

Investigating the effect of positional isomerism on the assembly of zirconium phosphonates based on tritopic linkers

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ELECTRONIC SUPPLEMENTARY INFORMATION

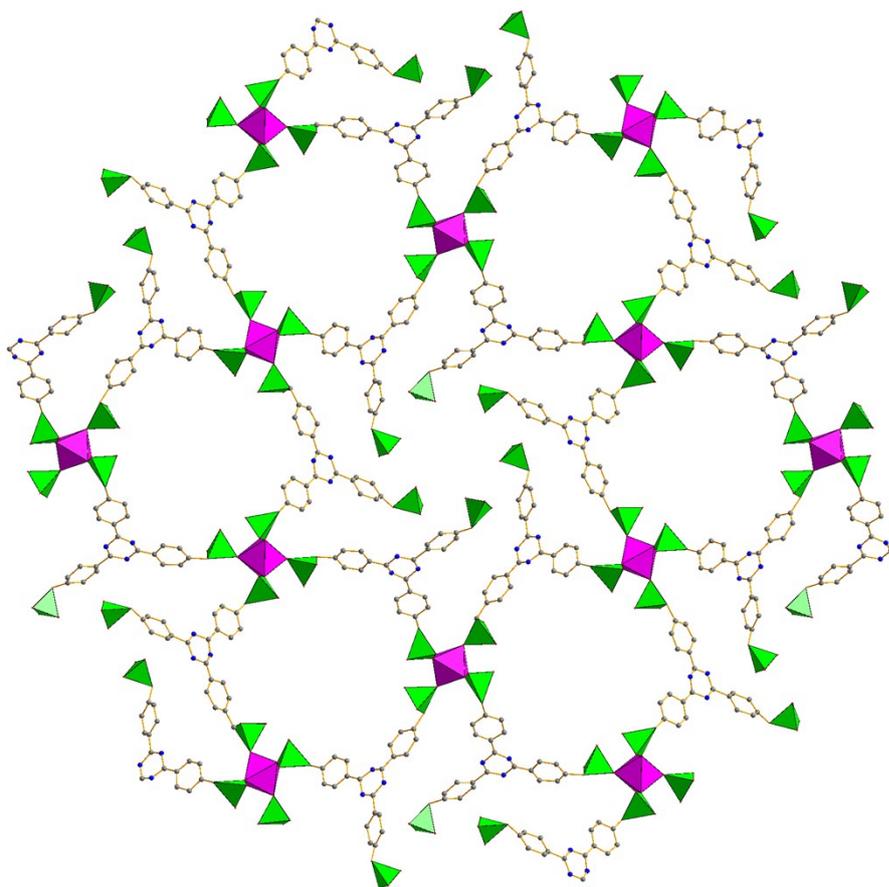


Figure S1. Crystal structure of UPG-1 seen along the *c* axis. Colour code: Zr, pink; P, green; N, blue; O, red; C, grey. Solvent molecules were removed for the sake of clarity.

Experimental Section

Chemicals.

Zirconium oxide chloride octahydrate was obtained from Merck Millipore. 3-bromomethylbenzonitrile, trifluoromethanesulfonic acid and chlorotrimethylsilane were obtained from Fluorochem. Triethylphosphite was obtained from VWR. Potassium iodide, concentrated ammonium hydroxide, isopropanol, hexane, diethyl ether, hydrofluoric acid and anhydrous acetonitrile were obtained from Sigma-Aldrich. Methanol was obtained from Carlo Erba Reagenti. All chemicals were used as received, with no further purification.

Analytical methods.

Nuclear magnetic resonance (NMR): ^1H and ^{31}P NMR spectra were recorded on a Bruker AV-500 instrument. All chemical shifts are reported in ppm and coupling constants are reported in Hz.

Mass spectrometry (MS): MS data for *mttbmBr* was acquired by atmospheric pressure chemical ionisation (APCI) via an atmospheric solids analysis probe (ASAP) on a Waters Xevo G2-S instrument. A small amount of solid sample was transferred to the tip of a glass capillary, which was then placed

within the ASAP source and inserted into the instrument. The vaporizer temperature was increased to 450°C, at which point ions were observed and acquired. Data was processed using vendor MassLynx software. MS data for Et₆mttbmp was acquired by positive mode nano-electrospray ionisation (nESI) via and Advion TriVersa NanoMate on a Thermo Fisher Scientific LTQ Orbitrap. The sample was prepared by dissolving in dichloromethane (DCM; HPLC grade, Fisher Scientific) and diluting into a solution of ammonium acetate (NH₄OAc; Sigma-Aldrich) in methanol (MeOH; HPLC grade, Fisher Scientific). An aliquot was loaded into the NanoMate microtiter plate well and infused into the Orbitrap instrument for acquisition. The Orbitrap tube lens voltage was +150V. Data was processed using vendor Xcalibur software. MS data for H₆mttbmp mass spectrometry data was acquired by negative mode nano-electrospray ionisation (nESI) via and Advion TriVersa NanoMate on a Thermo Fisher Scientific LTQ Orbitrap. The sample was prepared by dissolving in a 1:1 (v:v) mixture of water:methanol (H₂O:MeOH; HPLC grade, Fisher Scientific) or 1:1 (v:v) mixture of water:acetonitrile (H₂O:MeCN; HPLC grade, Fisher Scientific), respectively, and diluting into a solution of diethyl amine (DEA; Sigma-Aldrich) in MeOH. An aliquot was loaded into the NanoMate microtiter plate well and infused into the Orbitrap instrument for acquisition. The Orbitrap tube lens voltage was –100V. Data was processed using vendor Xcalibur software.

Attenuated-total reflectance infrared (ATR-IR) spectroscopy: a Thermo Scientific Nicolet iS10 FT-IR Spectrometer was used to collect the ATR-IR spectra of all samples. Spectra were recorded in the 650 – 4000 cm⁻¹ region with 16 scans.

Elemental analysis: The zirconium and phosphorus contents were obtained by inductively coupled plasma optical emission spectroscopy using a Varian Liberty Series II instrument working in axial geometry, after mineralization of the sample with concentrated hydrofluoric acid. The carbon, hydrogen, and nitrogen contents were obtained with an EA 1108 CHN Fisons instrument.

Thermogravimetric analysis (TGA): TGA was performed using a Netzsch STA490C thermoanalyser under a 20 mL min⁻¹ air flux with a heating rate of 5 °C min⁻¹.

Powder X-ray diffraction (PXRD): the PXRD pattern for structure solution and Rietveld refinement was collected in the 4-80 °2θ range, with 0.017 ° step size and 150 s step⁻¹ counting time, using the Cu Kα radiation on a PANalytical X'PERT PRO diffractometer, PW3050 goniometer, equipped with an X'Celerator detector. The long fine focus (LFF) ceramic tube operated at 40 kV and 40 mA.

Proton conductivity and water uptake: Conductivity measurements were carried out on pellets of pressed powder by impedance spectroscopy as described elsewhere.¹ The pellet conductivity was determined at 100 °C and decreasing relative humidity (RH) from 95% to 40%. All of the conductivity values here reported refer to measurements carried out after the conductivity had reached a constant

value for at least 2 hours. Water uptake at 100 °C, and RH of 40% and 100%, was determined by means of a cell, having the same size and shape as the conductivity cell, where the pellet holder was replaced by a glass container hosting the sample.¹ After one day equilibration at the desired RH value, the water content was calculated on the basis of the weight change after sample drying at 120 °C, by taking into account the amount of water trapped in the sample container at the temperature and RH of the experiment.

Synthesis of 2,4,6-tris[3'-(bromomethyl)phenyl]-1,3,5-triazine (mttbmBr).

3-bromomethylbenzonitrile (5 g, 6.38 mmol) was placed in a 100 mL Schlenk flask and kept in a water-ice bath. Trifluoromethanesulfonic acid (5 mL) was progressively added under N₂. After the addition, the flask was closed, and the mixture was warmed to room temperature and stirred for 20 h. Then, the mixture was poured in ice and neutralised with concentrated ammonium hydroxide. The solid phase was collected by filtration and washed with water and ethanol. The white solid was dried in a hot air oven at 60 °C. 4.95 g of product was recovered (Yield: 99%).

¹H NMR (CDCl₃, 500 MHz): δ = 8.74 – 8.61 (m, 6H, aromatic), 7.61 (m, 3H, aromatic), 7.52 (m, 3H, aromatic), 4.62 (s, 6H, *Ph*-CH₂-Br) ppm (Figure S2).

The low solubility of mttbmBr in the deuterated solvents we have available in our laboratory (CDCl₃, CD₃OD, *d*₆-DMSO) prevented us from obtaining well resolved ¹³C NMR and HSQC spectra.

Mass spectrometry: 585.9136 m/z [M+H]⁺ (Figure S3).

Attenuated total reflectance infrared (ATR-IR) analysis also clearly shows that the 3-bromomethylbenzonitrile starting material and the mttbmBr product produce very different spectra (Figure S6).

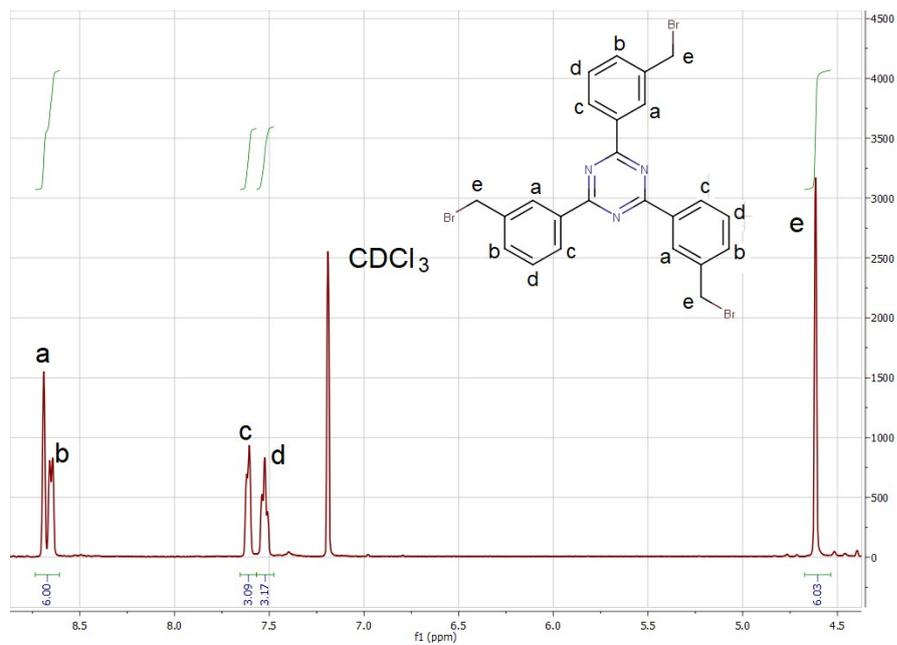


Figure S2. $^1\text{H-NMR}$ spectrum of *mttbmBr*.

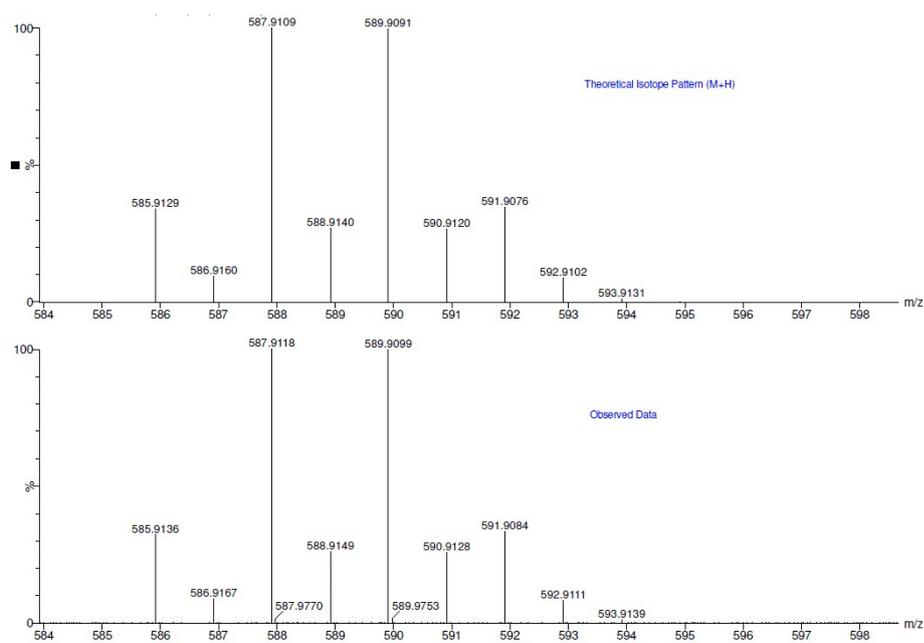


Figure S3. Mass spectrum of *mttbmBr* (bottom) and theoretical isotope pattern for the $[\text{M}+\text{H}]^+$ species (bottom).

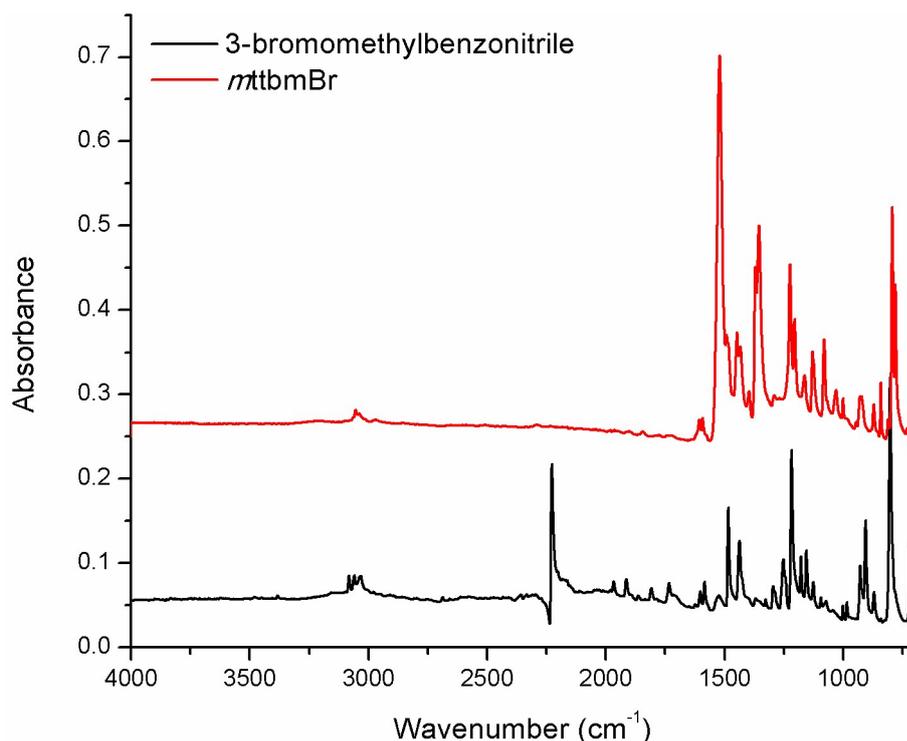


Figure S4. ATR-IR spectra of 3-bromomethylbenzonitrile (black) and *mttbmBr* (red). The band at 2227 cm^{-1} in the spectrum of 3-bromomethylbenzonitrile is assigned to the stretching of the nitrile group. The band has a weird shape because it falls in the same region as the asymmetric stretching of CO_2 , which is accounted for in the background spectrum. This band completely disappears in the spectrum of *mttbmBr*, while a new band at 1518 cm^{-1} appears, which is assigned to the stretching of the C=N double bonds in the triazine ring.

Synthesis of hexaethyl [1,3,5-triazine-2,4,6-triyltris(3,1-phenylenemethylene)]tris(phosphonate) (Et_6mttbmp).

mttbmBr (4.64 g, 8.0 mmol) and triethylphosphite (8.2 mL, 47.8 mmol) were introduced in a 100 mL round bottom flask. The mixture was heated under reflux for 4.5 h under a N_2 atmosphere. After cooling, a viscous liquid was obtained, which was stirred overnight in 200 mL of hexane under a N_2 atmosphere, forming a white solid. The white solid was filtered and dried in a desiccator under vacuum. 4.45 g of product was recovered (Yield: 74%).

^1H NMR (CDCl_3 , 500 MHz): δ = 8.74 – 8.63 (m, 6H, aromatic), 7.62 (m, 3H, aromatic), 7.56 (t, J = 7.6 Hz, 3H, aromatic), 4.10 (dq, J = 8.0, 7.1 Hz, 12H, O- CH_2), 3.37 (d, J = 21.6 Hz, 6H, *Ph*- CH_2 -P), 1.30 (t, J = 7.1 Hz, 18H, $-\text{CH}_3$) ppm (Figure S5).

^{13}C NMR (CDCl_3 , 500 MHz): δ = 171.47, 136.46, 133.99, 132.32, 130.17, 128.94, 127.75, 62.40, 34.82 (d), 16.38 ppm. (Figures S6-7).

^{31}P NMR (CDCl_3 , 500 MHz): $\delta = 26.09$ (m) ppm (Figure S8).

Mass spectrometry: 760.2656 m/z $[\text{M}+\text{H}]^+$; 777.2942 $[\text{M}+\text{NH}_4]^+$ (Figure S9).

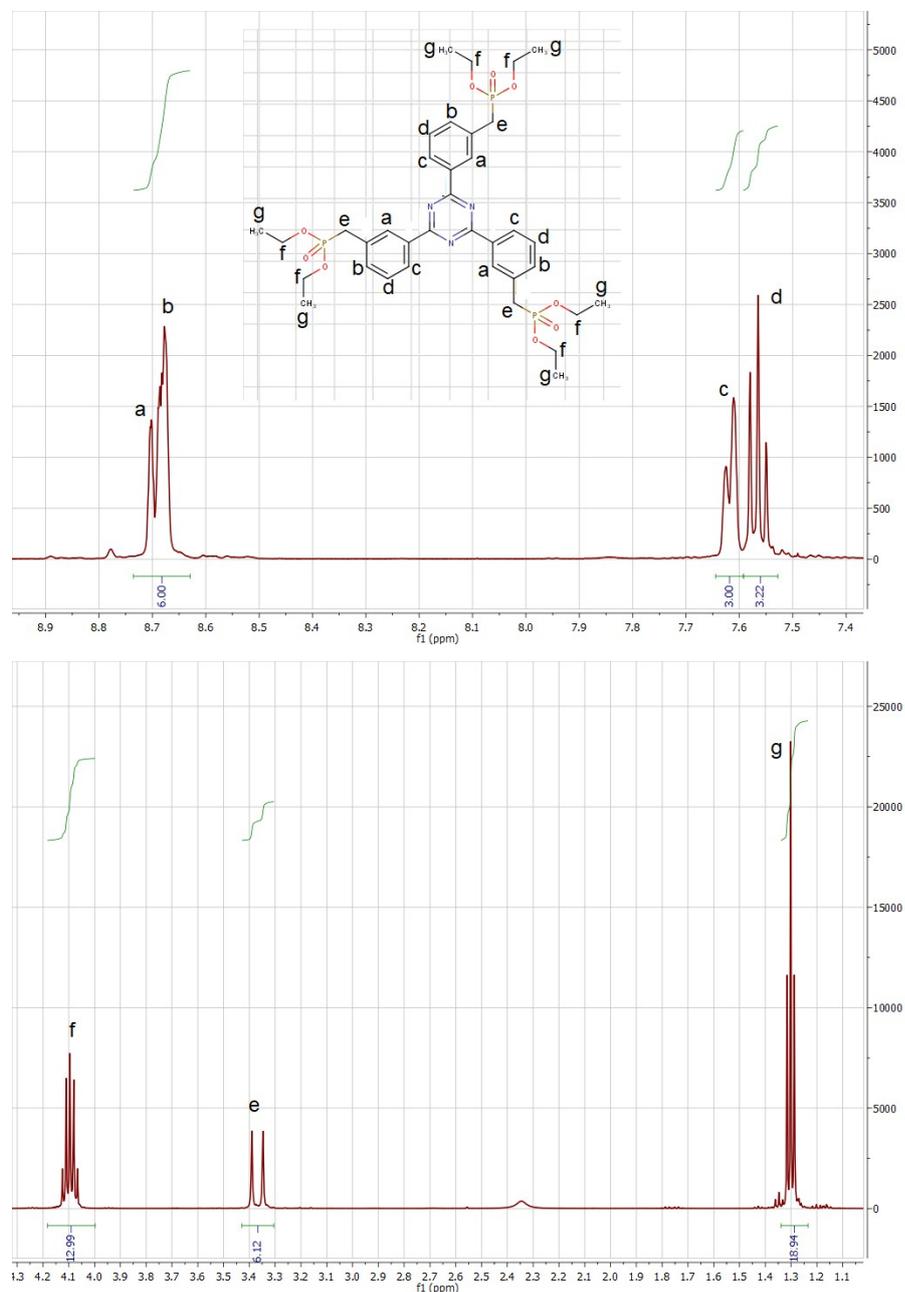


Figure S5. ^1H -NMR spectrum of Et_6mttbmP : aromatic protons region (top) and aliphatic protons region (bottom). For the sake of consistency, the labelling of H atoms in Figure S2 is transferred here and additional labels are used for the ethyl groups' protons.

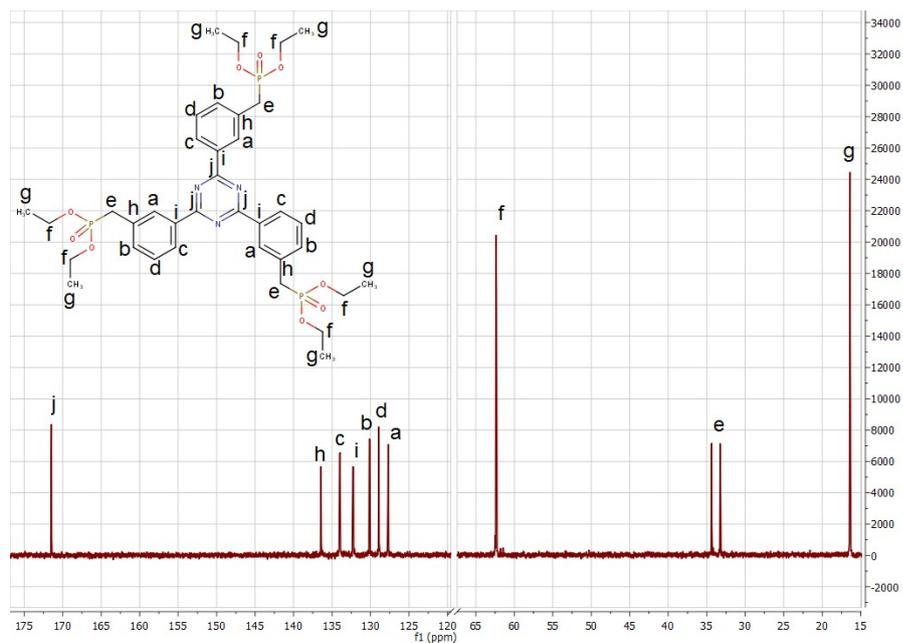


Figure S6. ^{13}C -NMR spectrum of Et_6mttbmP . For the sake of consistency, the labelling of H atoms in Figure S5 has been translated to the corresponding C atoms.

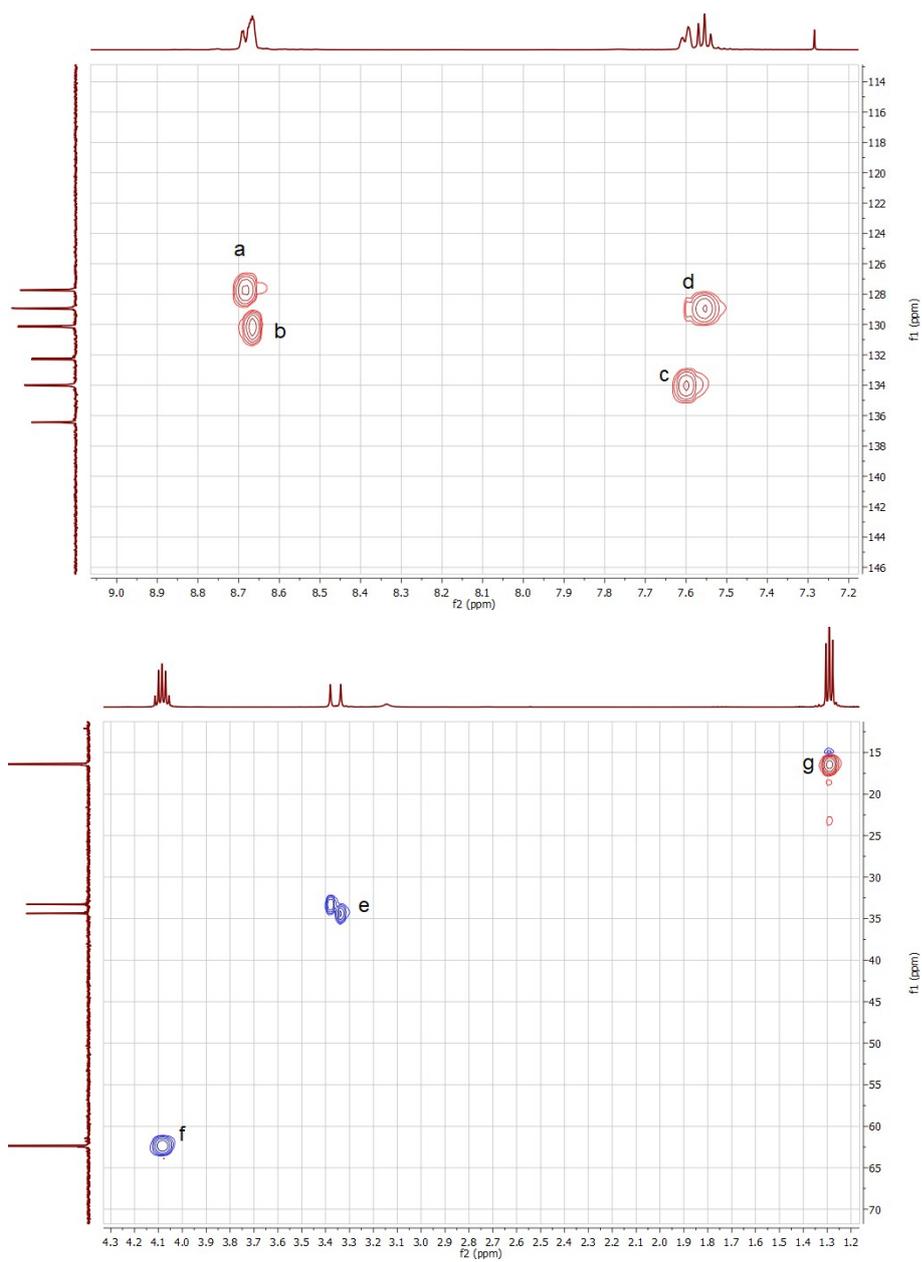


Figure S7. HSQC spectrum of Et₆mttbmP: aromatic signals region (top) and aliphatic signals region (bottom). Labelling is the same as in Figures S5-6.

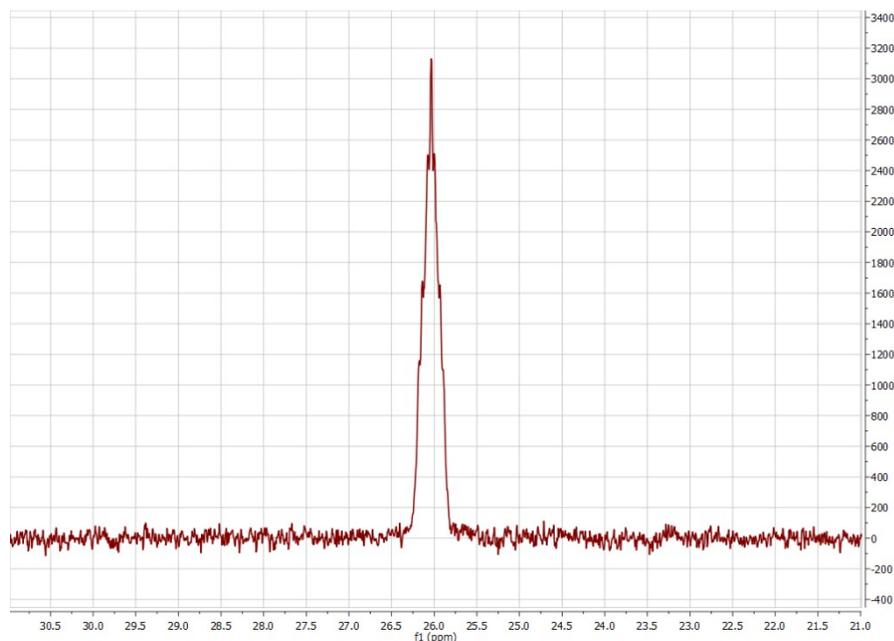


Figure S8. ^{31}P -NMR spectrum of Et_6mttbmP .

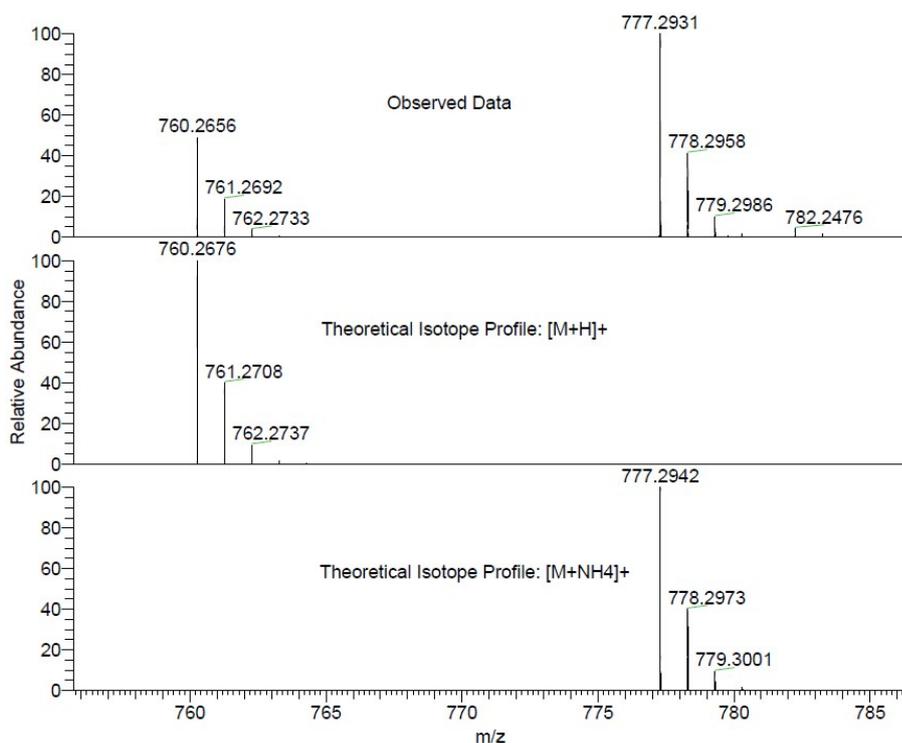


Figure S9. Mass spectrum of Et_6mttbmP (top) and theoretical isotope profiles for the $[\text{M}+\text{H}]^+$ (centre) and the $[\text{M}+\text{NH}_4]^+$ species (bottom).

Synthesis of 2,4,6-tris[3-(phosphonomethyl)phenyl]-1,3,5-triazine (H_6mttbmP).

Et_6mttbmP (3.0 g, 4.0 mmol) was dissolved in anhydrous acetonitrile (50 mL) inside a 250 mL round bottom flask under N_2 flow. Then, chlorotrimethylsilane (4.5 mL, 36.0 mmol) and potassium iodide (5.94 g, 36.0 mmol) were added. The mixture was heated to reflux under a N_2 atmosphere for 3.5 h.

Then, the mixture was filtered to remove potassium chloride, the mother liquor was dried in a rotary evaporator to remove acetonitrile and the excess chlorotrimethylsilane and water was added. After hydrolysis of the trimethylsilylester, the mixture was washed with diethyl ether to remove the trimethylsilanol side product. The water phase was recovered and dried in a rotary evaporator. The white solid was washed in isopropanol, filtered and dried in a hot air oven at 60 °C. 1.35 g of product was recovered (Yield: 58%).

^1H NMR ($\text{D}_2\text{O} + \text{K}_2\text{CO}_3$, 500 MHz): $\delta = 8.37$ (m, 3H, aromatic), 8.31 (dq, $J = 7.7, 1.6$ Hz, 3H aromatic), 7.56 (dq, $J = 7.7, 1.7$ Hz, 3H, aromatic), 7.47 (t, $J = 7.7$ Hz, 3H, aromatic), 2.92 (d, $J = 19.5$ Hz, 6H, *Ph-CH*₂-P) ppm. (Figure S10)

^{13}C NMR ($\text{D}_2\text{O} + \text{K}_2\text{CO}_3$, 500 MHz): $\delta = 172.66, 139.45, 135.03, 134.26, 130.12, 128.72, 126.03, 37.39$ (d) ppm. (Figures S11-12).

^{31}P NMR ($\text{D}_2\text{O} + \text{K}_2\text{CO}_3$, 500 MHz): $\delta = 17.30$ (t, $J = 19.3$ Hz) ppm. (Figure S13)

Mass spectrometry: 590.0656 m/z [*M*-H]⁻ + [2*M*-2H]²⁻ (Figure S9); 294.5290 m/z [*M*-2H]²⁻; 305.5198 m/z [*M*-3H+Na]²⁻. (Figure S14)

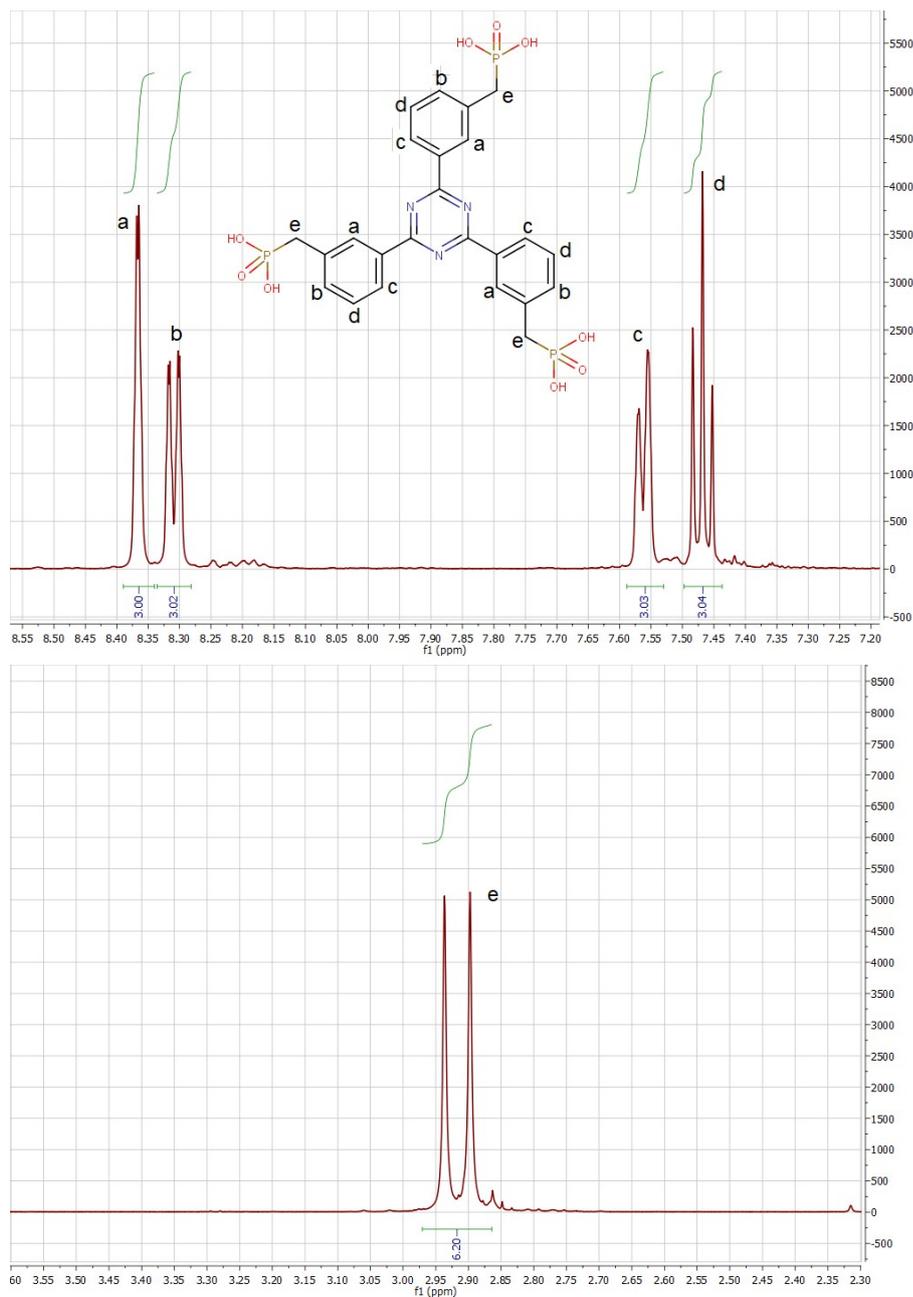


Figure S10. ¹H-NMR spectrum of H₆mttbmP: aromatics proton region (top) and methylene protons region (bottom).

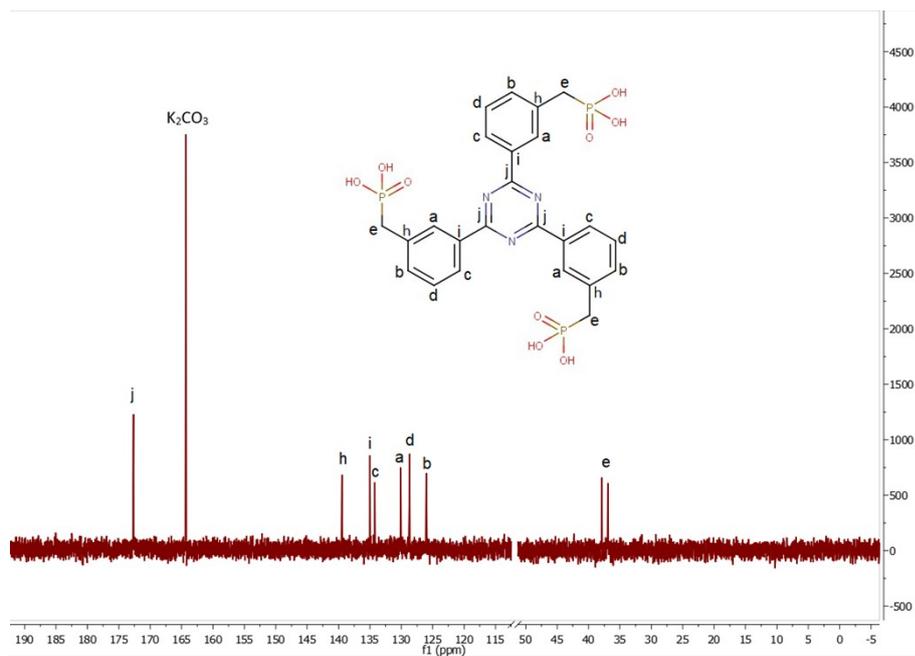


Figure S11. ^{13}C -NMR spectrum of H_6mttbmP . For the sake of consistency, the labelling of H atoms in Figure S10 has been translated to the corresponding C atoms.

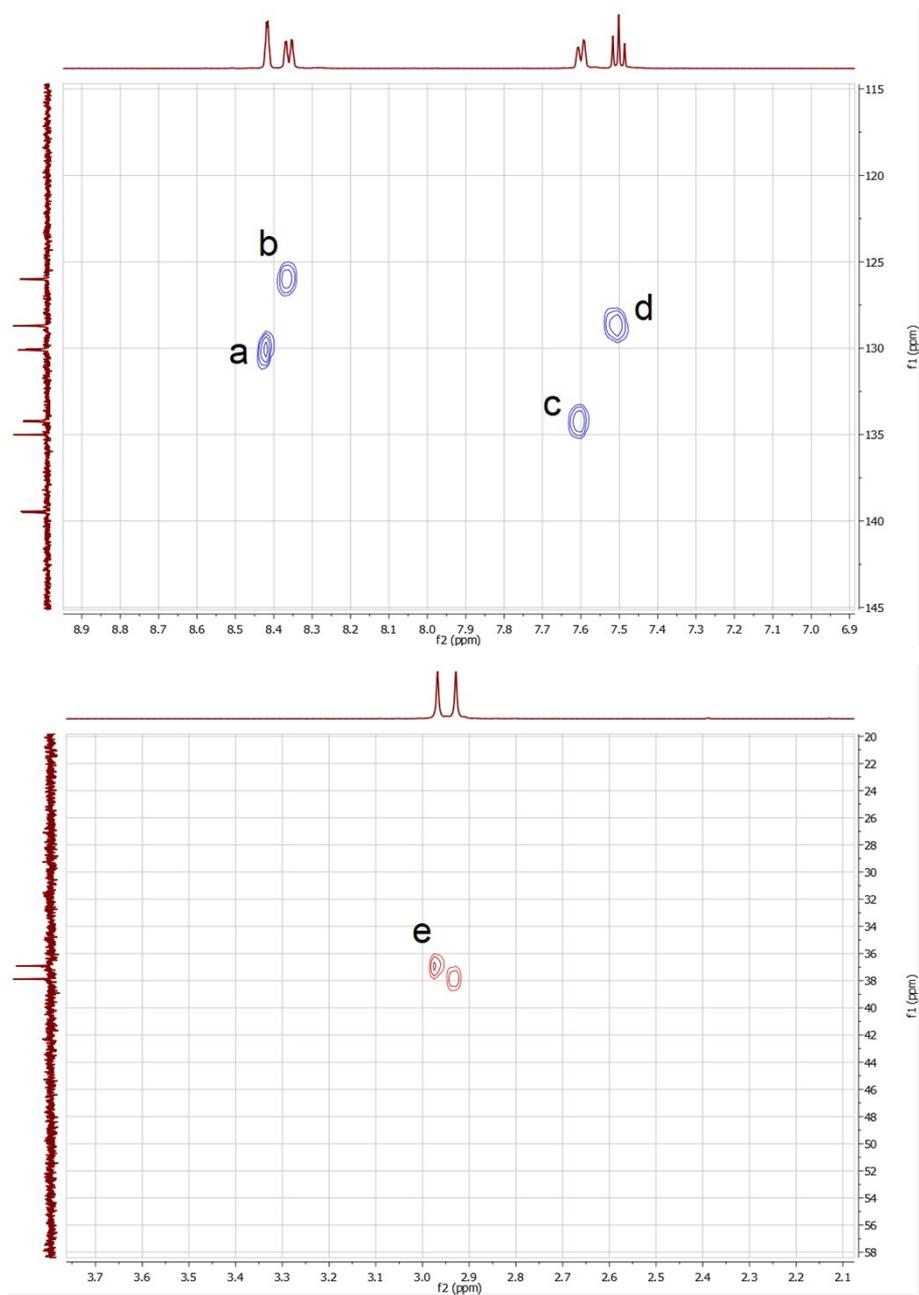


Figure S12. HSQC spectrum of H₆mttbmP: aromatic signals region (top) and methylene signals region (bottom). Labelling is the same as in Figures S10-11.

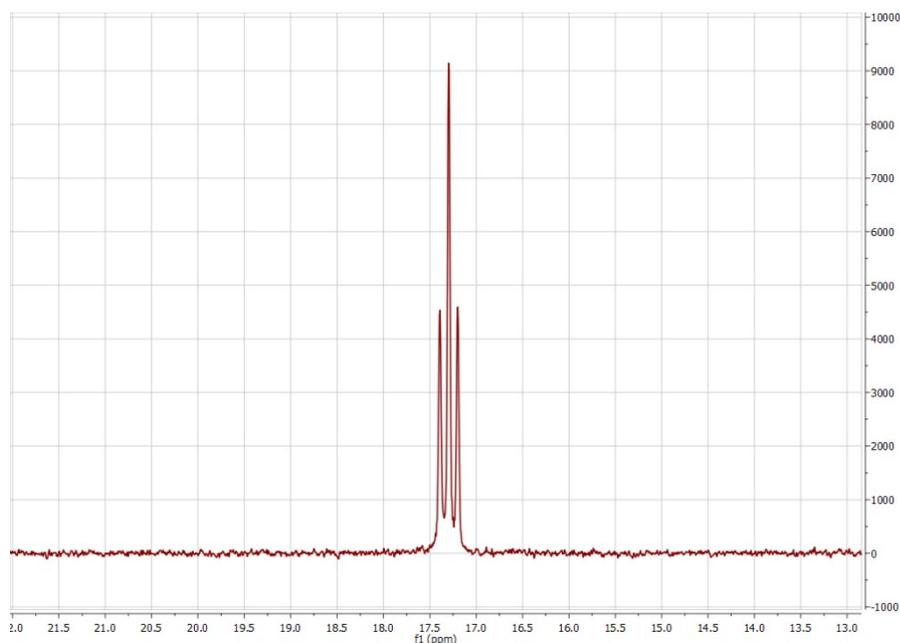


Figure S13. ^{31}P -NMR spectrum of H_6mttbmP .

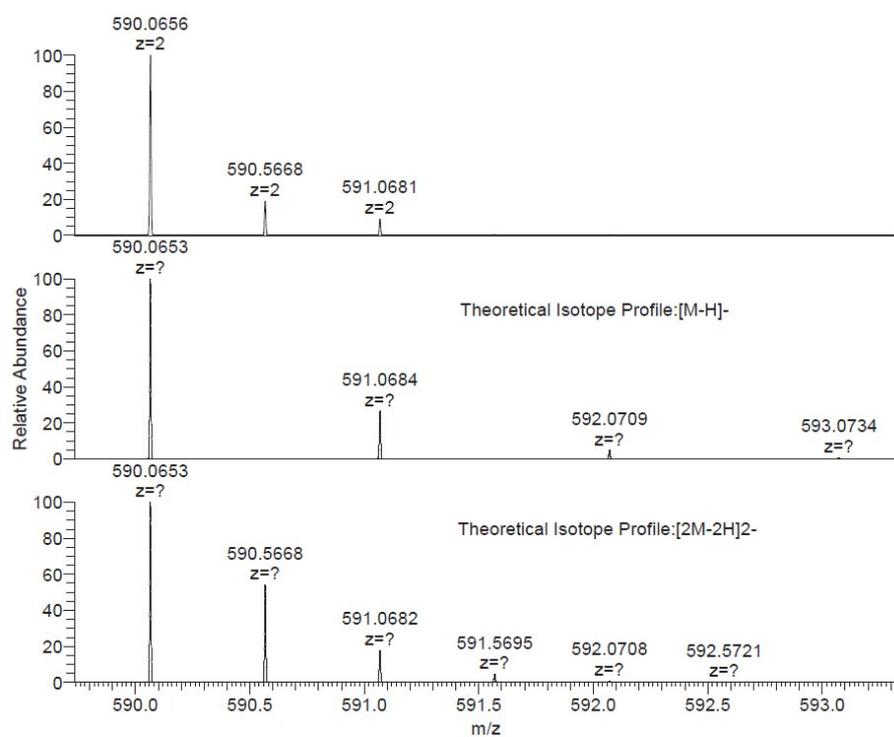


Figure S14. Mass spectrum of H_6mttbmP in the 589.5-593.5 m/z region (top) and theoretical isotope profiles for the $[\text{M}-\text{H}]^-$ (centre) and the dimeric $[2\text{M}-2\text{H}]^{2-}$ species (bottom).

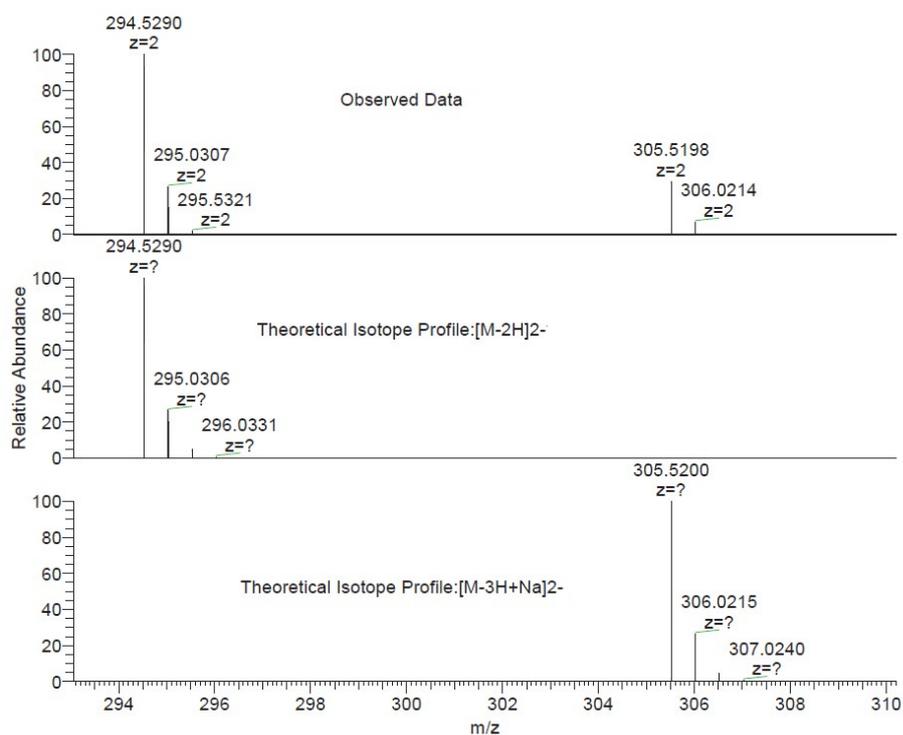


Figure S15. Mass spectrum of $H_6mttbmp$ in the 293-310 m/z region (top) and theoretical isotope profiles for the $[M-2H]^{2-}$ (centre) and the $[M-3H+Na]^{2-}$ species (bottom).

Synthesis of $Zr(H_4mttbmp)_2 \cdot 3H_2O$ (UPG-2).

$ZrOCl_2 \cdot 8H_2O$ (64 mg, 0.2 mmol) was dissolved in HF 2.9 M (3.5 mL, 10 mmol) in a plastic bottle. The mixture was diluted with water (8.0 mL), then $H_6mttbmp$ (118 mg, 0.2 mmol) was added. The bottle was closed and kept in an oven at 80 °C for seven days. The white solid was then filtered under vacuum, washed with water and methanol, and dried at room temperature. 108 mg of product was recovered (Yield: 80%, based on $H_6mttbmp$).

Analysis: Calcd for $C_{48}H_{50}N_6O_{21}P_6Zr$: Zr = 6.9%, P = 14.1%, C = 43.5%; H = 3.8%, N = 6.3%; Found: Zr = 7.1%, P = 12.9%, C = 46.3%; H = 4.5%, N = 6.1%.

Structure Determination and Refinement.

The crystal structure of UPG-2 was solved *ab initio* from PXRD data. Indexing was performed using the TREOR program,² using the positions of 49 peaks in the 5-30 °2 θ range and finding a triclinic cell with $M(20) = 26$ and no unindexed lines. The structural model was determined using the real space global optimization methods implemented in the FOX program:³ one *mttbmp* fragment and one ZrO_6 octahedron, placed in the inversion center, were input, according to the observed P/Zr ratio of 6. Trial structures were generated using the “Parallel Tempering” algorithm⁴ implemented in FOX, using the following antibump distances: P-Zr = 3 Å, P-P = 3 Å, C-Zr = 4 Å, C-O = 2.5 Å, O-O = 2.5 Å, O-N = 4 Å, P-N

= 4 Å. Rietveld refinement of the structural model was performed using the GSAS program.⁵ First, zero-shift, unit cell, background, and profile-shape parameters were refined. A corrected pseudo-Voigt profile function (six terms) with two terms for the correction of asymmetry at the low-angle region was used. Then, atomic coordinates were refined by restraining the bond distances to the following values: Zr-O = 2.00(5) Å, P-O = 1.55(5) Å, P-C = 1.80(5) Å, aromatic C-C = 1.39(5) Å, and C-N = 1.32(5) Å. The statistical weight of these restraints was decreased as the refinement proceeded. The position of water molecules was determined using difference Fourier maps, which showed two peaks of residual electron density in the interlayer space. The occupancy of these water molecules was arbitrarily set to 0.75, in agreement with the observed weight loss from TGA, discussed herein. Finally, atomic displacement parameters were refined by constraining them to have the same value. At the end of the refinement, the shifts in all parameters were less than their standard deviations.

Table S1 lists the crystal data and refinement details. Figure S16 shows the final Rietveld and difference plots.

Table S1. Structural data and refinement details for UPG-2.

empirical formula	C ₄₈ H ₅₀ N ₆ O ₂₁ P ₆ Zr
formula weight	1323
crystal system	triclinic
space group	<i>P</i> -1
<i>a</i> /Å	8.8147(4)
<i>b</i> /Å	9.6066(5)
<i>c</i> /Å	16.338(1)
α /°	88.426(4)
β /°	83.914(4)
γ /°	85.607(4)
volume/Å ³	1371.4(2)
Z	1
calculated density/g cm ⁻³	1.59
data range/°2 θ	4-80
wavelength/Å	1.54056
n. of data points	4470
n. of reflections	1626
n. of parameters	151
n. of restraints	136

R_p^a	0.0395
R_{wp}^b	0.0511
R_{f2}^c	0.05960
GOF^d	2.91

^a $R_p = \sum |I_o - I_c| / \sum I_o$; ^b $R_{wp} = [\sum w(I_o - I_c)^2 / \sum w I_o^2]^{1/2}$; ^c $R_{f2} = \sum |F_o^2 - F_c^2| / \sum |F_o^2|$; ^d $GOF = [\sum w(I_o - I_c)^2 / (N_o - N_{var})]^{1/2}$

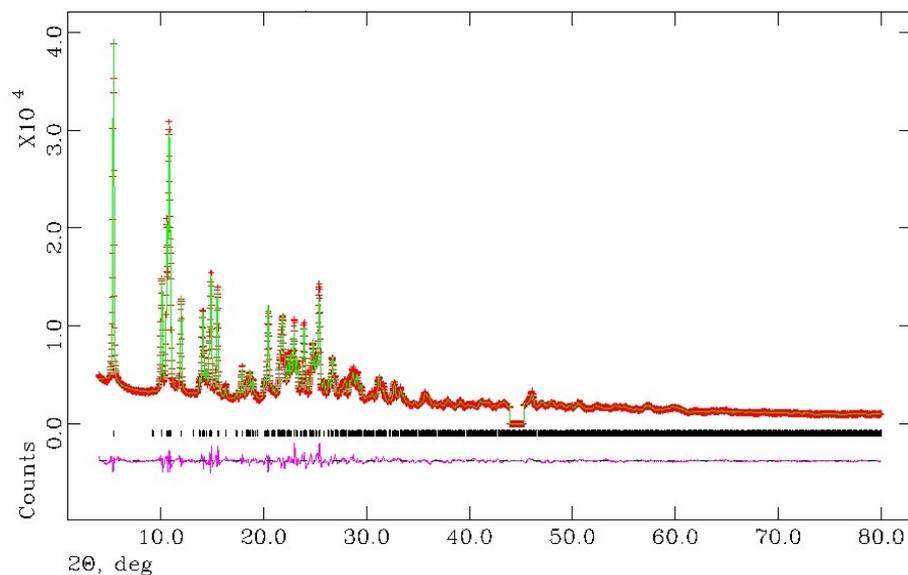


Figure S16. Final Rietveld plot for UPG-2, reporting the observed pattern (red symbols), the calculated pattern (green line), and their difference (pink line). Black markers at the bottom indicate the calculated positions of peaks.

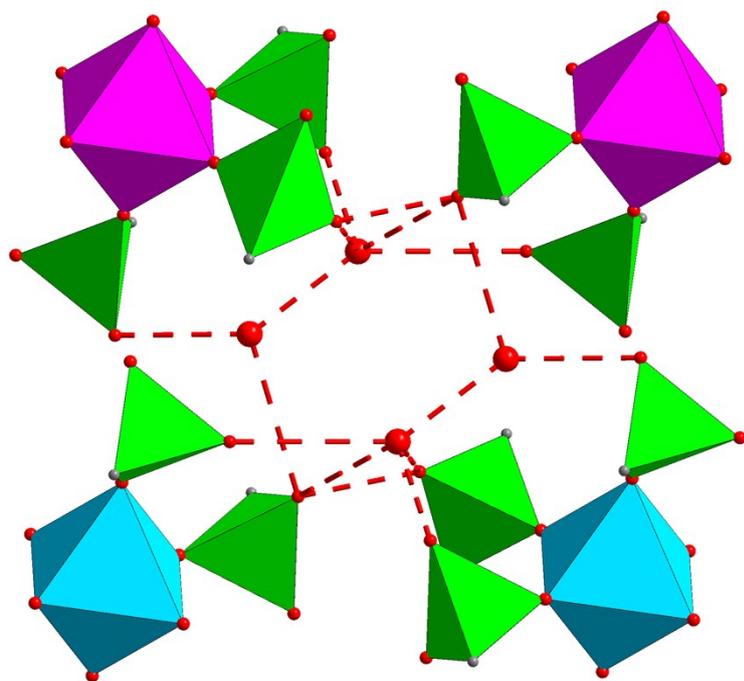


Figure S17. View of the hydrogen bonding network existing between the layers of UPG-2. Zr octahedra belonging to adjacent layers are coloured different for the sake of clarity. Colour code: Zr, pink/light blue; P, green; O, red; C, grey. Hydrogen bonds are represented as red dashed lines.

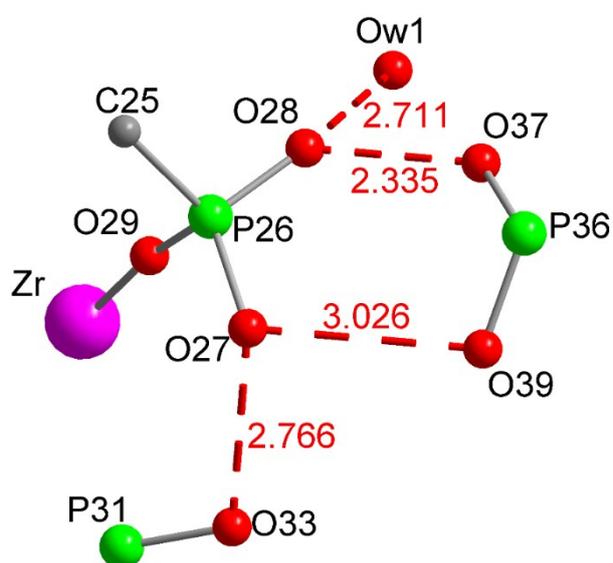


Figure S18. View of the hydrogen bonding interactions involving the phosphonate group centred around P26. Colour code: Zr, pink; P, green; O, red; C, grey. Hydrogen bonds are represented as red dashed lines.

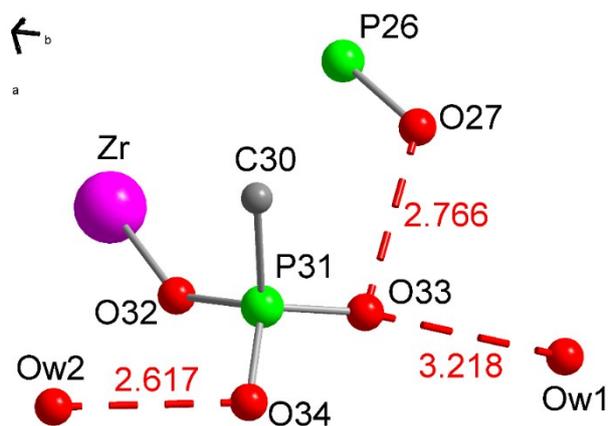


Figure S19. View of the hydrogen bonding interactions involving the phosphonate group centred around P31. Colour code: Zr, pink; P, green; O, red; C, grey. Hydrogen bonds are represented as red dashed lines.

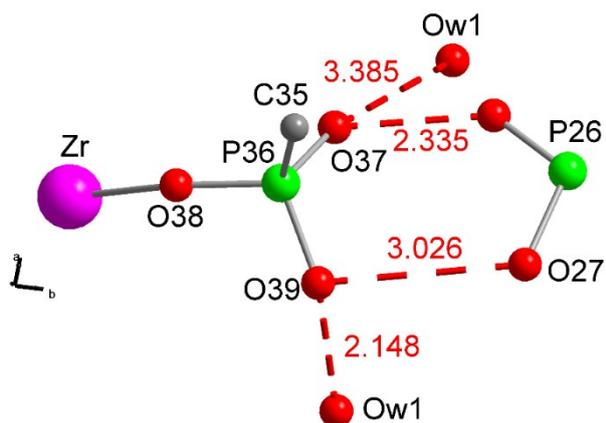


Figure S20. View of the hydrogen bonding interactions involving the phosphonate group centred around P36. Colour code: Zr, pink; P, green; O, red; C, grey. Hydrogen bonds are represented as red dashed lines.

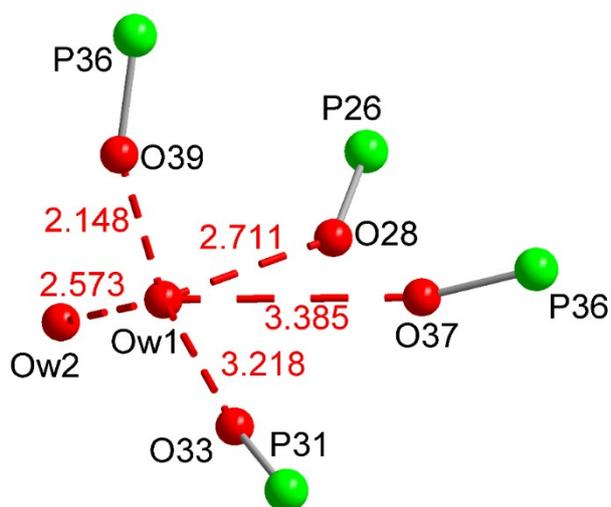


Figure S21. View of the hydrogen bonding interactions involving Ow1. Colour code: P, green; O, red. Hydrogen bonds are represented as red dashed lines.

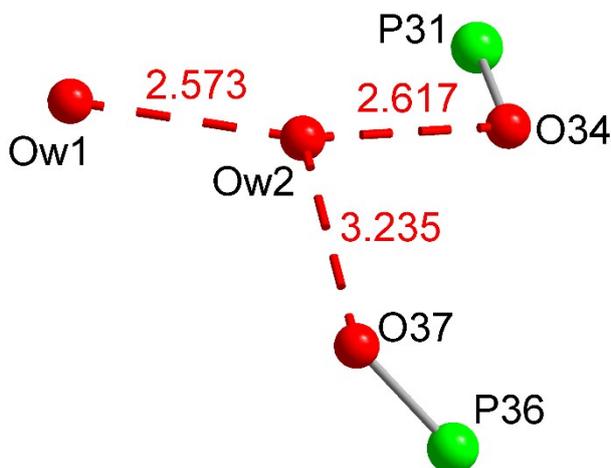


Figure S22. View of the hydrogen bonding interactions involving Ow2. Colour code: P, green; O, red. Hydrogen bonds are represented as red dashed lines.

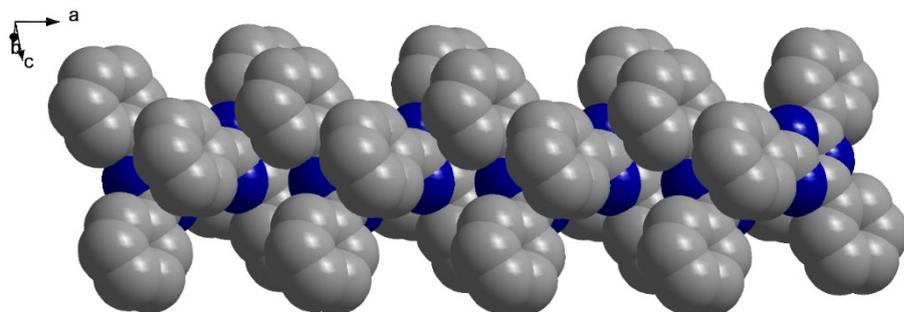


Figure S23. Space filling model view of the system of π - π stacking interactions extending along the a axis. Colour code: N, blue; C, grey.

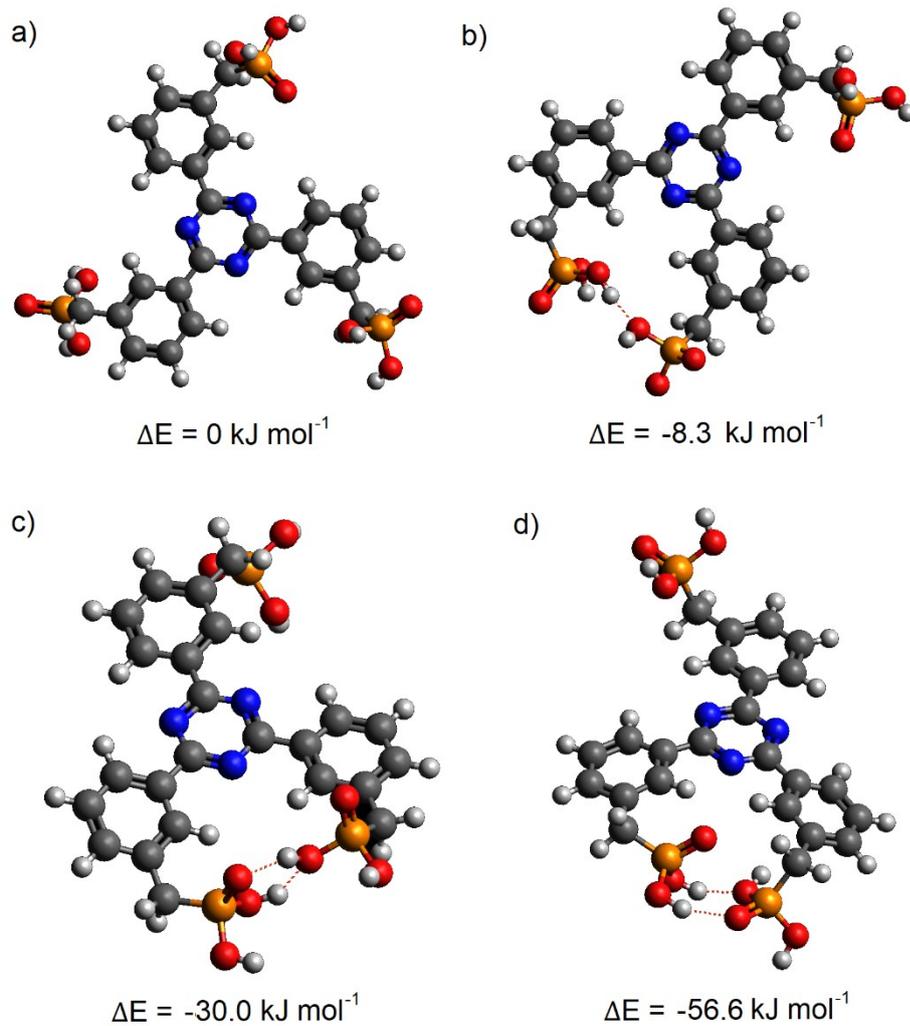


Figure S24. Optimised conformations of the H₆mttbmp linker and their relative energy, normalised to the energy of the least stable conformer (a). Colour code: P, yellow; O, red; N, blue; C, grey; H, white. Hydrogen bonds are represented as red dashed lines.

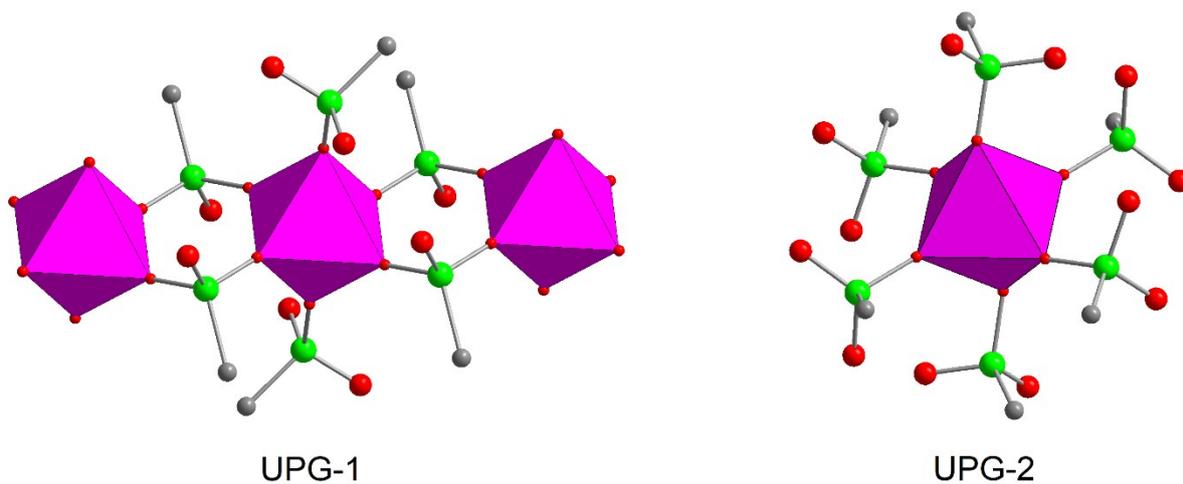


Figure S25. Comparison of the 1D IBU found in UPG-1 (left) and the 0D IBU in UPG-2 (right). Colour code: Zr, pink; P, green; O, red; C, grey.

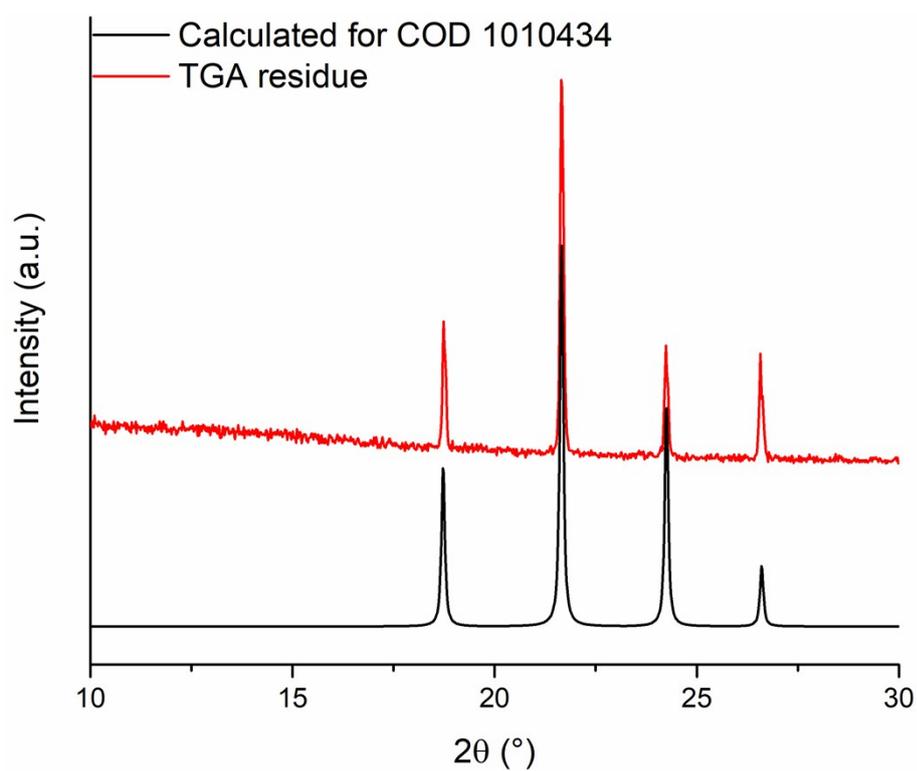


Figure S26. Calculated PXRD pattern for ZrP₂O₇ (COD 1010464) (black) and PXRD pattern of the TGA residue for UPG-2 (red).

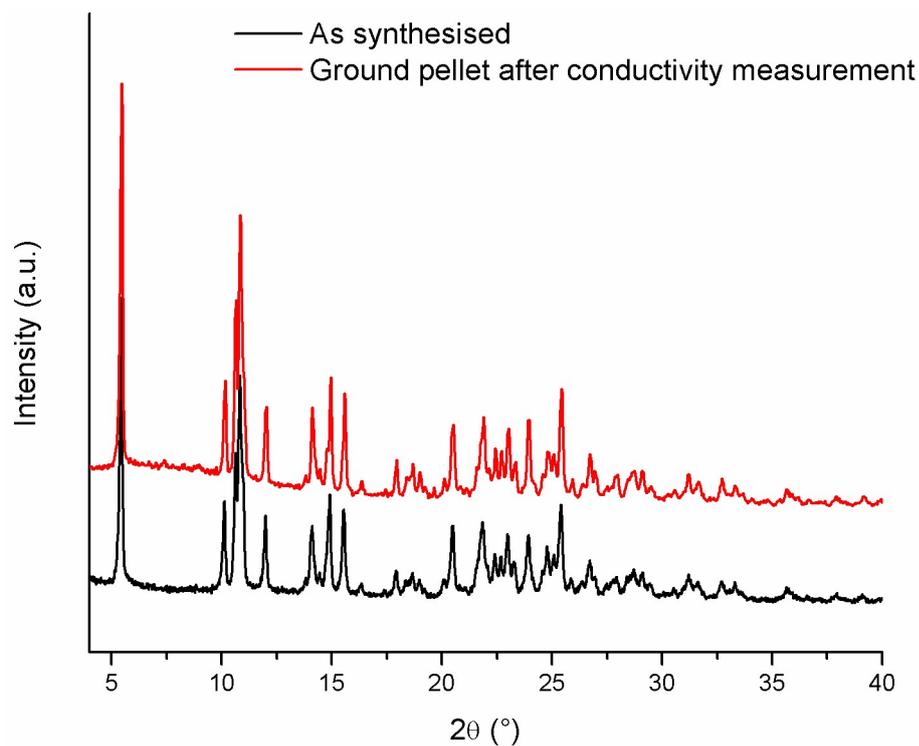


Figure S27. PXRD patterns of UPG-2 as synthesised (black) and after the conductivity measurement (red).

REFERENCES

1. M. Taddei, A. Donnadio, F. Costantino, R. Vivani and M. Casciola, *Inorg. Chem.*, 2013, **52**, 12131-12139.
2. P.-E. Werner, L. Eriksson and M. Westdahl, *J. Appl. Crystallogr.*, 1985, **18**, 367-370.
3. V. Favre-Nicolin and R. Cerny, *J. Appl. Crystallogr.*, 2002, **35**, 734-743.
4. M. Falcioni and M. W. Deem, *J. Chem. Phys.*, 1999, **110**, 1754-1766.
5. A. C. Larson and R. B. V. Dreele, "General Structure Analysis System (GSAS)" Los Alamos National Laboratory Report LAUR 86-748, 2000.