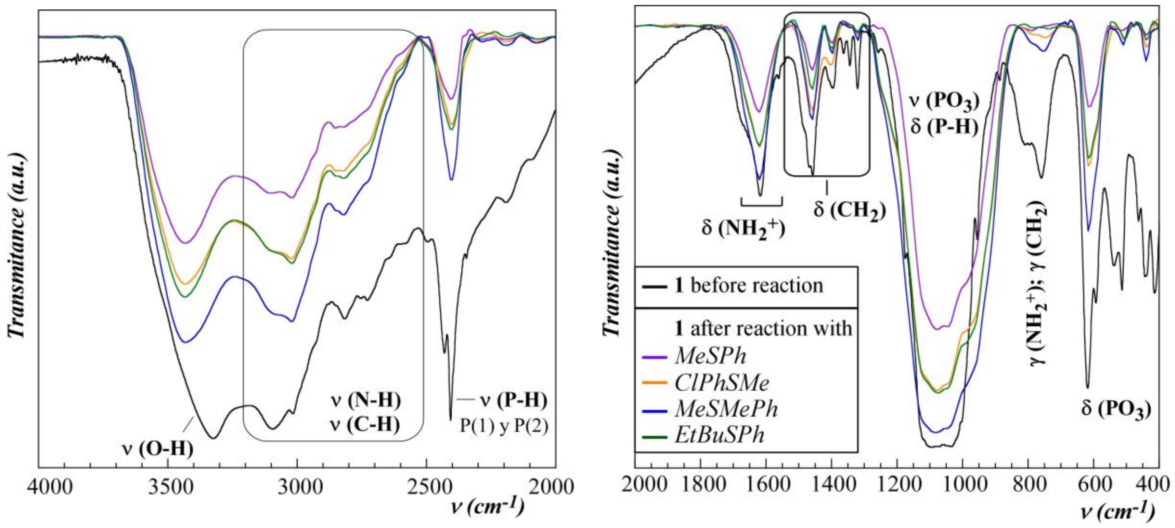

Figure S5.3 IR spectra of catalyst **1** before and after the reactions with various alkyl aryl sulfides with H_2O_2 as oxidizing agent.

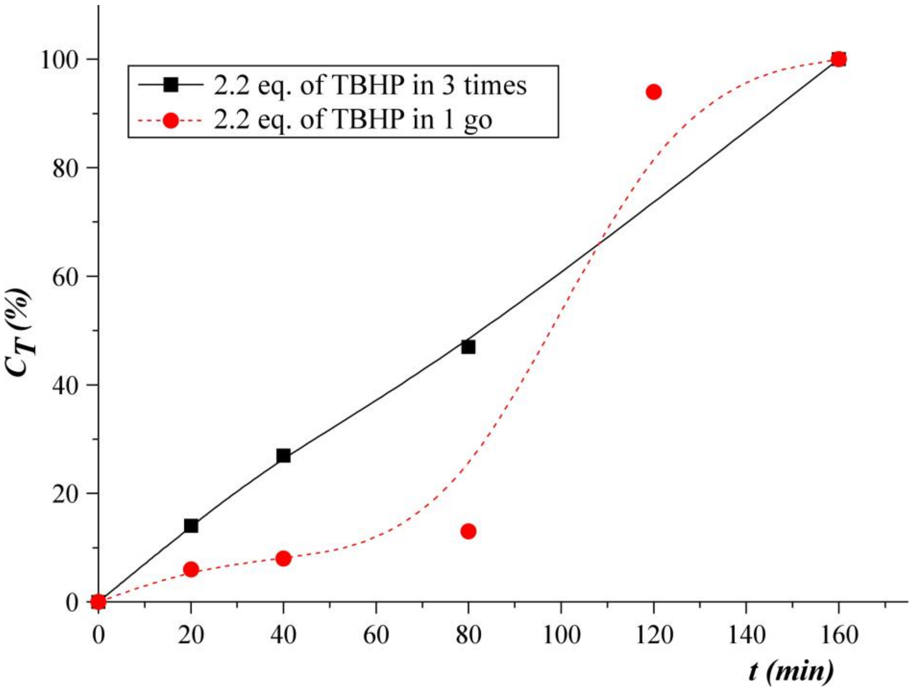

Figure S5.4. Kinetic profiles of the oxidation reaction of methyl phenyl sulfide (MeSPh), over catalyst **1** with 2.2 eq. of TBHP as oxidizing agent added gradually or in one go.

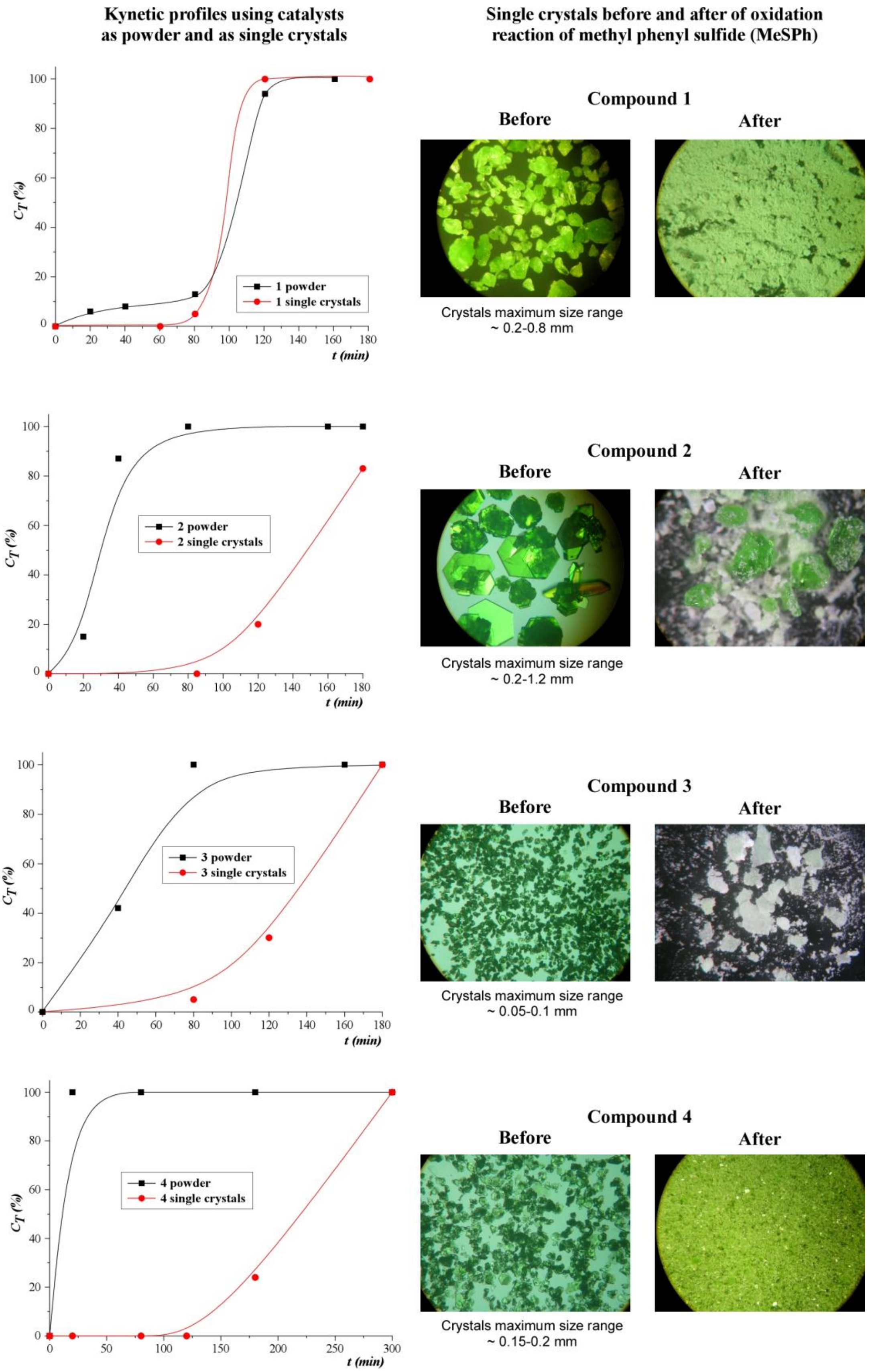

Figure S5.5. Kinetic profiles of the oxidation reaction of methyl phenyl sulfide (MeSPh), over catalyst **1-4** as powder and as crystals with TBHP as oxidizing agent. Photos of the catalysts used as single crystals before and after the reaction.