Supporting Information for the manuscript:

New Architectures for Zirconium Polyphosphonates With a Tailor-Made Open Framework Structure

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Synthesis

1 and **2** were prepared according to Moedritzer-Irani method.[1]

3 was prepared as follows: a clear solution containing 0.05 mol L^{-1} of $ZrOCl_2 \cdot 8H_2O$, 0.1 mol L^{-1} of **1**, and 0.75 mol L^{-1} of HF was prepared using 1:2 (V/V) water/methanol as solvent. 50 mL of the reaction mixture were maintained at 80°C for 3 days in a closed Teflon bottle. The white solid formed was separated by centrifugation, washed three times with the same solvent used for the synthesis and dried at 75% r.h.

Analysis: Calcd. for $ZrP_4O_{16}N_2C_8H_{28}$ (found) Zr, 14.64 (14.9); P, 19.90 (20.12); N, 4.49 (4.45); C, 15.40 (15.31); H, 4.49 (4.23) %.

4 was prepared reacting 0.05 mol L^{-1} of $ZrOCl_2 \cdot 8H_2O$ with 0.05 mol L^{-1} of **2**, 0.25 mol L^{-1} of NaOH, and 0.5 mol L^{-1} of HF, using water as solvent. 50 mL of the reaction mixture were maintained at 80°C overnight in a closed Teflon bottle. The white solid formed was treated as above.

Analysis: Calcd. for $ZrNa_2P_4O_{17}N_2C_{10}H_{30}$ (found): Zr, 12.82 (12.75); P, 17.44 (17.30); N, 3.94 (3.88); C, 16.87 (16.70) ; Na, 6.47 (6.33); H, 4.22 (4.32) %.

Analytical procedures

Chemical analysis: C, N, and H contents were determined using a C. Erba 1106 Analyser.

Zirconium and phosphorus contents were determined as ZrO_2 and phosphates, respectively, after mineralisation of the samples.[2] Phosphates were determined by ion chromatography using a Dionex 2000 i/sp instrument. Na was determined by atomic emission spectrophotometry using a Perkin Elmer 3100 instrument.

Crystal structure determination and refinement: X-ray powder diffraction patterns were collected on a Philips X'PERT APD Bragg-Brentano diffractometer, PW3020 goniometer (CuKα, λ = 1.5418 Å) equipped with a graphite monochromator in the diffracted beam. The generator was operated at 40 kV and 40 mA. Unit cell parameters were determined using the TREOR program.[3]

The structural determination of **3** and **4** was performed using the direct space global optimisation methods, implemented in the FOX program.[4] The building blocks used were one Zr atom and one half of the tetraphosphonic group, described in terms of restrained bond lengths and angles. These were left to freely change within a 0.15 Å and 10° range from their literature values, respectively. These models were optimised over their diffraction patterns using integrated *wRp* value as the cost function. The Parallel Tempering algorithm[5] was used in order to find the global minimum of the cost function that corresponded to the correct solution. Extraframework water molecules and Na ions were found using difference Fourier calculations alternating with Rietveld refinement cycles.

Rietveld refinements were performed using the GSAS program.[6] Cell parameters, sample displacement, background and profile were first refined, then atomic coordinates and isotropic displacement factors were also refined. A 6 term Pseudo-Voigt profile function, with 2 terms for the modelling of asymmetry at low angles, was used. For both compounds, atomic parameters were refined applying the following bond distance restraints: Zr-O 2.05(5) Å, P-O 1.56(3) Å, P-C 1.83(3) Å, C-N 1.54(5) Å, C-C 1.45(5) Å, in order to avoid divergence at the first stages of the refinement. The statistical weight of these restraints was decreased as the refinement proceeded, but it was not possible to set it to zero, due to some unrealistic light atom bond distances. Isotropic thermal factors for Zr and P were refined freely. Isotropic displacement factors of the light atoms (C, N, O) in **3** were refined constraining the program to apply the same shifts while those of **4** were fixed and not refined.

At the end of the refinement, the shifts in all parameters were less than their standard deviations.

The final Rietveld plots for **3** and **4** are reported in Figures 1s and 2s, while their asymmetric units are shown in Figures 3s and 4s, respectively. Tables 1s - 5s report the significant crystallographic data for the two compounds.

Table 1s Crystal data and refinement details for **3** and **4**

Sample code	**3**	**4**
Empirical formula	$Zr_1\ P_4\ O_{16}\ C_8\ N_2\ H_{28}$	$Zr_1\ P_4\ O_{17}\ C_{10}\ N_2\ Na_2\ H_{32}$
Formula weight	623.2	713.2
Crystal system	Monoclinic	Monoclinic
Space group	*P* 2/*c*	*C* 2/*c*
a/Å	10.7337(3)	18.923(1)
b/Å	12.8604(3)	16.5046(7)
c/Å	7.8919(2)	7.8437(3)
β/°	104.91(2)	91.868(3)
V/Å^3	1052.71(4)	2448.46(5)
Z	2	4
Calculated density/g·cm^{-3}	1.880	1.848
N. of data	6800	6332
N. of reflections	1997	2099
N. of variables	82	83
N. of restraints	16	44
R_p [a]	0.066	0.082
R_{wp} [b]	0.088	0.110
R_F2 [c]	0.040	0.082
χ [d]	3.13	3.87

[a] $R_p = \Sigma\ |I_o\text{-}I_c| / \Sigma\ I_o$; [b] $R_{wp} = [\Sigma\ w(I_o\text{-}I_c)^2 / \Sigma\ wI_o^2]^{1/2}$; [c] $R_F2 = \Sigma\ |F_o^2 - F_c^2| / \Sigma\ |F_o^2|$; [d] $\chi = [\Sigma\ w(I_o\text{-}I_c)^2 / (N_o - N_{var})]^{1/2}$

Table 2s Fractional coordinates and thermal factors for **3**

Atom name	x/*a*	y/*b*	z/*c*	U_{iso}x100
Zr(1)	0	0.1329(2)	0.25	1.05(7)
P(2)	0.2252(4)	0.3241(3)	0.1807(6)	1.8(2)
P(3)	0.1911(4)	0.0837(3)	-0.3283(5)	1.5(2)
O(4)	0.1298(7)	0.2397(6)	0.190(1)	2.2(1)
O(5)	0.1989(8)	0.4269(6)	0.265(1)	2.2
O(6)	0.3616(7)	0.2761(6)	0.261(1)	2.2
O(7)	0.3247(8)	0.0560(6)	-0.358(1)	2.2
O(8)	0.0980(8)	0.1391(7)	-0.4804(7)	2.2
O(9)	0.1227(7)	-0.0139(5)	-0.289(1)	2.2
C(10)	0.206(1)	0.3496(9)	-0.066(1)	2.2
C(11)	0.197(1)	0.1743(9)	-0.143(2)	2.2
N(12)	0.257(1)	0.2738(8)	-0.165(1)	2.2
C(13)	0.398(1)	0.2780(9)	-0.147(1)	2.2
C(14)	0.4281(7)	0.3619(9)	-0.263(2)	2.2
OW1	0.5747(6)	0.1023(5)	0.1215(9)	2.2
OW2	0.1150(7)	0.3974(6)	-0.4289(9)	2.2

Table 3s Selected bond distances and angles for **3**

Bond	Lenght/ Å	Angle	Amplitude/deg.
ZR(1)-O(4)	2.097(5)	O(4)-P(2)-O(5)	113.2(6)
ZR(1)-O(8)	2.119(5)	O(4)-P(2)-O(6)	105.9(5)
ZR(1)-O(9)	2.091(5)	O(4)-P(2)-C(10)	105.8(6)
P(2)-O(4)	1.507(6)	O(5)-P(2)-O(6)	114.9(6)
P(2)-O(5)	1.539(7)	O(5)-P(2)-C(10)	107.9(5)
P(2)-O(6)	1.564(7)	O(6)-P(2)-C(10)	108.7(6)
P(2)-C(10)	1.94(1)	O(7)-P(3)-O(8)	115.5(5)
P(3)-O(7)	1.553(8)	O(7)-P(3)-O(9)	110.7(5)
P(3)-O(8)	1.527(7)	O(7)-P(3)-C(11)	114.6(6)
P(3)-O(9)	1.526(6)	O(8)-P(3)-O(9)	107.0(5)
P(3)-C(11)	1.86(1)	O(8)-P(3)-C(11)	102.1(5)
N(12)-C(10)	1.44(1)	O(9)-P(3)-C(11)	106.0(5)
N(12)-C(11)	1.46(1)	C(10)-N(12)-C(11)	107.(1)
N(12)-C(13)	1.49(2)	C(10)-N(12)-C(13)	116(1)
C(14)-C(13)	1.50(1)	C(13)-C(14)-C(14)	107.2(9)
C(14)-C(14)#2	1.50(2)		
H-bonds			
O(6)...OW1	2.45(1)		
O(7)...OW1#1	2.61(1)		
OW2...N(12)#2	2.75(1)		
OW2...O(5)	2.79(1)		
OW2...O(5) #3	2.75(1)		
O(3)….OW1#2	2.47(2)		

#1 1-x, y, -0.5-z
#2 -x, y, 0.5-z
#3 x, 1-y, -1+z.

Table 4s Atomic coordinates and isotropic thermal factor for **4**

Atom type	x/*a*	y/*b*	z/*c*	U_{iso} x100
Zr(1)	0	0.8914(2)	0.75	2.0(1)
P(1)	0.0672(4)	0.7236(4)	-0.0114(8)	4.8(3)
P(2)	0.1045(4)	0.9460(4)	0.4063(9)	3.4(3)
O(1)	0.0629(5)	0.8014(5)	-0.137(1)	4.5
O(2)	0.0837(8)	0.6472(6)	-0.120(1)	4.5
O(3)	-0.0016(5)	0.7084(9)	0.063(1)	4.5
O(4)	0.1717(5)	0.9680(7)	0.504(1)	4.5
O(5)	0.0660(5)	1.0237(5)	0.353(1)	4.5
O(6)	0.0570(6)	0.8973(8)	0.538(1)	4.5
C(1)	0.1190(8)	0.8753(7)	0.236(1)	4.5
C(2)	0.1823(7)	0.789(1)	0.432(1)	4.5
C(3)	0.2534(8)	0.804(1)	0.345(2)	4.5
C(4)	0.1872(7)	0.705(1)	0.510(2)	4.5
C(5)	0.1365(7)	0.737(1)	0.157(1)	4.5
N(1)	0.1245(6)	0.790(1)	0.298(2)	4.5
Na	0.2639(5)	0.956(1)	0.780(1)	4.5
Ow2	0.0386(6)	0.4437(5)	-0.0489(7)	4.5
Ow3	0.1505(7)	0.5107(8)	-0.088(2)	4.5
Ow1	0	0.453(1)	0.25	4.5

Table 5s Selected bond distances and angles for **4**

Bond	Distance/Å	Bond	Angle/deg.
Zr(1)-O(1)	2.082(7)	O(1)-Zr(1)-O(1)	89.1(5)
Zr(1)-O(5)	2.028(7)	O(1)-Zr(1)-O(5)#3	176.8(5)
Zr(1)-O(6)	2.016(8)	O(1)-Zr(1)-O(5)	89.2(3)
P(1)-O(1)	1.619(7)	O(1)-Zr(1)-O(6)	94.1(4)
P(1)-O(2)	1.561(8)	O(1)-Zr(1)-O(6)#4	89.9(4)
P(1)-O(3)	1.467(8)	O(1)-Zr(1)-O(5)	176.8(5)
P(1)-C(5)	1.824(9)	O(1)-P(1)-O(2)	108.3(6)
P(2)-O(5)	1.526(9)	O(1)-P(1)-O(3)	110.6(8)
P(2)-O(4)	1.506(8)	O(1)-P(1)-C(5)	111.0(7)
P(2)-O(6)	1.60(1)	O(2)-P(1)-O(3)	106.1(8)
P(2)-C(1)	1.803(9)	O(3)-P(1)-C(5)	109.4(7)
N(1)-C(1)	1.495(10)	O(5)-P(2)-C(1)	111.2(8)
N(1)-C(2)	1.493(9)	O(5)-P(2)-O(4)	108.9(7)
N(1)-C(5)	1.45(1)	O(5)-P(2)-O(6)	108.9(8)
C(3)-C(2)	1.53(1)	C(1)-P(2)-O(4)	112.6(8)
C(3)-C(4)	1.56(1)	O(4)-P(2)-O(6)	106.0(8)
C(2)-C(3)	1.54(1)	C(1)-N(1)-C(5)	109(1)
C(2)-C(4)	1.52(1)	C(1)-N(1)-C(2)	106(1)
Na-O(4)	2.75(2)	C(3)-N(1)-O(6)	108.1(7)
Na-O(4)#2	2.81(2)	C(5)-N(1)-C(2)	112.8(9)
Na-Ow3	2.42(1)	C(2)-C(3)-C(4)	108(1)
Na-Ow3#1	2.92(2)	N(1)-C(2)-C(3)	109(1)
H bonds		N(1)-C(2)-C(4)	109(1)
Ow3...Ow2	2.42(2)		
Ow1...Ow2	2.48(1)		
Ow1...Ow2#2	2.52(1)		
Ow2...Ow2#1	2.45(1)		
Ow1...O(2)	2.49(2)		
N(1)...O(3)#3	2.95(2)		

Simmetry codes
#1: 0.5-x, 0.5-y, -z
#2: -x, -y, -z
#3: x, 1-y, 0.5+z
#4: -x, y, 0.5-z

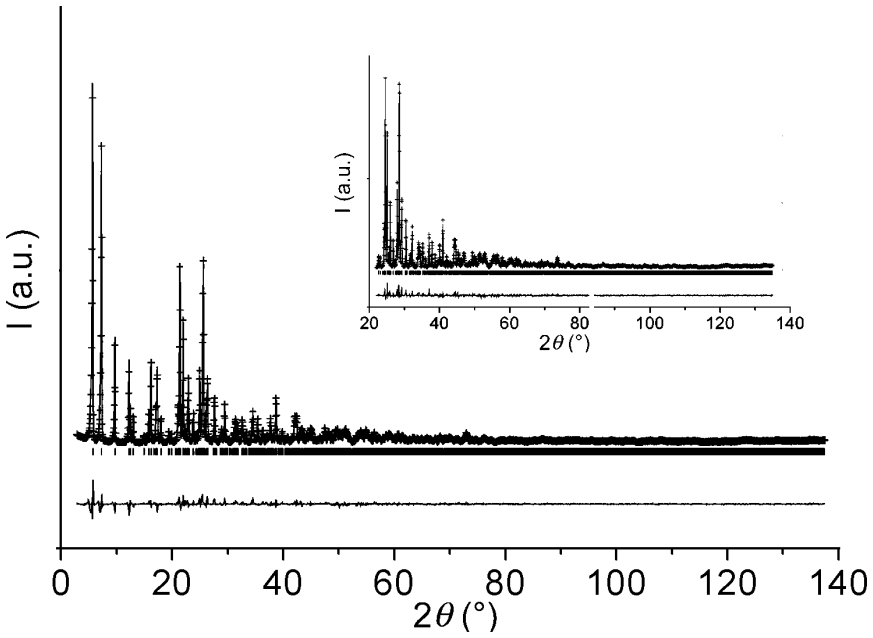

Figure 1s. Rietveld and difference plot for **3.** The insert shows the high-angle region.

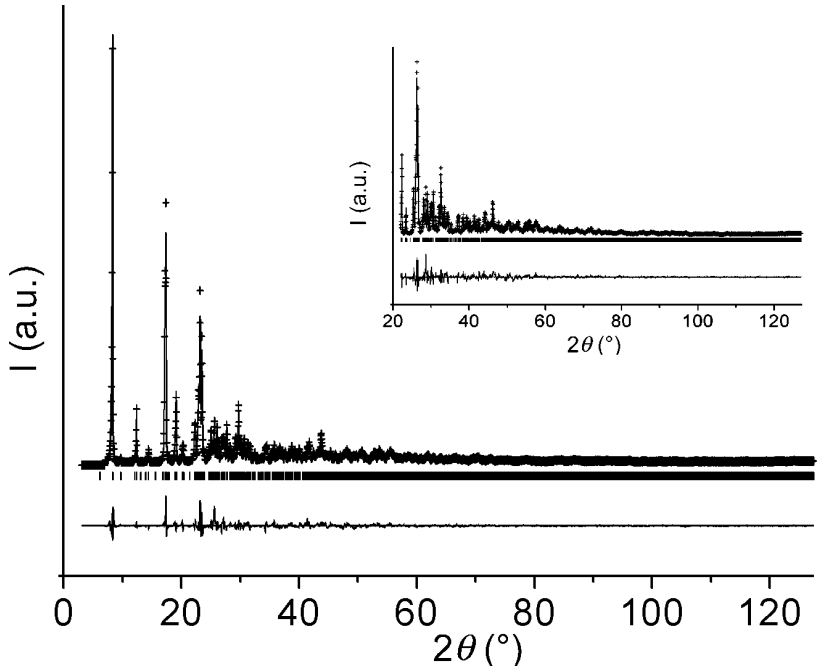

Figure 2s. Rietveld and difference plot for **4.** The insert shows the high-angle region.

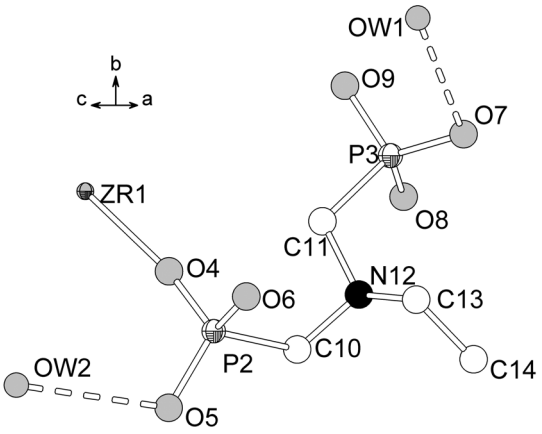

Figure 3s. Asymmetric unit and labelling scheme for **3**.
Thermal displacement spheres are drawn at the 50% probability level.

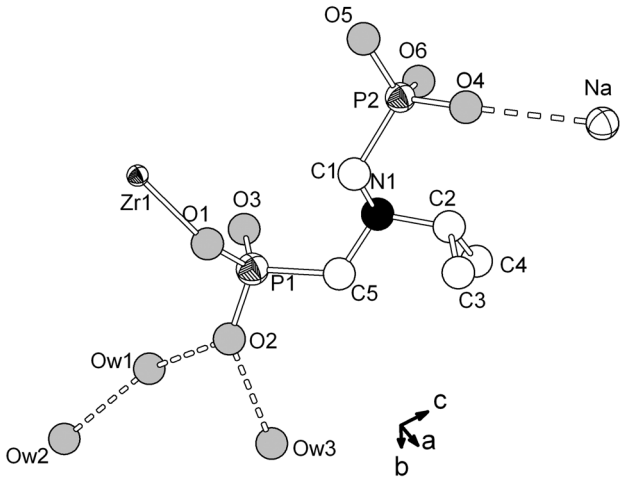

Figure 4s. Asymmetric unit and labelling scheme for **4.**
Thermal displacement spheres are drawn at the 50% probability level.

Thermal Analysis: Coupled TG-DTA measurements were performed using a Netzsch STA490C thermoanalyser with a heating rate of 5°C min^{-1} under a 20 mL min^{-1} air flux.

Figures 5s and 6s show the coupled TG and DTA curve for **3** and **4.**

Compound **3**: The first weight loss, at about 100°C (11.1%) is due to the crystallization water loss.

The second weight loss starts around 280°C up to 580°C and is correlated to a sharp exothermic peak on the DTA curve. It should be ascribed to the decomposition of organics together with P_2O_5 loss from the phosphorus excess. At the end of the analysis (1200°C) only cubic ZrP_2O_7 was found. The calculated weight loss (57.48%) is in good agreement with the experimental value (56.45%)

Compound **4**: The first weight loss (12.0%) is related to the loss of crystallization water. This first weight loss is divided in two steps: the first one (at about 100°C) corresponds to the loss of about four water molecules while the second one (at about 150°C) should be due to the loss of the fifth water molecule. This behaviour may depend on the different interactions of the water molecules inside the extra-framework region.

The second step (about 300°C) can be related to the combustion of the organic part, after that, weight continues to be lost up to about 1000°C. At the end of the analysis the $NaZr_2(PO_4)_3$ phase was observed.

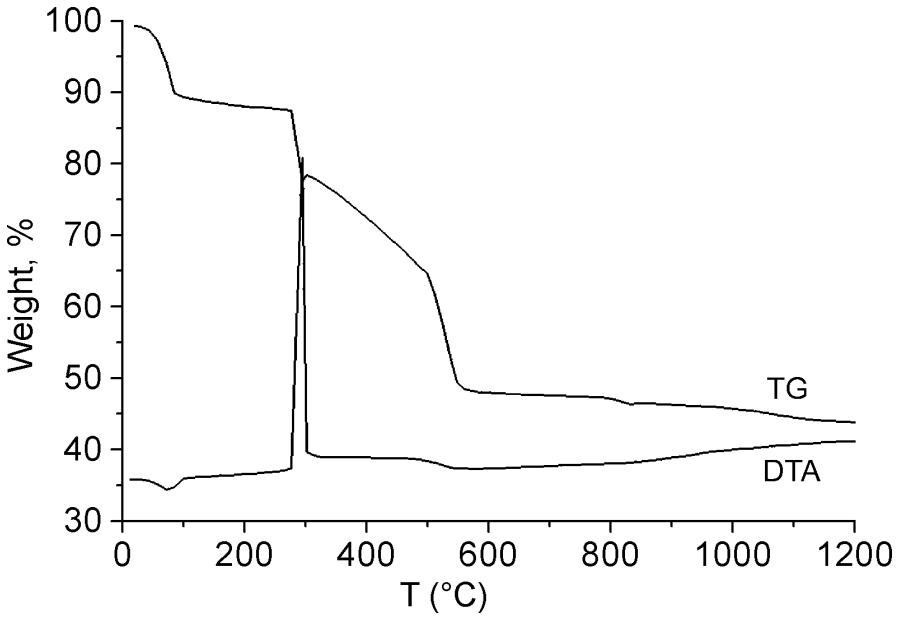

Figure 5s. Coupled TG and DTA curves for **3**.

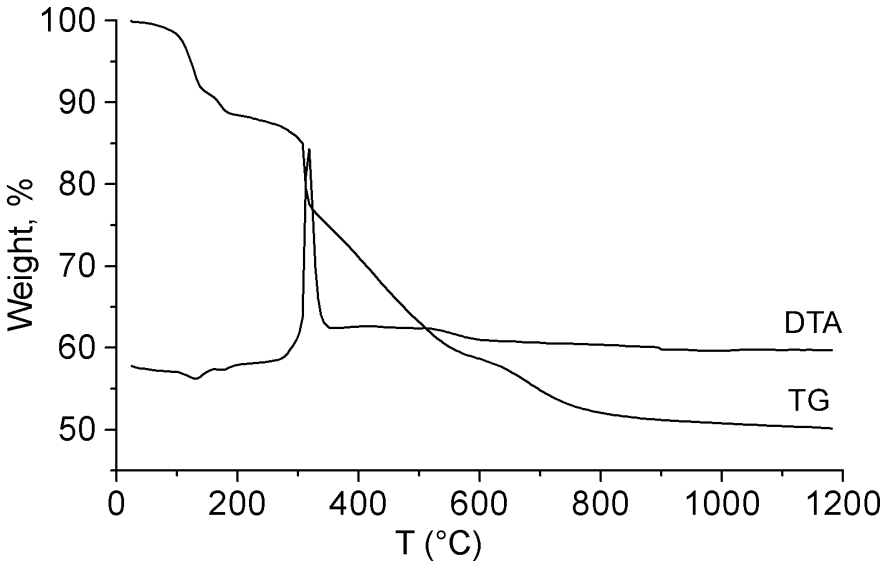

Figure 6s. Coupled TG and DTA curves for **4**.

Ion exchange properties: Figure 7s shows the titration curves related to the ion exchange with Na^+/H^+ and Li^+/H^+ for **3.** The solid was titrated with 0.1 M NaOH or 0.1 M LiOH in the presence of the respective 1M chloride salts. In both titration curves, after a first pH increase, a long plateau is observed, assessing the occurrence of the ion exchange process, until an inflexion point is reached. The total upload is close to 2 mol of cation per mol of compound, showing the presence of two protons of similar acidic strength. The high pH value needed for cation exchange may be related to a high activation energy required for the process, that should be due to the high rigidity of layers.

Figure 8s shows the XRPD patterns of Na- and Li-exchanged phases.

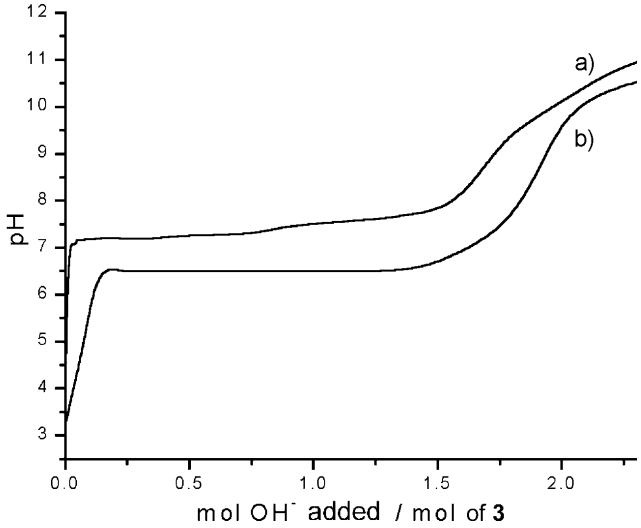

Figure 7s. Titration curves of **3** with 0.1 M NaOH a) and LiOH b) in the presence of 1M added salt.

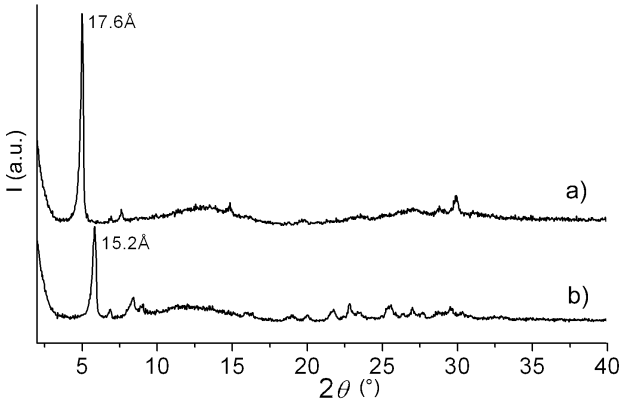

Figure 8s. XRPD patterns of **3** after Na^+ a) and Li^+ b) exchange processes.

References

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