Supporting Information

For

Tuning Proton Conductivity in Alkali Metal Phosphonocarboxylates by Cation Size-Induced and Water-Facilitated Proton Transfer Pathways

Montse Bazaga-García,[#] Maria Papadaki,[‡] Rosario M.P. Colodrero,[#] Pascual Olivera-Pastor,[#] Enrique R. Losilla,[#] Belén Nieto-Ortega,[§] Miguel Ángel G. Aranda,[#†] Duane Choquesillo-Lazarte,[⊥] Aurelio Cabeza,[#] and Konstantinos D. Demadis*[‡]*

[#] Universidad de Málaga, Departamento de Química Inorgánica, Campus Teatinos s/n, Málaga-29071, Spain.

[‡] Crystal Engineering, Growth and Design Laboratory, Department of Chemistry, University of Crete, Voutes Campus, Crete, GR-71003, Greece.

[§] Universidad de Málaga, Departamento de Química Física, Campus Teatinos s/n, Málaga-29071, Spain.

[†] ALBA Synchrotron, Ctra. BP1413 km 3.3, 08290 Cerdanyola del Vallès, Barcelona, SPAIN

[⊥] Laboratorio de Estudios Cristalográficos, IACT, CSIC-Universidad de Granada, Granada-18100, Spain.

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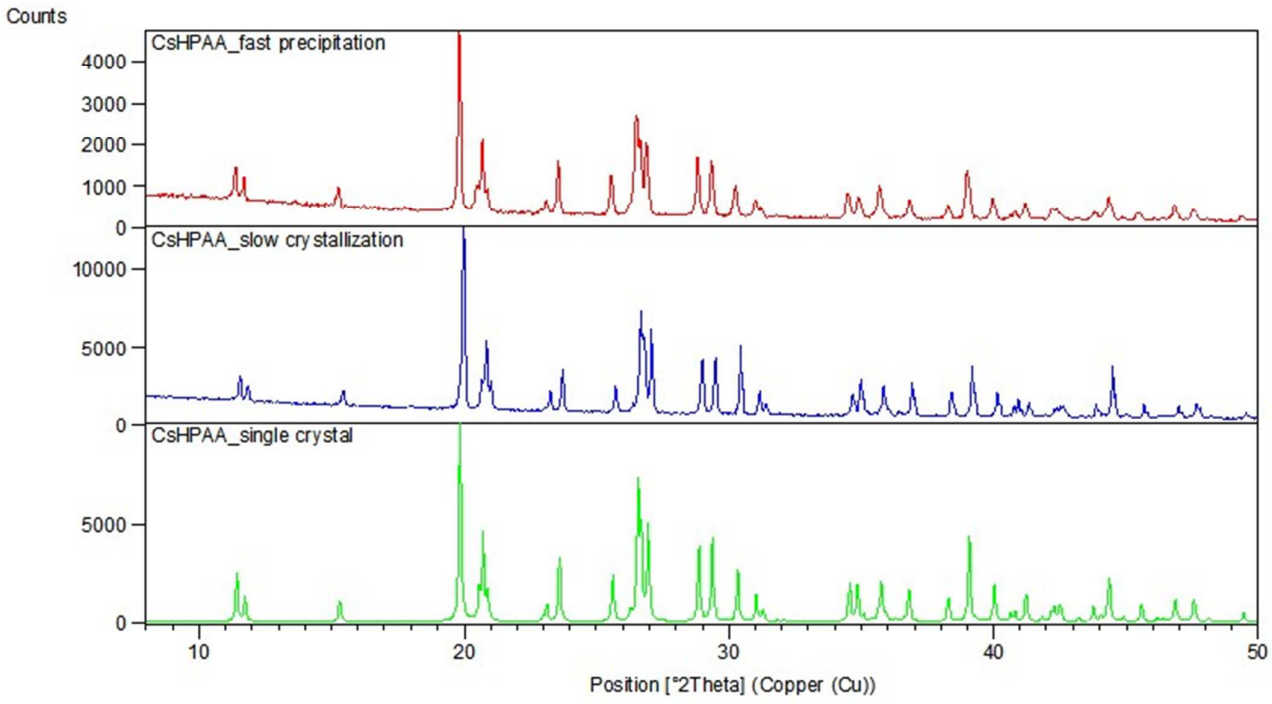

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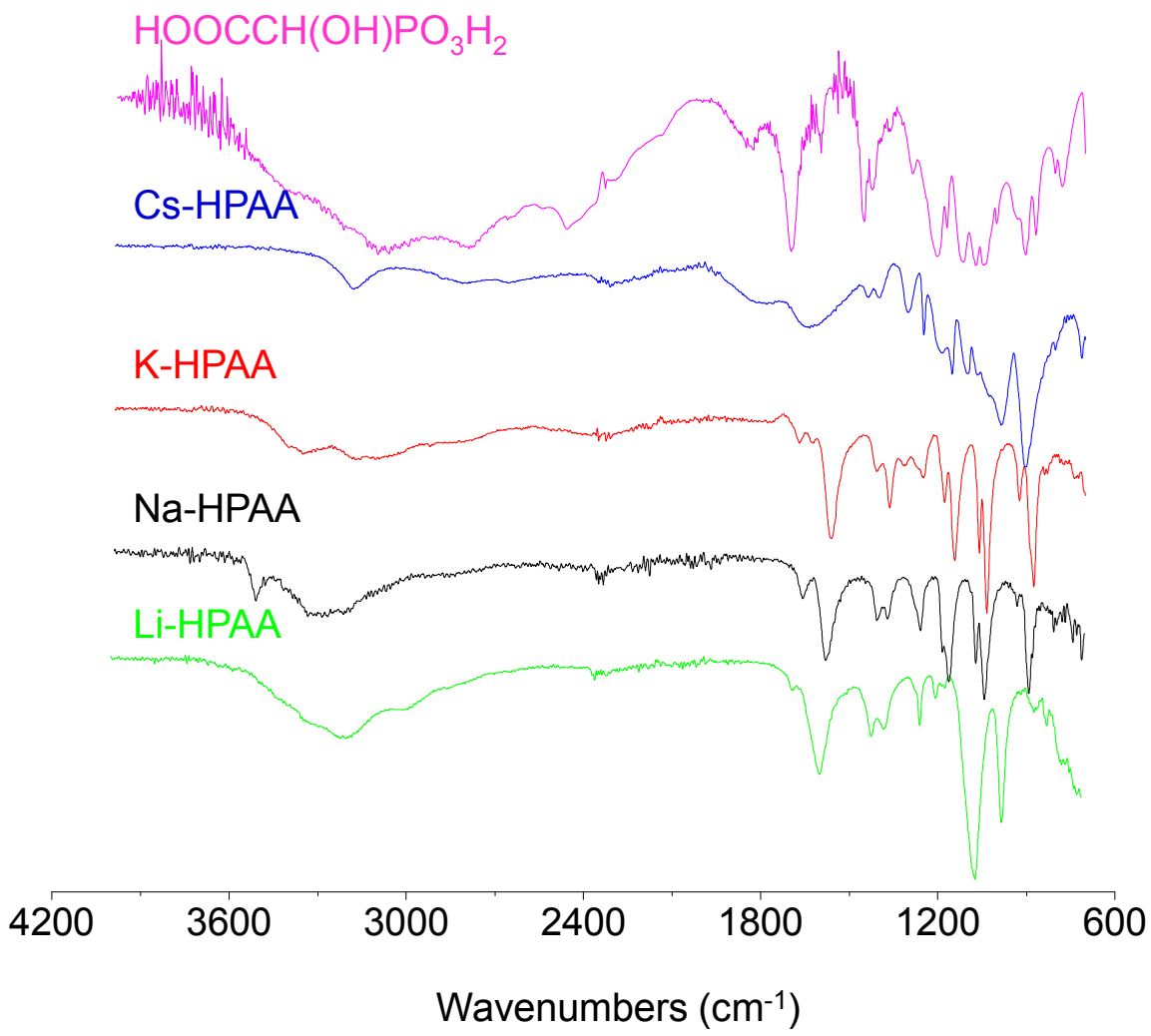

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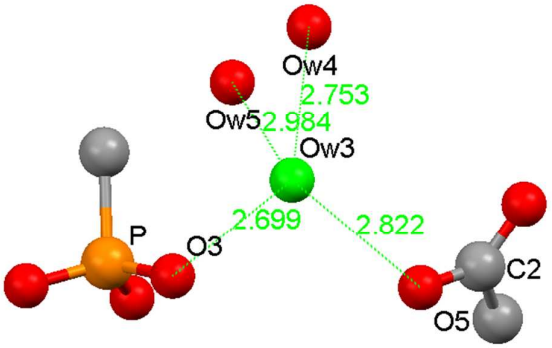

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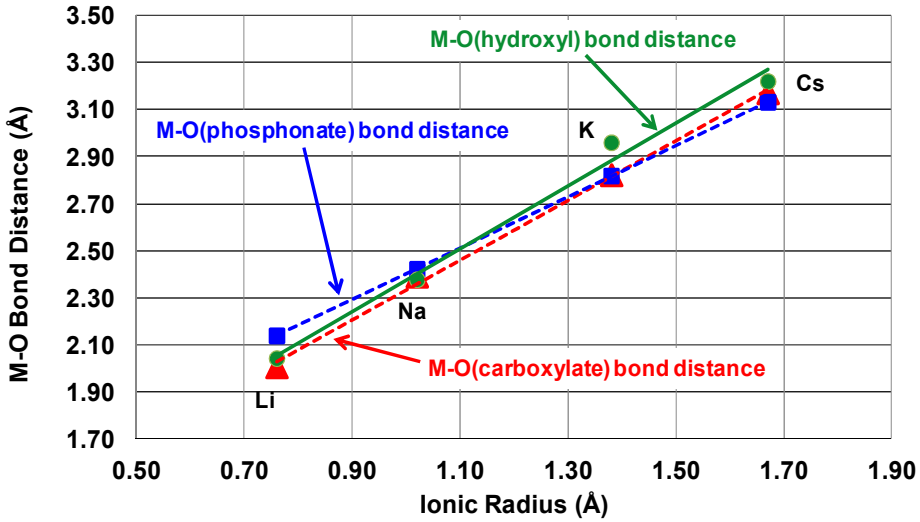

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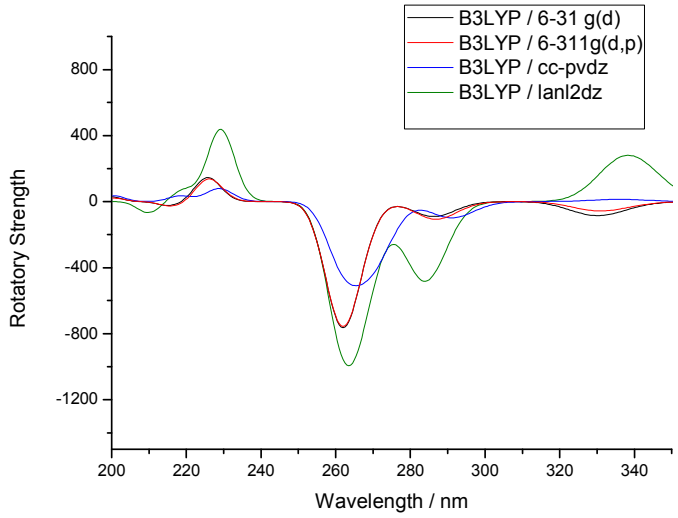

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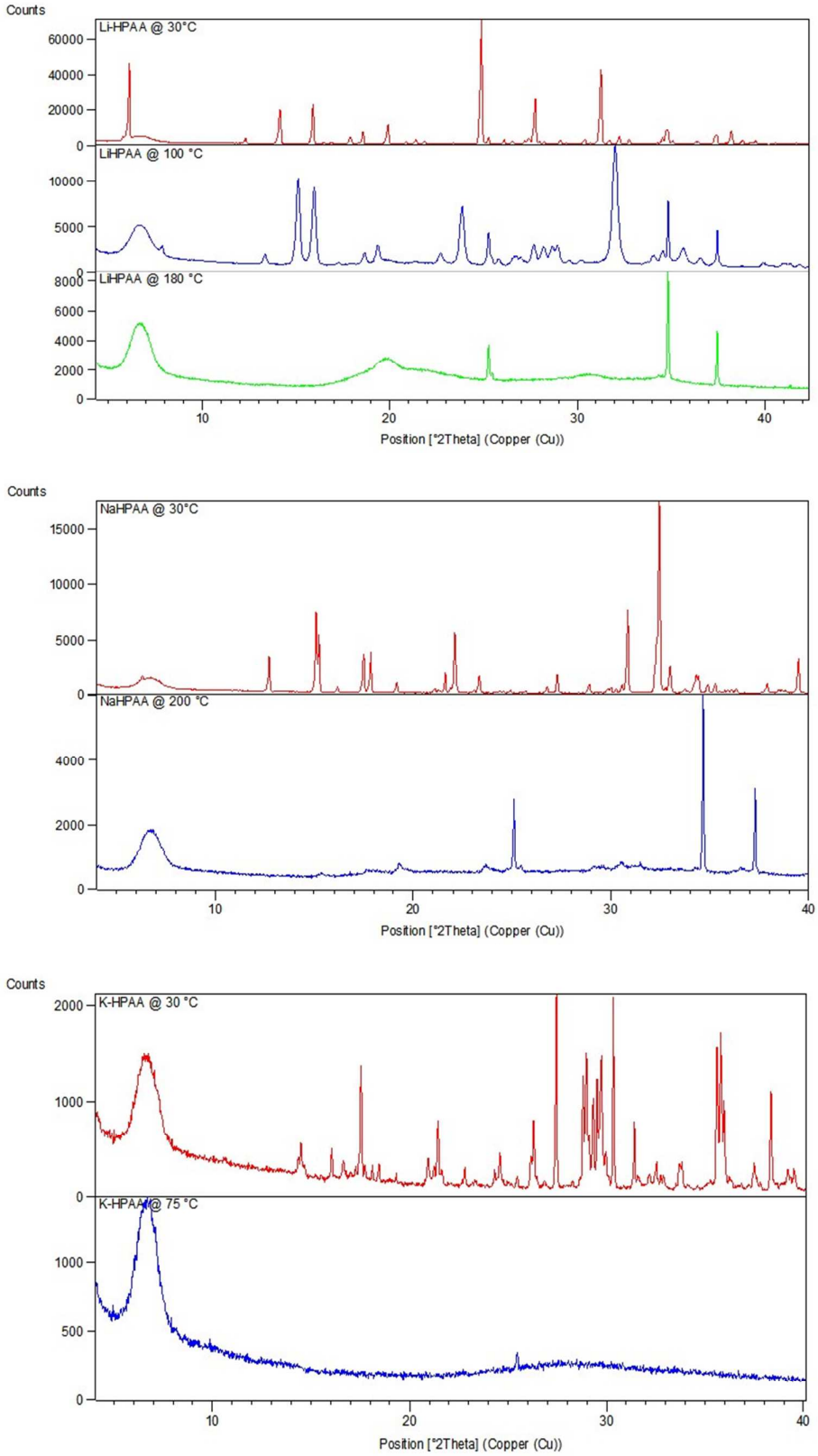

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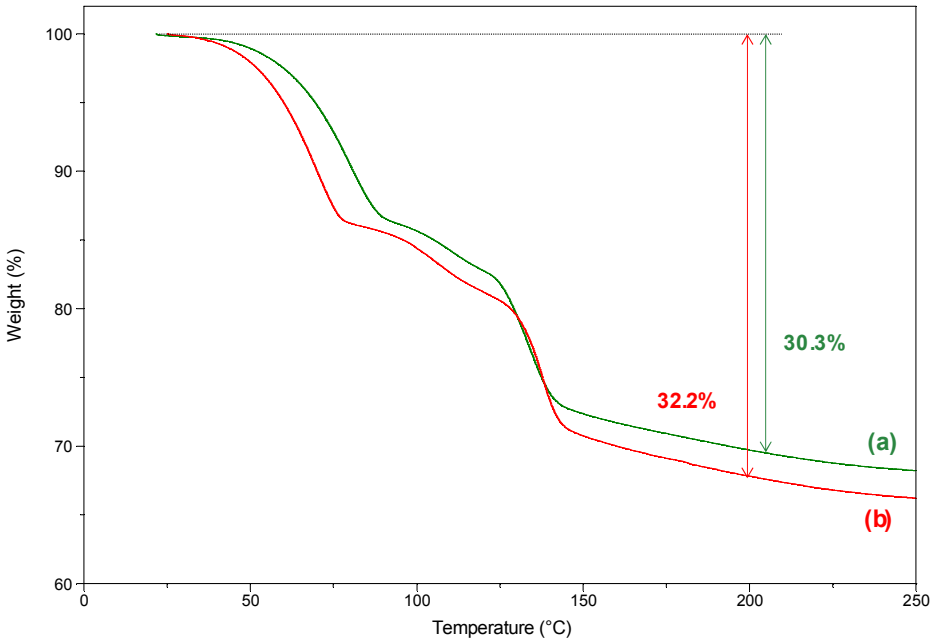

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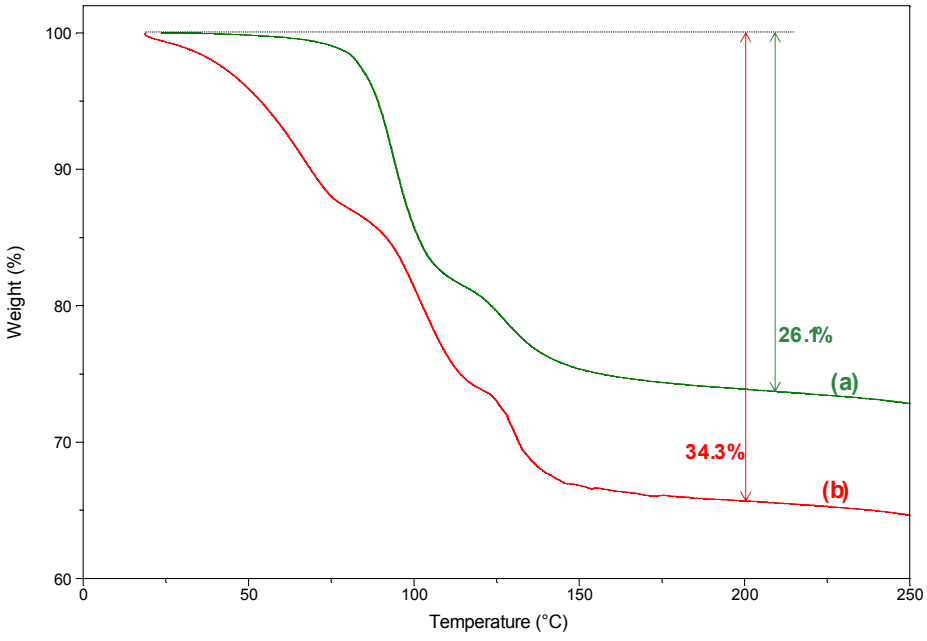

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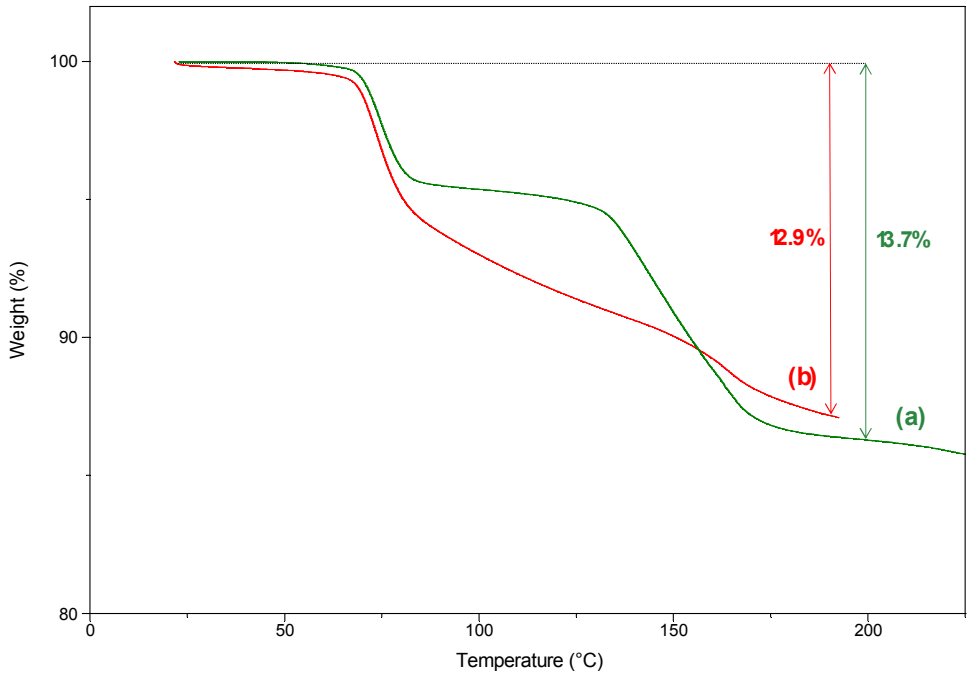

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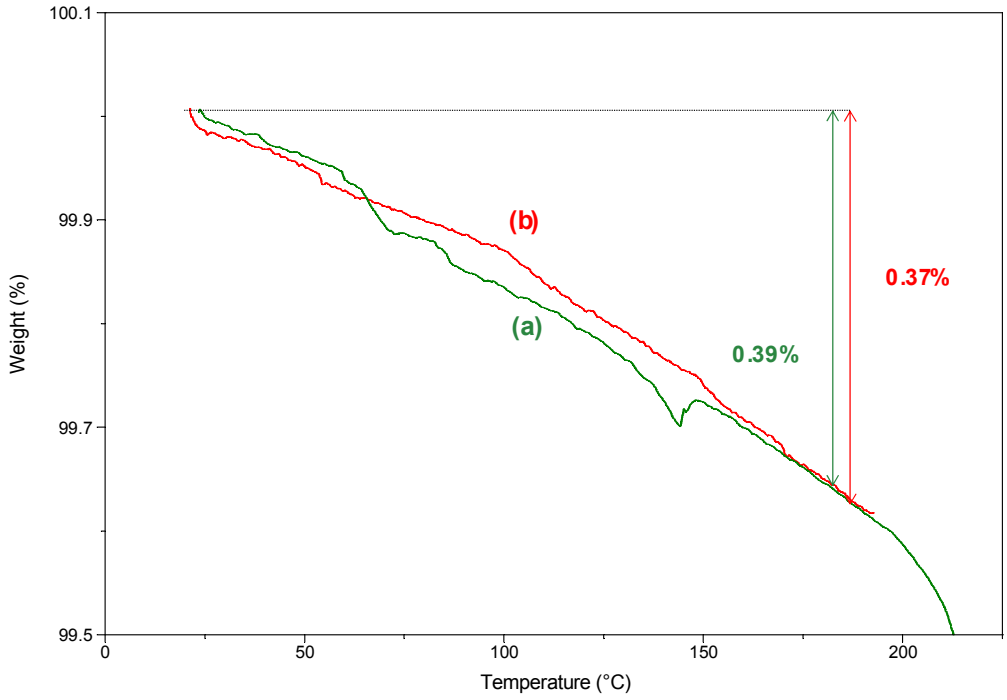

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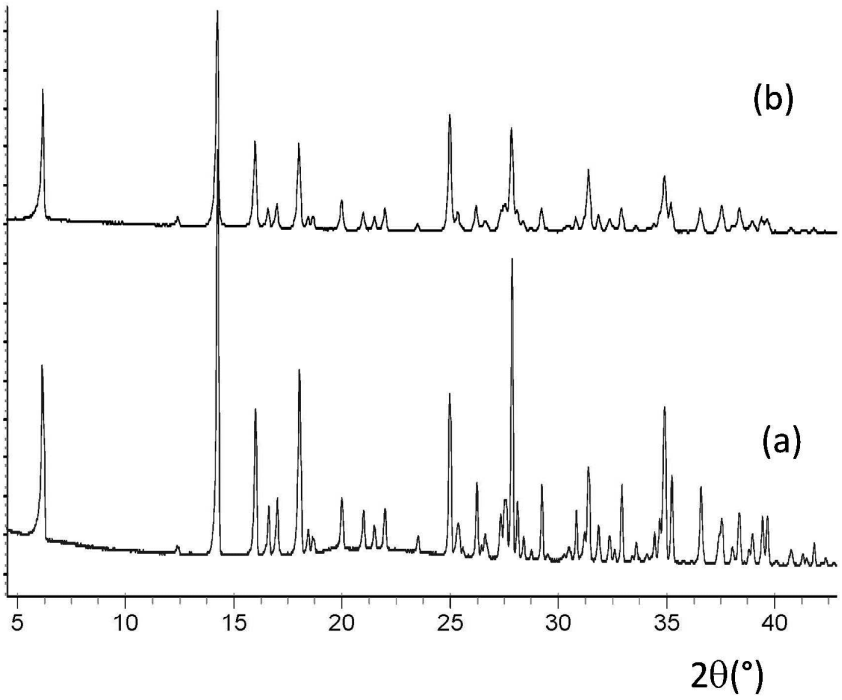

Figure S-11. Powder X-ray diffraction patterns for $[Li_3(HPAA)(H_2O)_4]\cdot H_2O$, Li-HPAA: (a) as synthesized and (b) after impedance analysis

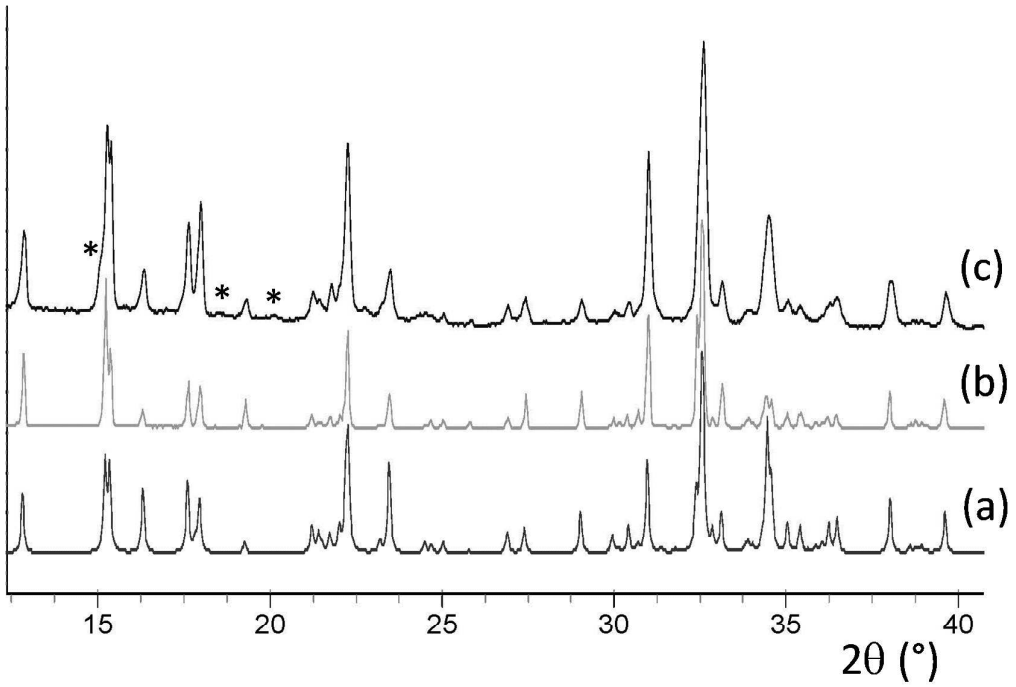

Figure S-12. Powder X-ray diffraction patterns for $Na_2(OOCCH(OH)PO_3H)(H_2O)_4$, Na-HPAA: (a) simulated from single crystal; (b) as synthesized and (c) after impedance analysis.

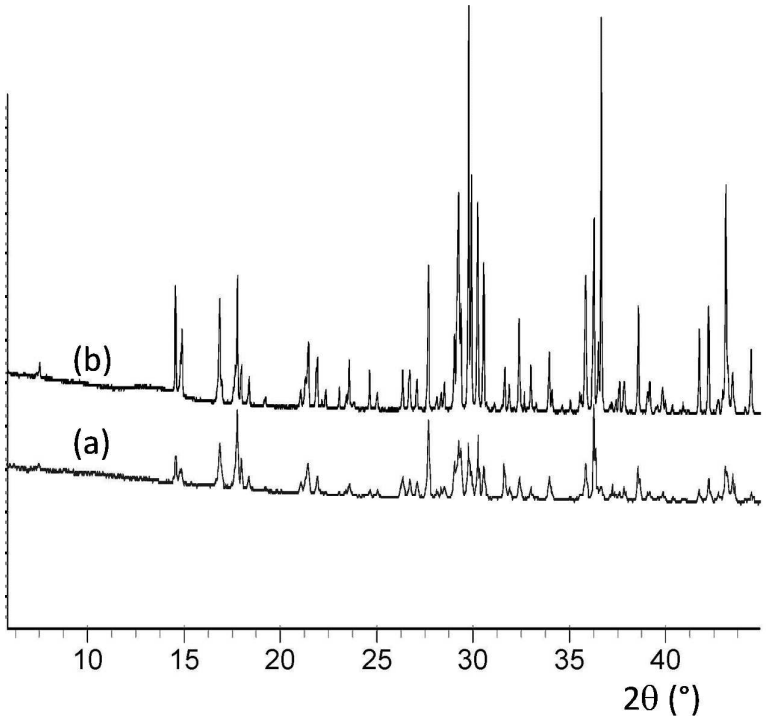

Figure S-13. Powder X-ray diffraction patterns for $K_2(OOCCH(OH)PO_3H)(H_2O)_2$, K-HPAA: (a) as synthesized and (b) after impedance analysis.

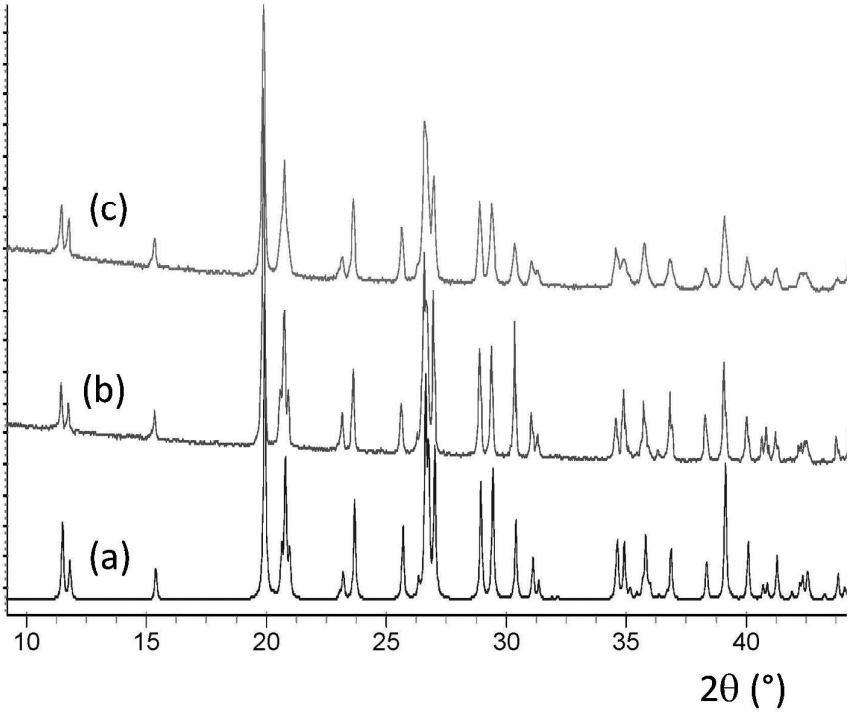

Figure S-14. Powder X-ray diffraction patterns $Cs(HOOCCH(OH)PO_3H)$, Cs-HPAA: (a) simulated from single crystal; (b) as synthesized and (c) after impedance analysis.

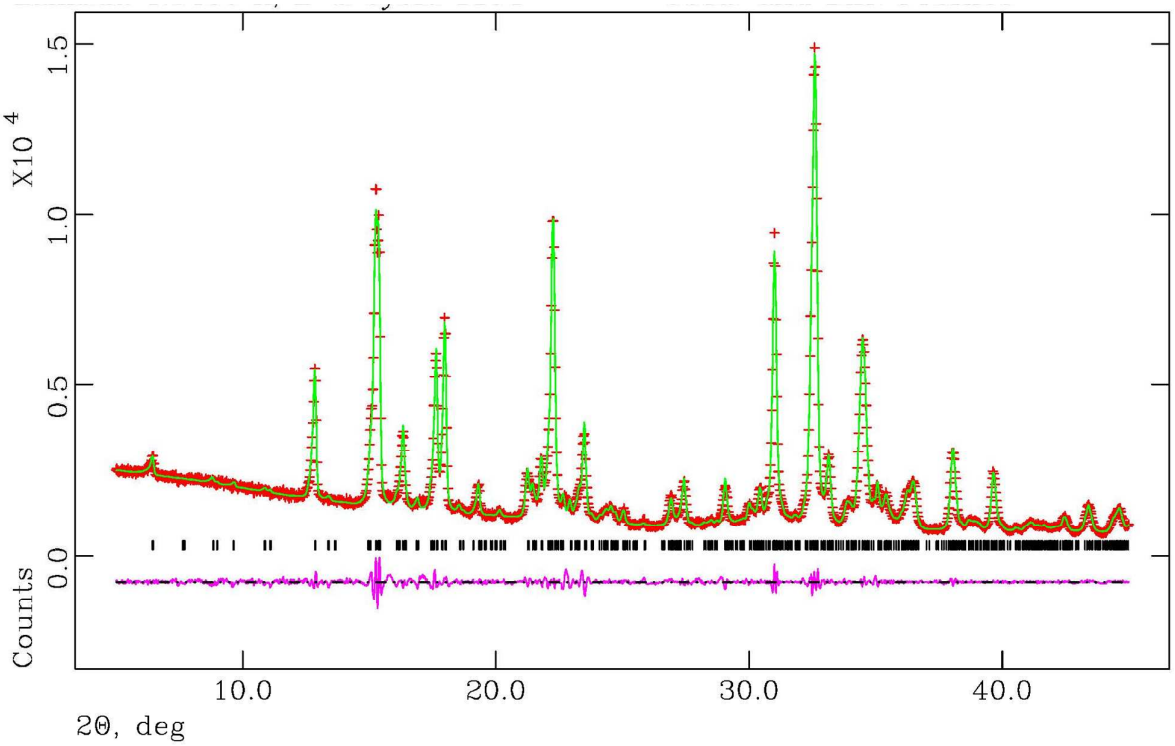

Figure S-15. Le Bail fit for $Na_2(OOCCH(OH)PO_3H)(H_2O)_4$ after impedance analysis. Final observed (crosses), calculated (solid line) and difference plots (in blue). Tick marks indicate calculated peak positions. Refined unit cell parameters: a = 11.8593(4) Å, b = 5.9084(2) Å, c = 28.117(1) Å, β = 100.984(2)°, V= 1934.1(1) $Å^3$ and s.g. P 2/m (R_{WP} = 0.0385 and R_P = 0.0258).

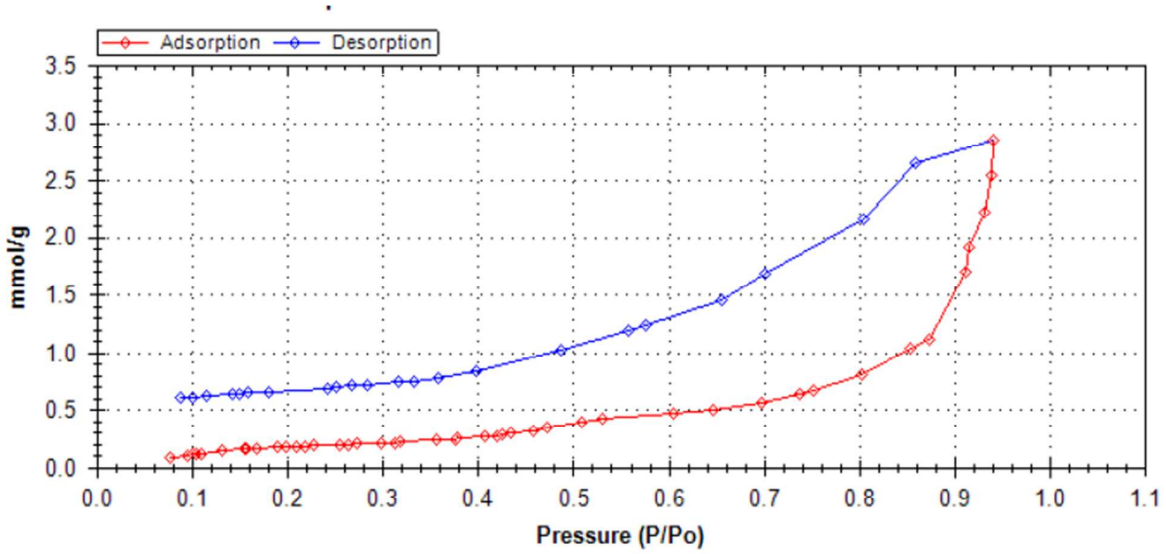

Figure S-16. Water vapor isotherm for $Na_2(OOCCH(OH)PO_3H)(H_2O)_4$ at 24 °C.

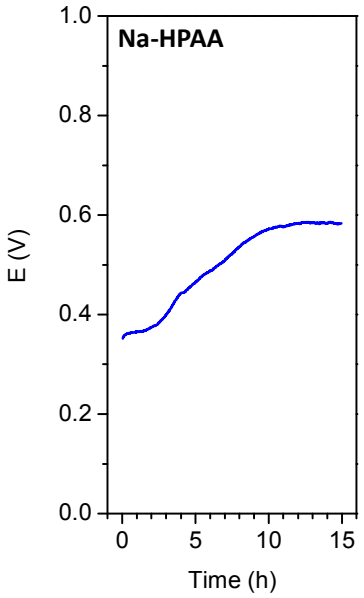

Figure S-17. Open Circuit Voltage curve of $Na_2(OOCCH(OH)PO_3H)(H_2O)_4$ at 24 °C and 98% relative humidity in flowing H_2 as fuel and static air as oxidant. Measurements were performed using Pt-C gas diffusion electrodes.

Table S-1. Selected bond distances (Å) for $[Li_3(OOCCH(OH)PO_3)(H_2O)_4]\cdot H_2O$, $Na_2(OOCCH(OH)PO_3H)(H_2O)_4$, $K_2(OOCCH(OH)PO_3H)(H_2O)_2$ and $Cs(HOOCCH(OH)PO_3H)$.

Li-HPAA, $[Li_3(OOCCH(OH)PO_3)(H_2O)_4]\cdot H_2O$					
Li_1-O5	2.209(14)	Li_2-O1	2.090(15)	Li_3-O1	1.966(15)
Li_1-O6	2.073(15)	Li_2-O2	2.001(15)	Li_3-O2	1.967(15)
Li_1-O4	2.044(15)	Li_2-Ow1	2.011(16)	Li_3-O5	1.949(15)
Li_1-Ow5	2.303(14)	Li_2-Ow2	1.986(15)	Li_3-Ow1	1.944(15)
Li_1-Ow4	2.099(16)				
Na-HPAA, $Na_2(OOCCH(OH)PO_3H)(H_2O)_4$					
Na(1)-O(11)	2.447(2)	Na(2A)-O(12)	2.390(2)	Na(2B)-O(12)$^{\#6}$	2.608(3)
Na(1)-O(10)	2.427(2)	Na(2A)-O(12)$^{\#5}$	2.547(3)	Na(2B)-O(9B)$^{\#3}$	2.428(5)
Na(1)-O(10)$^{\#1}$	2.473(2)	Na(2A)-O(13)	2.518(2)	Na(2B)-O(9B)	2.440(5)
Na(1)-O(2A)	2.439(3)	Na(2A)-O(9A)	2.435(3)	Na(2B)-O(6B)	2.361(6)
Na(1)-O(3A)$^{\#2}$	2.359(3)	Na(2A)-O(9A)$^{\#4}$	2.440(3)	Na(2B)-O(12)	2.385(3)
Na(1)-O(8A)	2.417(3)	Na(2A)-O(6A)	2.358(4)	Na(2B)-O(13)	2.529(3)
Na(1)-O(2B)	2.279(4)				
Na(1)-O(3B)$^{\#2}$	2.539(4)				
Na(1)-O(8B)	2.459(4)				
K-HPAA, $K_2(OOCCH(OH)PO_3H)(H_2O)_2$					
K_1-O17	2.983(6)	K2-O1	2.708(5)	K3-O15	2.821(6)
K_1-O1	2.863(5)	K2-O12	2.729(5)	K3-O3	2.706(5)
K1-O16	2.747(5)	K2-O14	2.944(6)	K3-O12	2.797(5)
K1-O2	2.810(5)	K2-O2	2.783(4)	K3-O6	2.790(5)
K1-O4	3.068(5)	K2-O4	2.995(5)	K3-O11	2.743(5)
K1-O5	2.965(5)	K2-O11	2.685(4)	K3-O13	3.020(4)
K1-O8	2.736(5)	K2-O13	2.868(5)	K3-O18	2.874(5)
K1-O7	2.908(4)				
K1-O16	3.255(5)				
K4-O3	2.904(5)	K4-O17	2.888(4)	K4-O18	2.863(5)
K4-O5	2.842(5)	K4-O8	3.016(5)		
K4-O7	2.874(5)	K4-O6	2.960(4)		
K4-O17	3.041(5)	K4-O16	2.780(5)		
Cs-HPAA, $Cs(HOOCCH(OH)PO_3H)$					
Cs-O(8)	3.062(6)	Cs-O(4)	3.470(6)	Cs-O(8)	3.130(6)
Cs-O(2)	3.117(5)	Cs-O(6)	3.470(6)	Cs-O(8)	3.287(6)
Cs-O(3)	3.128(6)	Cs-O(6)	3.224(5)	Cs-O(9)	3.117(6)

Table S-2. H-bond interactions (Å) for for **Li-HPAA**, $[Li_3(OOCCH(OH)PO_3)(H_2O)_4]\cdot H_2O$

Ow1_O1	3.158(13)
Ow1_O1	3.208(12)
Ow1_O2	2.892(12)
Ow1_O2	2.749(13)
Ow1_O3	2.508(12)
Ow1_O5	3.363(13)
Ow1_Ow2	3.032(12)
Ow1_Ow2	3.340(12)
Ow2_O1	2.844(12)
Ow2_O1	3.405(12)
Ow2_O3	2.718(12)
Ow3_O3	2.781(12)
Ow3_O5	2.847(13)
Ow3_Ow4	2.775(11)
Ow3_Ow5	3.389(13)
Ow3_Ow5	2.930(12)
Ow4_O4	3.384(13)
Ow4_O4	2.906(13)
Ow4_O6	2.660(13)
Ow4_O6	3.101(13)
Ow4_Ow4	2.986(18)
Ow4_Ow5	3.063(12)
Ow4_Ow5	2.954(13)
Ow5_O6	3.057(13)

Table S-3. Hydrogen bonds for **Na-HPAA**, $Na_2(OOCCH(OH)PO_3H)(H_2O)_4$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(11)-H(11A)...O(3A)#8	0.86	2.03	2.851(3)	159.5
O(11)-H(11A)...O(3B)#8	0.86	2.24	2.901(4)	133.9
O(11)-H(11B)...O(2A)#1	0.86	1.93	2.780(3)	170.6
O(11)-H(11B)...O(3B)#1	0.86	2.11	2.814(5)	138.2
O(12)-H(12A)...O(4A)#9	0.82	2.02	2.844(7)	172.7
O(12)-H(12A)...O(4B)#9	0.82	2.05	2.857(10)	166.3
O(12)-H(12B)...O(9A)#5	0.81	1.94	2.710(3)	157.4
O(10)-H(10A)...O(2B)#10	0.84	2.26	3.064(4)	159.1
O(10)-H(10B)...O(11)#11	0.85	2.01	2.844(3)	166.1
O(13)-H(13A)...O(4B)#3	0.85	1.97	2.787(7)	159.5
O(13)-H(13B)...O(8A)#5	0.85	1.99	2.785(3)	154.8
O(13)-H(13B)...O(8B)#5	0.85	2.26	2.797(4)	121.7
O(4A)-H(4A)...O(13)#3	0.82	1.95	2.740(5)	163.0
O(6A)-H(6A)...O(3A)	0.85	2.44	2.960(4)	120.1
O(6A)-H(6A)...O(8A)#7	0.85	2.05	2.759(4)	140.4
O(6B)-H(6B)...O(2B)	0.85	2.46	2.988(7)	121.0
O(6B)-H(6B)...O(8B)	0.85	2.12	2.756(7)	131.1
O(4B)-H(4B)...O(12)#12	0.82	2.14	2.857(10)	146.9

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,-z+1 #2 x,y+1,z #3 -x+2,y+1/2,-z+1/2

#4 -x+2,y-1/2,-z+1/2 #5 -x+1,y-1/2,-z+1/2 #6 -x+1,y+1/2,-z+1/2

#7 x,y-1,z #8 x-1,y+1,z #9 x-1,y,z #10 -x+3,-y+2,-z+1

#11 -x+2,-y+3,-z+1 #12 x+1,y,z

Table S-4. Hydrogen bonds for **K-HPAA**, $K_2(OOCCH(OH)PO_3H)(H_2O)_2$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5)...O(8)#2	0.87(8)	1.95(9)	2.816(7)	178(8)
O(6)-H(6)...O(1)#7	0.88(8)	1.94(9)	2.773(7)	158(8)

Symmetry transformations used to generate equivalent atoms:

#2 x,y+1,z #7 x,y-1,z

Table S-5. Hydrogen bonds for **Cs-HPAA**, Cs(HOOCCH(OH)PO_3H) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(3)-H(3)...O(4)#9	0.85	1.78	2.561(7)	151.4
O(6)-H(6)...O(4)#8	0.85	1.88	2.708(8)	165.3
O(9)-H(9)...O(2)#1	0.83	1.66	2.485(7)	172.2

Symmetry transformations used to generate equivalent atoms:

#1 -x,y-1/2,-z+3/2 #2 x-1,y-1,z #3 x-1,y,z

#4 x-1/2,-y+1/2,-z+1 #5 -x,y+1/2,-z+3/2 #6 x+1,y+1,z

#7 x+1/2,-y+1/2,-z+1 #8 x+1,y,z #9 x+1/2,-y+3/2,-z+1