Electronic Supplementary Material (ESI) for Dalton Transactions.

Water-based synthesis and nitrate release properties of a Zr^{IV}-based metal-organic framework derived from *L*-aspartic acid

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ELECTRONIC SUPPLEMENTARY INFORMATION

Experimental Section

Chemicals

L-aspartic acid (Fluorochem), Zirconium oxynitrate hydrate (Sigma-Aldrich), Zirconium tetrachloride (Sigma-Aldrich), Nitric acid, 65% (Sigma-Aldrich), Concentrated sulfuric acid, 98% (Sigma-Aldrich), Ethanol (Sigma-Aldrich), Salicyclic acid (Sigma-Aldrich), Sodium sulfate (Sigma-Aldrich), Sodium chloride (Sigma-Aldrich), Sodium hydroxide (Carlo-Erba), Potassium nitrate (Carlo-Erba).

Synthesis of $Zr_6O_4(OH)_4(Asp)_6(HNO_3)_6$ (MIP-202-NO_3)

L-aspartic acid (2.80 g, 21.1 mmol) was dissolved in 8.25 mL of water. $ZrO(NO_3)_2{\cdot}4H_2O$ (3.00 g, 10.0 mmol) was added with 1.25 mL concentrated nitric acid (65%, 16 M, 20.0 mmol). The mixture was stirred at 1000 rpm until all reactants dissolved. The mixture was then placed on a heating block at 100 °C for 1 h without stirring. The product was separated from the mother liquor by centrifugation, washed once in water (40 mL) and twice in ethanol (40 mL each time). The white solid product obtained was dried in an oven at 80 °C overnight. Yield: 2.39 g.

Synthesis of $Zr_6O_4(OH)_4(Asp)_6(HCl)_{7.4}$ (MIP-202-Cl)

The synthesis of MIP-202-Cl was performed according to the literature procedure, with increased time: *L*-aspartic acid (1.40 g, 10.5 mmol) was added to 2.5 mL of water. $ZrCl_4$ (1.17 g, 5.03 mmol) was then added, followed by the further addition of 2.5 mL water. The mixture was heated at 100 °C for 24 hours without stirring. The product was separated from the mother liquor by centrifugation and washed twice in a 50:50 water/ethanol mixture (20 mL each time). The white solid product obtained was dried in an oven at 80 °C overnight. Yield: 1.50 g.

Analytical procedures

Powder X-ray diffraction (PXRD) patterns were collected in reflection geometry in the 4-40° 2θ range, with a 30 s step^{-1} counting time and with a step size of 0.033° 2θ on a PANalytical X'PERT PRO diffractometer, PW3050 goniometer, equipped with an X'Celerator detector and using a Cu Kα radiation source. The long fine focus (LFF) ceramic tube operated at 40 kV and 40 mA.

Attenuated total reflectance infrared (ATR-IR) spectra were collected on an Agilent Cary 630 spectrometer in the 700-4000 cm^{-1} wavenumber range.

^{1}H and ^{35}Cl Quantitative Nuclear Magnetic Resonance (NMR) analysis of hydrolysed solids was performed at 298 K on a Jeol JNM-ECZ500S instrument equipped with a RoyalProbe Broadband probe. About 15-20 mg of solid was introduced into a glass vial and kept at 120 °C for two hours. Afterwards, the vial was capped while still hot and weighed to determine the mass of the desolvated solid (the cap had previously been weighed alongside the vial). 1 mL of 1 M NaOH in D_2O, spiked with 0.1 M fumaric acid as a ^{1}H internal standard, was then added to the vial and the mixture briefly sonicated and left to digest overnight. The NMR tubes were then loaded with the solution, taking care to avoid transferring solid particles in the tubes. Quantification of ^{35}Cl content was performed against a 0.050 M NaCl solution in 1 M aqueous NaOH as external standard. Chemical shifts (expressed in parts per million) are referenced to the residual solvent peaks. ^{1}H-

NMR experiments were performed with a relaxation delay of 25 s, four scans and a receiver gain of 42. ^{35}Cl-NMR experiments were performed with a relaxation delay of 0.35 s, 600 scans and a receiver gain of 50.

Ultraviolet-visible (UV-Vis) spectra for nitrate quantification were acquired with an Ultrospec 2100 pro spectrophotometer in the 350-550 nm wavelength range.

Carbon, hydrogen and nitrogen (CHN) analysis were performed on a Vario MICRO cube instrument (Elementar).

Scanning electron microscopy (SEM) images were acquired with a FEI Quanta 450 ESEM FEG, working at 15.00 kV acceleration voltage. The samples were sputtered with graphite prior to the analysis.

Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) analyses were performed on a Thermo Scientific iCAP 7000 Series ICP-OES instrument. 3% HNO_3 was used for the preparation of Zr standards solutions (15 ppm, 10 ppm, 6 ppm, 3 ppm, 1 ppm) and dilution of samples. The supernatant liquids after stability test were directly injected to determine Zr leaching.

N_2 adsorption isotherms were recorded using a 3P micro 300 instrument (3P Instruments) at the temperature of 77 K. Before the measurement, the samples were degassed at 100 °C for 16 h under dynamic vacuum.

Ion exchange experiments

100 mg of MIP-202-NO_3 was dispersed in 10 mL of HCl 0.1 M for 1 h. The solid was recovered by centrifugation, washed with ethanol (10 mL) and dried in an oven at 80 °C.

100 mg of MIP-202-NO_3 was dispersed in 10 mL of NaCl 0.1 M for 1 h. The solid was recovered by centrifugation, washed with a 50:50 water/ethanol mixture (10 mL) and dried in an oven at 80 °C.

100 mg of MIP-202-Cl was dispersed in 10 mL of HNO_3 0.1 M for 1 h. The solid was recovered by centrifugation, washed with ethanol (10 mL) and dried in an oven at 80 °C.

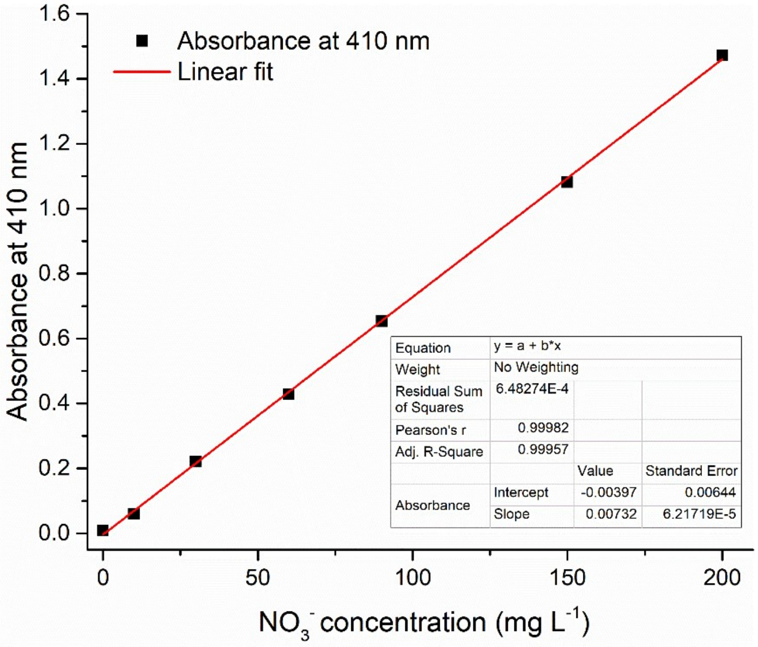
100 mg of MIP-202-Cl was dispersed in 10 mL of $NaNO_3$ 0.1 M for 1 h. The solid was recovered by centrifugation, washed with a 50:50 water/ethanol mixture (10 mL) and dried in an oven at 80 °C.

Nitrate release experiments

200 mg of MIP-202-NO_3 was dispersed in either 200 or 20 mL of deionized water, 200 or 20 mL of ethanol, 200 mL of aqueous NaCl solutions (0.01 and 0.001 M) and 200 mL of Na_2SO_4 solutions (0.01 and 0.001 M). The suspension was kept under stirring for two hours at room temperature. The pH was monitored with a Vio pH 7 portable pH-meter.

A slight modification of the methods reported by Cataldo *et al.* (ref. 25 in manuscript) and Robarge & Edwards (ref. 24 in manuscript) was employed for nitrate determination. 10 mL aliquots of the suspension were taken at set times and centrifuged. From the centrifuged sample, 0.5 mL of the supernatant was taken, introduced into a test tube and treated with 1.0 mL 5% (w/v) salicylic acid in concentrated H_2SO_4 and mixed using a vortex, followed by the addition of 10 mL of 4 M NaOH solution and further mixing with a vortex. The mixture was left to cool for five minutes, after which the absorbance at 410 nm was measured using a UV-Vis spectrometer.

A calibration curve was built using KNO_3 standards having concentrations of 10, 30, 60, 90, 150 and 200 mg L^{-1}, respectively (Figure S1).



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	6.48274E-4		
Pearson's r	0.99982		
Adj. R-Square	0.99957		
		Value	Standard Error
Absorbance	Intercept	-0.00397	0.00644
	Slope	0.00732	6.21719E-5

Figure S1. Calibration curve used for the quantification of nitrate released in aqueous solution by MIP-202-NO_3.

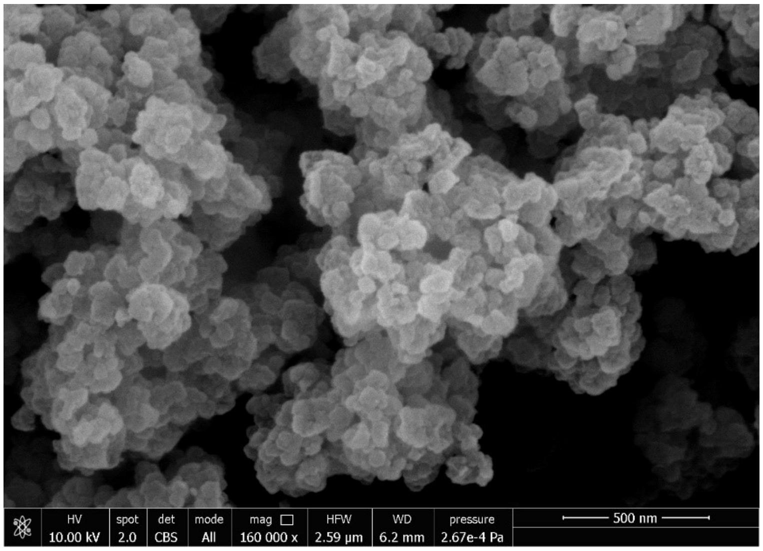


Figure S2. SEM micrograph of MIP-202-NO_3.

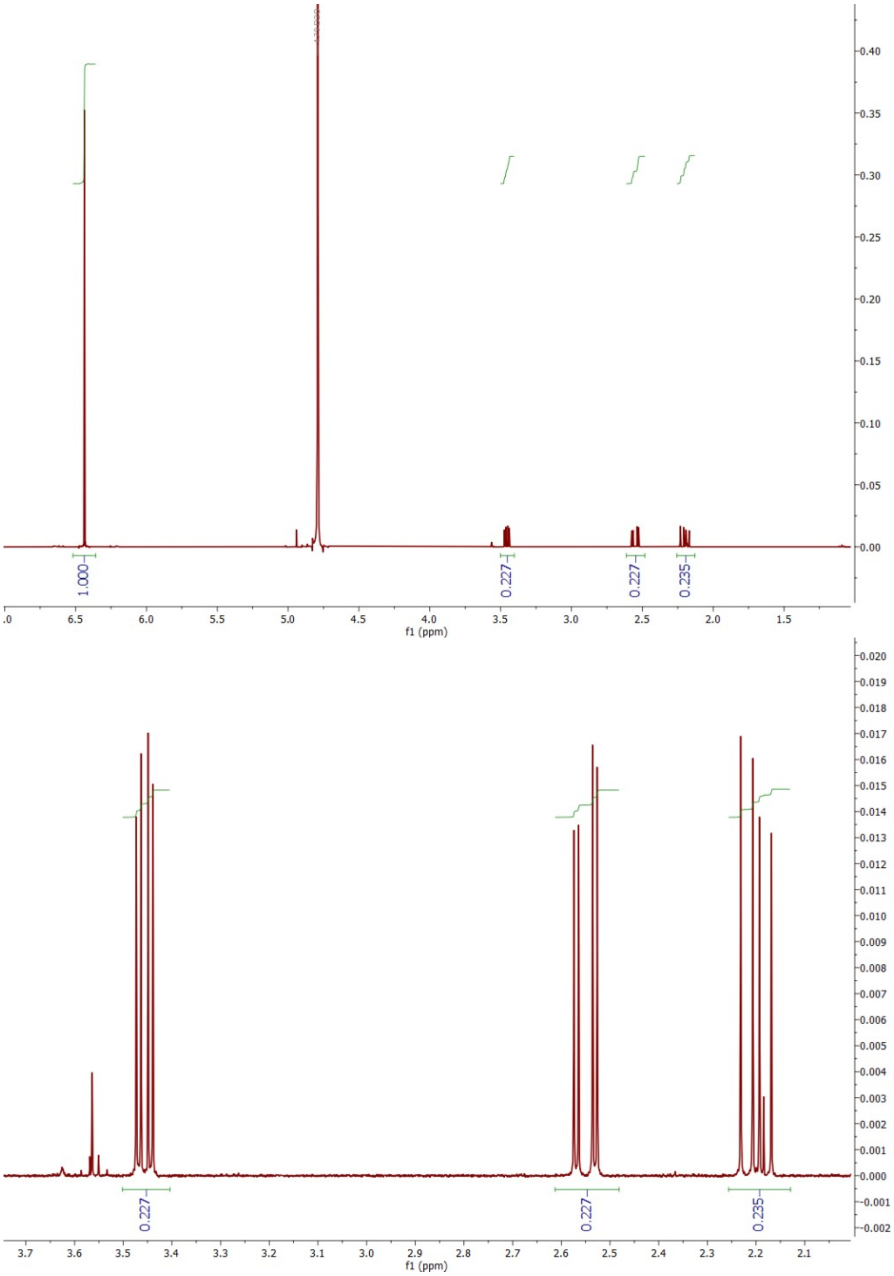


Figure S3. Full ^{1}H-NMR spectrum (top) and zoom on the region where the signals of Asp appear (bottom) of 14.2 mg of dry MIP-202-NO_3 digested in 1 mL of 1 M NaOH in D_2O in the presence of 0.101 M fumaric acid. Each signal of Asp accounts for one proton. The averaged integral for Asp is 0.230. The signal of fumaric acid accounts for two protons. The integral of fumaric acid is 1.000, which is normalised to 0.500. The concentration of Asp is derived to be 0.0465 M, corresponding to 6.09 mg of Asp in the original solid (42.9 wt%).

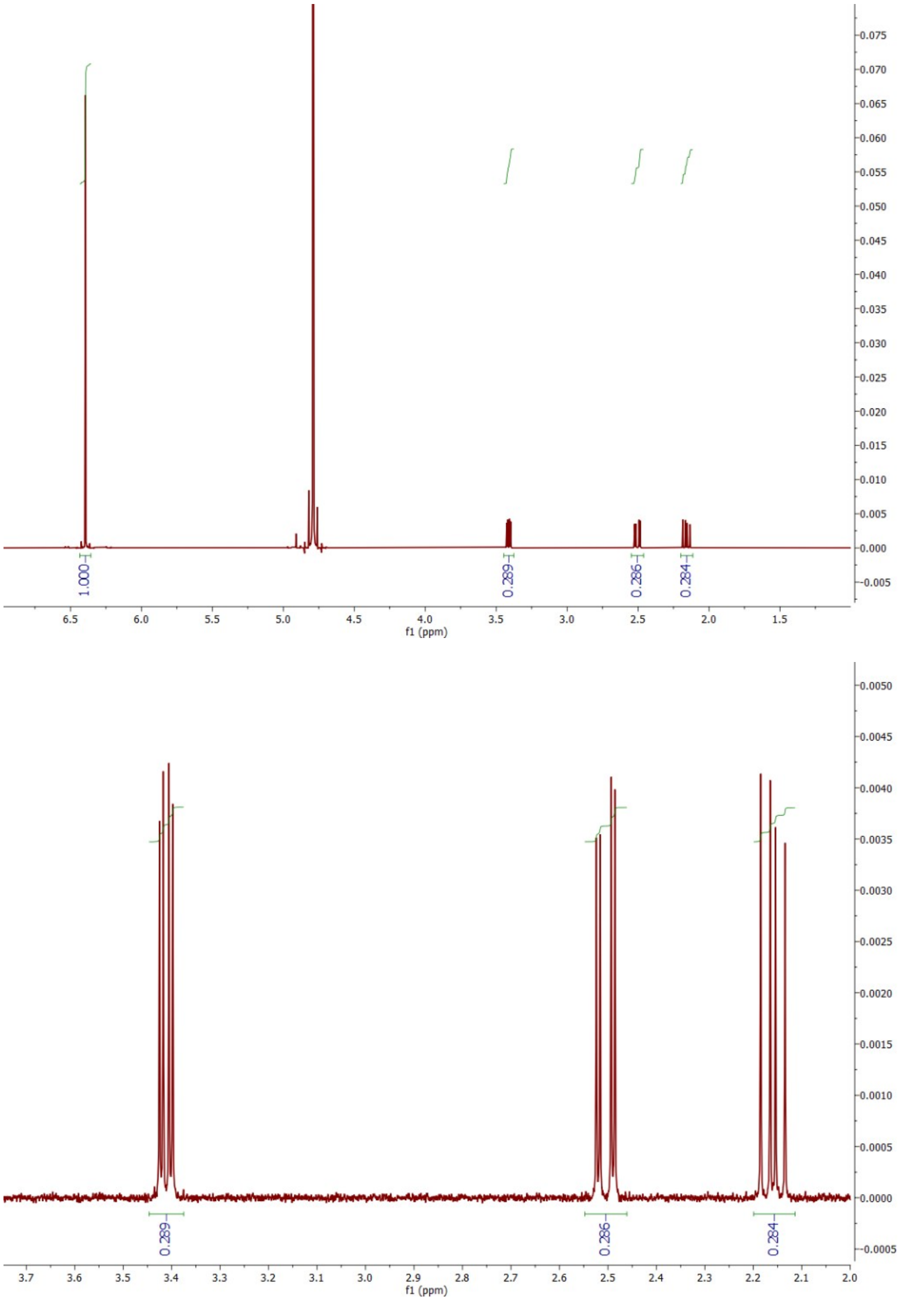


Figure S4. Full ^{1}H-NMR spectrum (top) and zoom on the region where the signals of Asp appear (bottom) of 16.5 mg of dry MIP-202-Cl digested in 1 mL of 1 M NaOH in D_2O in the presence of 0.100 M fumaric acid. Each signal of Asp accounts for one proton. The averaged integral for Asp is 0.286. The signal of fumaric acid accounts for two protons. The integral of fumaric acid is 1.000, which is normalised to 0.500. The concentration of Asp is derived to be 0.0573 M, corresponding to 7.50 mg of Asp in the original solid (45.5 wt%).

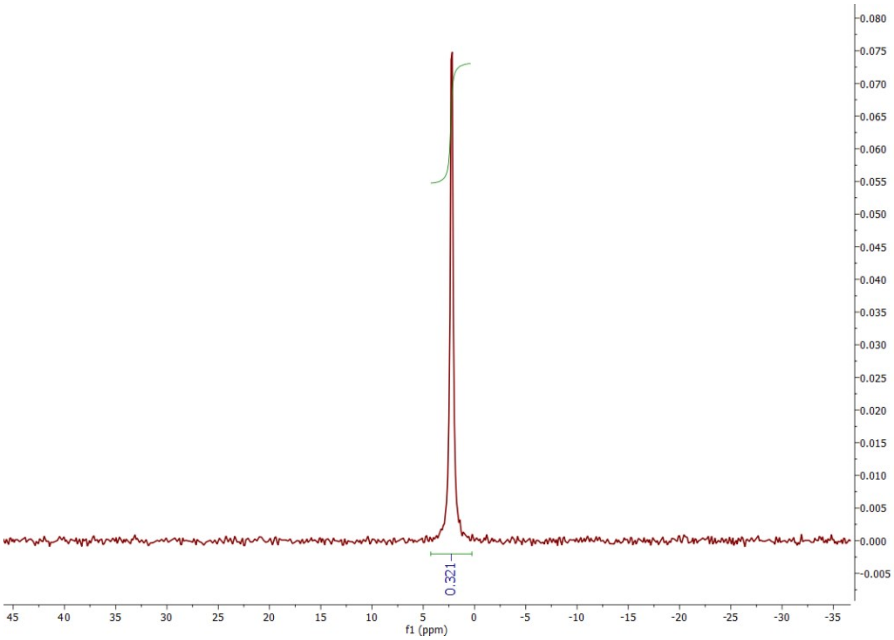


Figure S5. ^{35}Cl-NMR spectrum of 16.5 mg of dry MIP-202-Cl digested in 1 mL of 1 M NaOH in D_2O in the presence of 0.100 M fumaric acid. The value shown for the integral (0.321) is the absolute value. The same signal for the external standard (0.050 M NaCl solution in 1 M aqueous NaOH) integrates 0.225. The concentration of chloride is derived to be 0.0713 M, corresponding to 2.53 mg of chloride in the original solid (15.3 wt%).

Table S1. CHN elemental analysis results for MIP-202-NO_3.

Sample	%C	%H	%N	C/N molar ratio
MIP-202-NO_3	14.51	2.94	8.35	2.03

Determination of the chemical formula of MIP-202-NO_3 and MIP-202-Cl

Based on ^{1}H-NMR analysis (Figure S4), dry MIP-202-NO_3 contains 42.9 wt% of Asp. The C/N ratio is 2.03, suggesting a nitrate/Asp ratio of 1.0 (based on the C/N ratio of Asp being 4). Assuming the formula $Zr_6O_4(OH)_4(Asp)_6(HNO_3)_6$ (FW = 1830 g mol^{-1}), 42.7 wt% of Asp is calculated, in excellent agreement with the experimental one. The percentages of C, H and N calculated on the basis of this formula are 15.74%, 2.19% and 9.18%, respectively. Looking at table S1, the experimental C and N percentages are lower than the calculated ones, while the experimental H percentage is higher. This can be explained by the fact that the sample for CHN analysis is not pre-dried and therefore contains solvent. If this solvent is taken to be water, the formula $Zr_6O_4(OH)_4(Asp)_6(HNO_3)_6 \cdot 9.6H_2O$ (FW = 2003 g mol^{-1}) can be proposed. The percentages of C, H and N calculated on the basis of this formula are 14.38%, 2.96% and 8.39%, respectively, in much better agreement with the experimental ones.

Based on ^{1}H-NMR analysis (Figure S4), dry MIP-202-Cl contains 42.9% of Asp and 15.3% of chloride, corresponding to a chloride/Asp ratio of 1.24. Assuming the formula $Zr_6O_4(OH)_4(Asp)_6(HCl)_{7.4}$ (FW = 1722 g mol^{-1}), 44.9 wt% of Asp and 15.2 wt% of chloride are expected, in excellent agreement with the experimental ones.

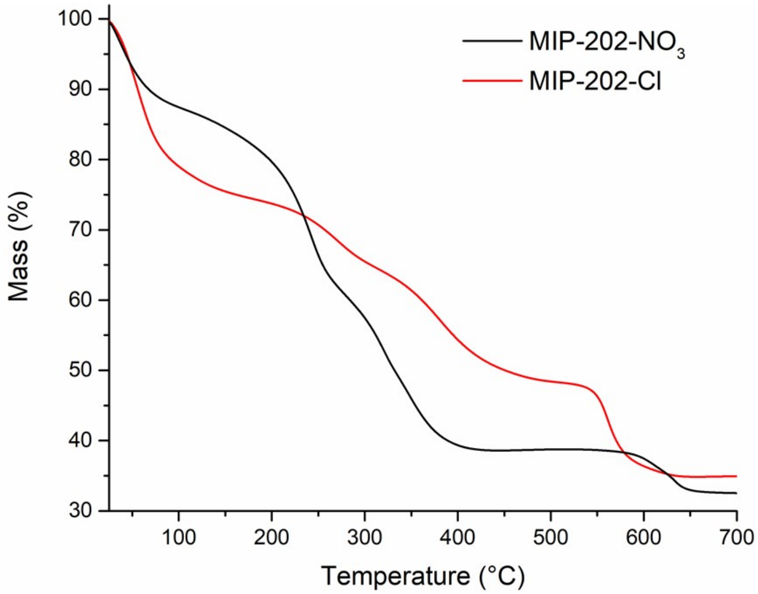


Figure S6. Thermogravimetric curves of $MIP\text{-}202\text{-}NO_3$ (black) and MIP-202-Cl (red).

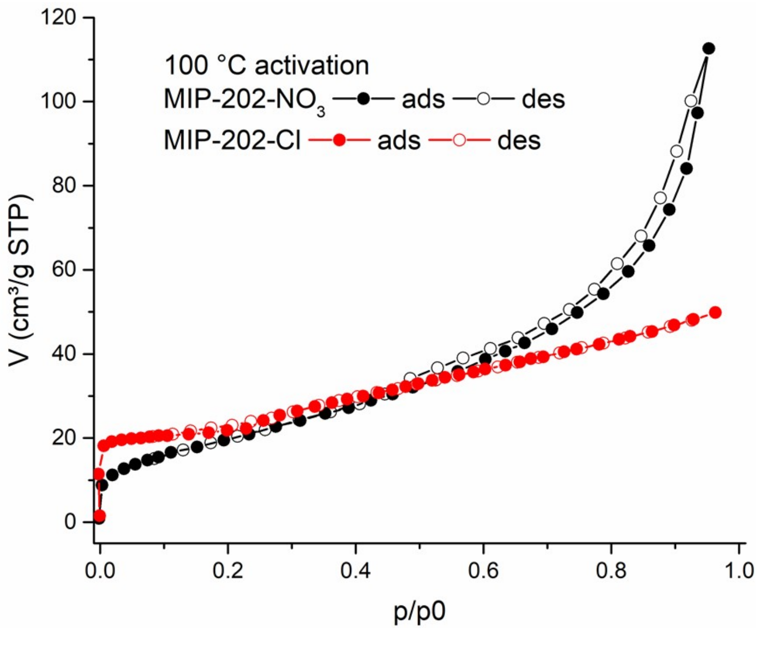


Figure S7. N_2 adsorption (filled symbols) and desorption (empty symbols) isotherms of MIP-202-NO_3 (black) and MIP-202-Cl (red) upon activation at 100 °C for 16 h.

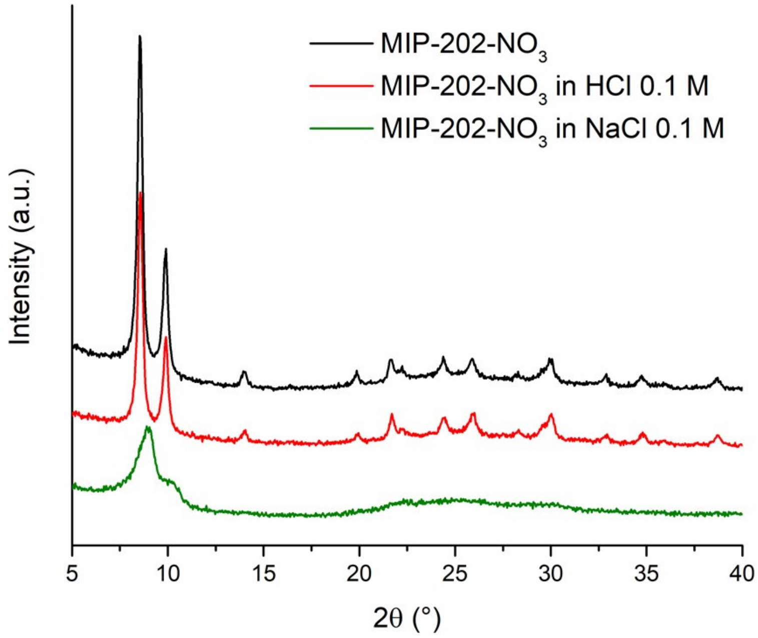


Figure S8. PXRD patterns of MIP-202-NO$_3$ as synthesised (black), after soaking in HCl 0.1 M (red) and after soaking in NaCl 0.1 M (green).

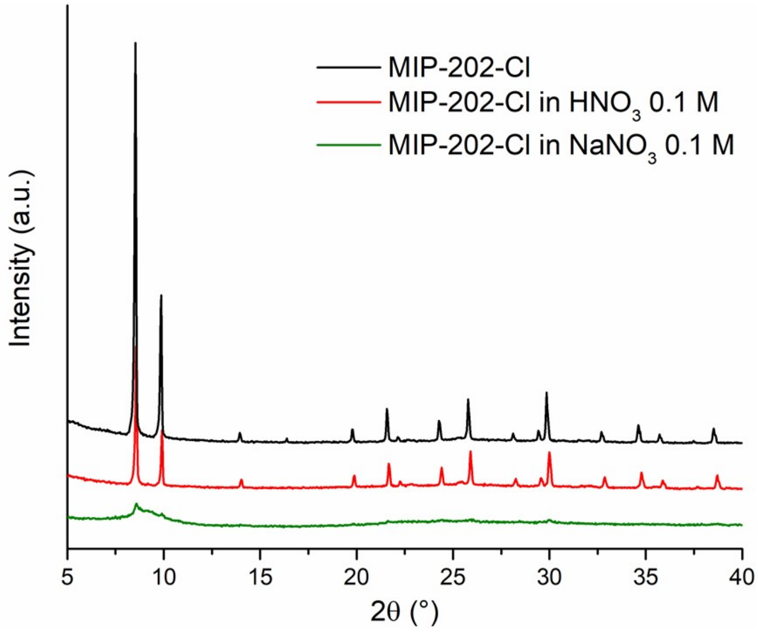


Figure S9. PXRD patterns of MIP-202-Cl as synthesised (black), after soaking in HNO$_3$ 0.1 M (red) and after soaking in NaNO$_3$ 0.1 M (green).

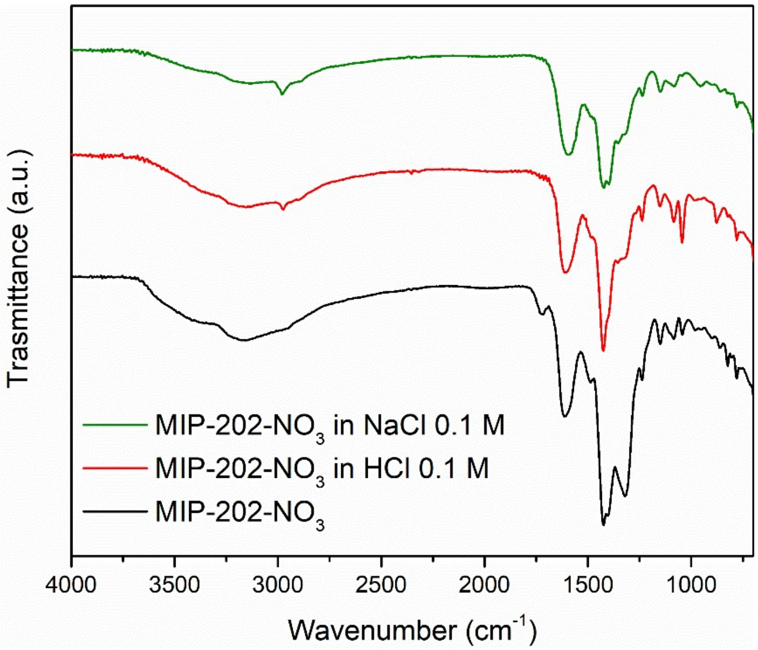


Figure S10. ATR-IR spectra of MIP-202-NO$_3$ as synthesised (black), after soaking in HCl 0.1 M (red) and after soaking in NaCl 0.1 M (green).

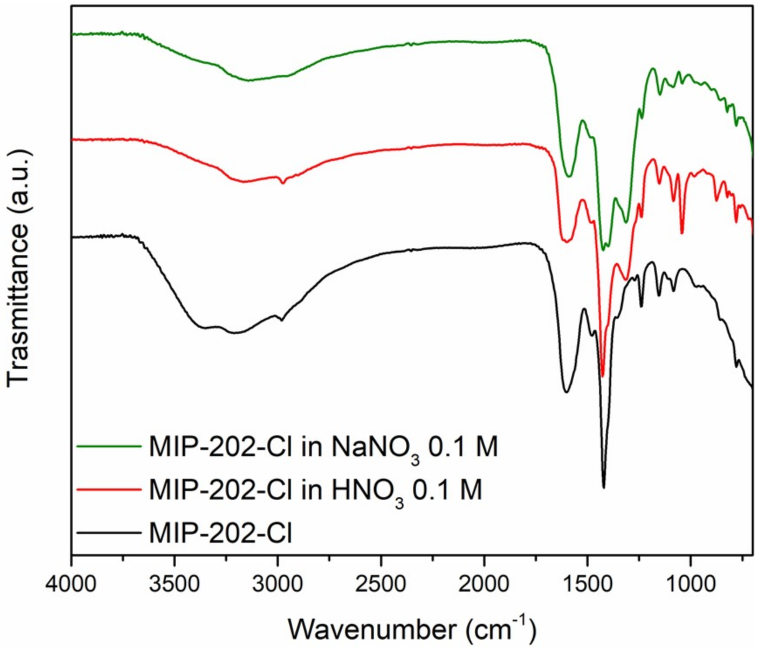


Figure S11. ATR-IR spectra of MIP-202-Cl as synthesised (black), after soaking in HNO$_3$ 0.1 M (red) and after soaking in NaNO$_3$ 0.1 M (green).

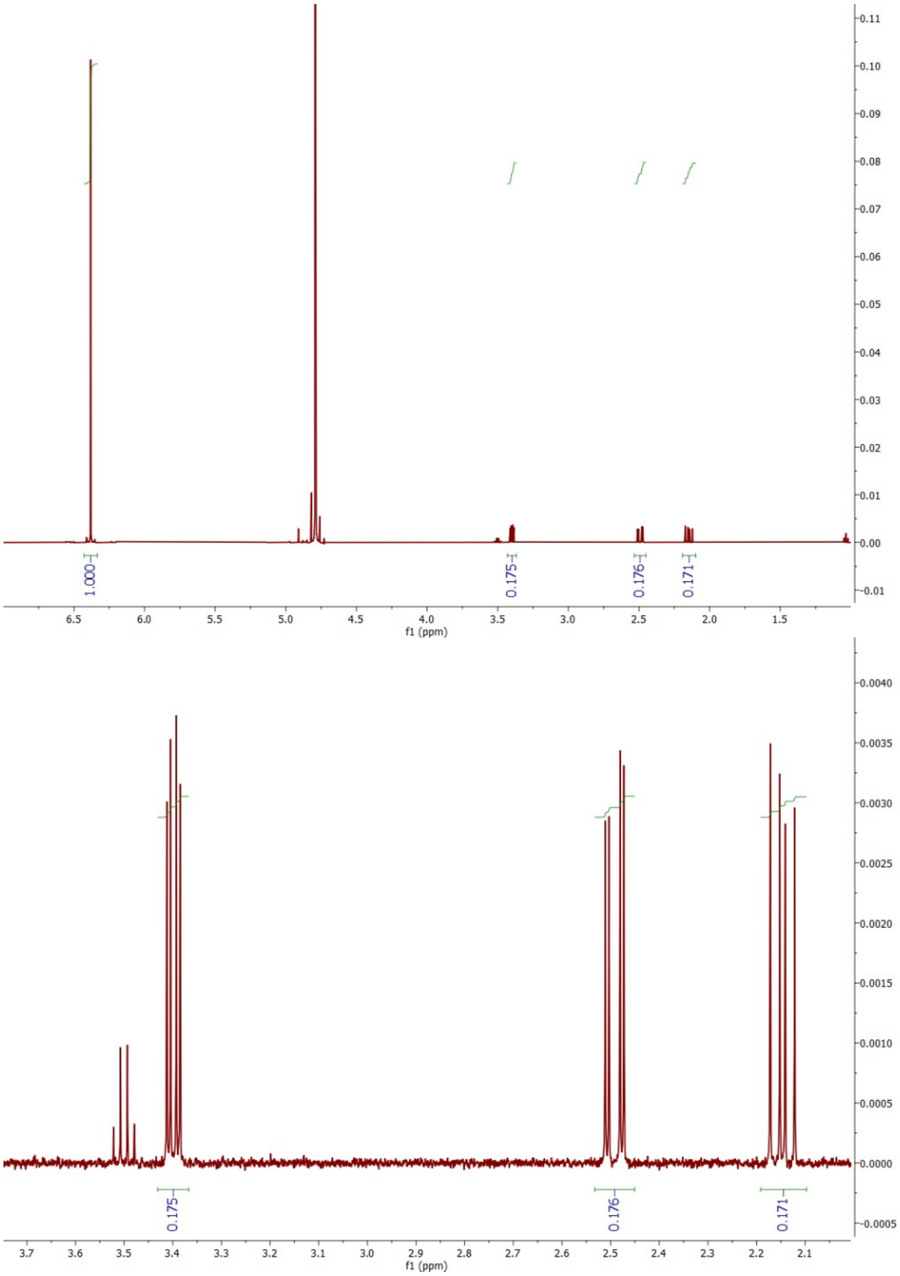


Figure S12. Full ^{1}H-NMR spectrum (top) and zoom on the region where the signals of Asp appear (bottom) of 11.1 mg of dry MIP-202-NO_3 soaked in 0.1 M HCl (hereafter MIP-202-NO_3/HCl) digested in 1 mL of 1 M NaOH in D_2O in the presence of 0.100 M fumaric acid. Each signal of Asp accounts for one proton. The averaged integral for Asp is 0.174. The signal of fumaric acid accounts for two protons. The integral of fumaric acid is 1.000, which is normalised to 0.500. The signals at about 1 and 3.5 ppm are due to residual ethanol, used to wash the solid. The concentration of Asp is derived to be 0.0348 M, corresponding to 4.56 mg of Asp in the original solid (41.1 wt%).

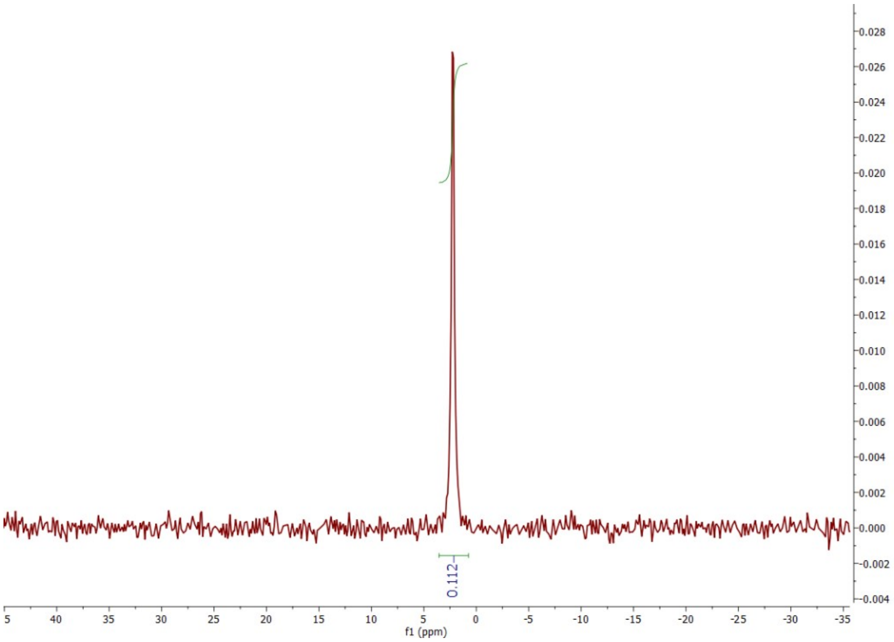


Figure S13. ^{35}Cl-NMR spectrum of 11.1 mg of dry MIP-202-NO_3/HCl digested in 1 mL of 1 M NaOH in D_2O in the presence of 0.100 M fumaric acid. The value shown for the integral (0.112) is the absolute value. The same signal for the external standard (0.050 M NaCl solution in 1 M aqueous NaOH) integrates 0.225. The concentration of chloride is derived to be 0.0249 M, corresponding to 0.88 mg of chloride in the original solid (7.9 wt%).

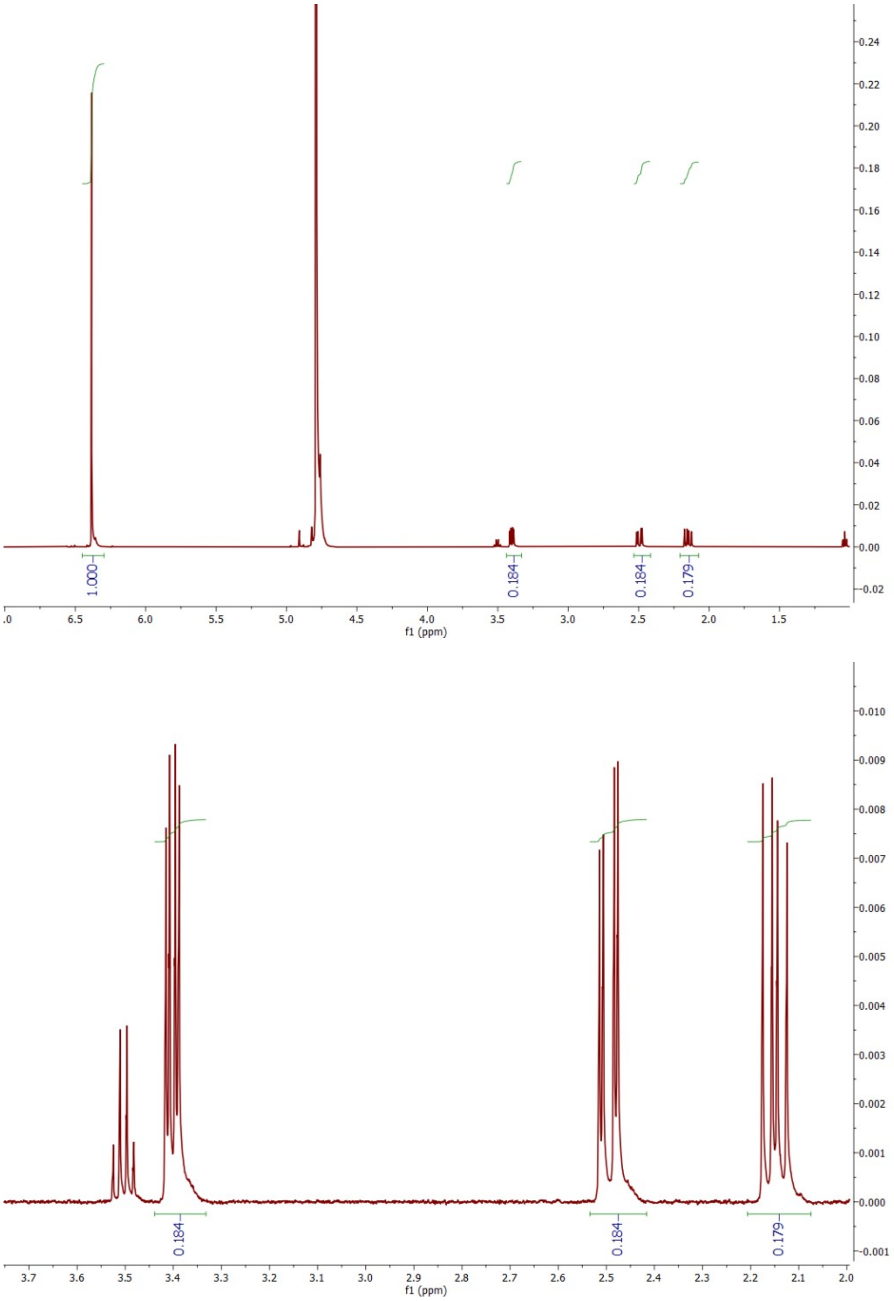


Figure S14. Full ^{1}H-NMR spectrum (top) and zoom on the region where the signals of Asp appear (bottom) of 12.8 mg of dry MIP-202-Cl soaked in 0.1 M HNO_3 (hereafter MIP-202-Cl/HNO_3) digested in 1 mL of 1 M NaOH in D_2O in the presence of 0.100 M fumaric acid. Each signal of Asp accounts for one proton. The averaged integral for Asp is 0.182. The signal of fumaric acid accounts for two protons. The integral of fumaric acid is 1.000, which is normalised to 0.500. The signals at about 1 and 3.5 ppm are due to residual ethanol, used to wash the solid. The concentration of Asp is derived to be 0.0365 M, corresponding to 4.78 mg of Asp in the original solid (37.3 wt%).

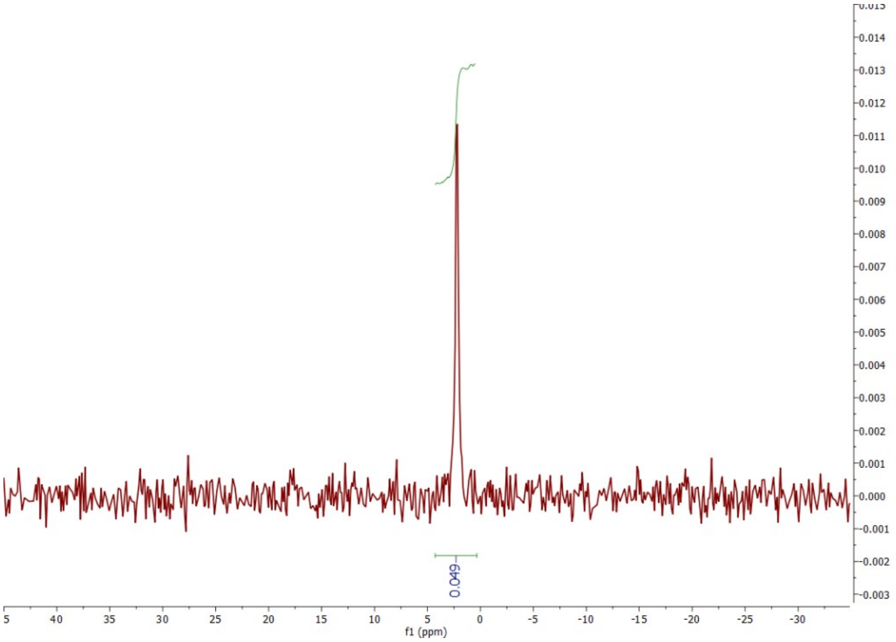


Figure S15. ^{35}Cl-NMR spectrum of 12.8 mg of dry MIP-202-Cl/HNO_3 digested in 1 mL of 1 M NaOH in D_2O in the presence of 0.100 M fumaric acid. The value shown for the integral (0.049) is the absolute value. The same signal for the external standard (0.050 M NaCl solution in 1 M aqueous NaOH) integrates 0.225. The concentration of chloride is derived to be 0.0107 M, corresponding to 0.38 mg of chloride in the original solid (3.0 wt%).

Table S2. CHN elemental analysis results for MIP-202-NO_3/HCl and MIP-202-Cl/HNO_3.

Sample	%C	%H	%N	C/N molar ratio
MIP-202-NO_3/HCl	12.51	3.56	4.81	3.03
MIP-202-Cl/HNO_3	12.17	3.79	6.44	2.20

Determination of the chemical formula of MIP-202-NO_3/HCl and MIP-202-Cl/HNO_3

Based on the NMR analyses of Figure S12 and Figure S13, dry MIP-202-NO_3/HCl contains 41.1 wt% of Asp and 7.9 wt% of chloride, corresponding to a chloride/Asp ratio of 0.71. The C/N ratio obtained from elemental analysis is 3.03, suggesting a nitrate/Asp ratio of 0.30. Assuming the formula $Zr_6O_4(OH)_4(Asp)_6(HCl)_{4.2}(HNO_3)_{1.8}$ (FW = 1730 g mol^{-1}), 45.4 wt% of Asp and 8.7 wt% of chloride are expected, in fair agreement with the experimental values.

Based on the analyses of Figure S14 and Figure S15, a chloride/Asp ratio of 0.29 is calculated for dry MIP-202-Cl/HNO_3. The C/N ratio obtained from elemental analysis is 2.20, suggesting a nitrate/Asp ratio of 0.82. Assuming the formula $Zr_6O_4(OH)_4(Asp)_6(HCl)_{1.8}(HNO_3)_{4.9}$ (FW = 1838 g mol^{-1}), 42.8 wt% of Asp and 3.5 wt% of chloride are expected, in fair agreement with the experimental ones.

The slightly lower experimental wt% could be due to either the presence of an amorphous inorganic residue deriving from partial decomposition of the MOFs or to the formation of some defects during the treatment in acidic conditions.

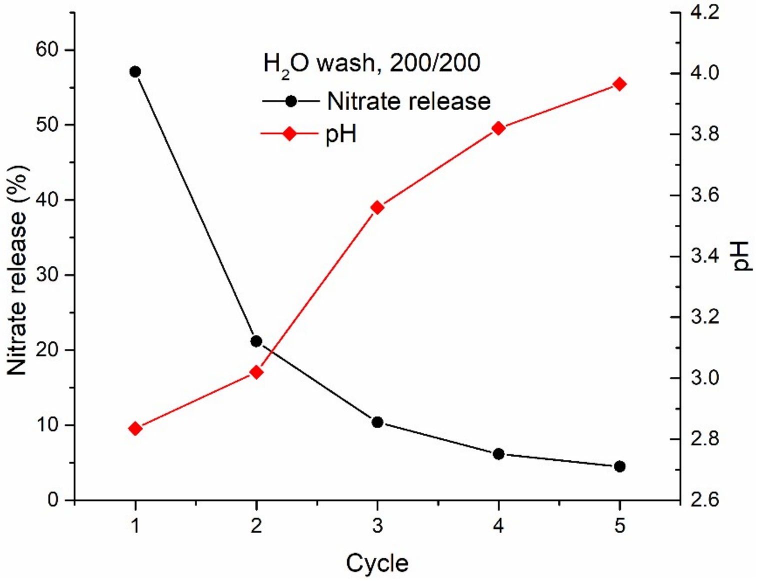


Figure S16. Nitrate release (black) and pH of the supernatant (red) during five cycles of washing of 200 mg of MIP-202-NO$_3$ in 200 mL water.

Table S3. Results of ICP-OES analysis on the supernatant after each washing cycle of 200 mg of MIP-202-NO$_3$ in 200 mL water.

Cycle	Concentration (ppm)	Mass of Zr leached (mg)	Zr leaching[a] (%)
1	15.146	3.03	5.5
2	2.523	0.50	0.9
3	1.200	0.24	0.4
4	0.479	0.10	0.2
5	0.644	0.13	0.2

[a] Determined based on 200 mg of hydrated MIP-202-NO$_3$ containing 54.6 mg of Zr

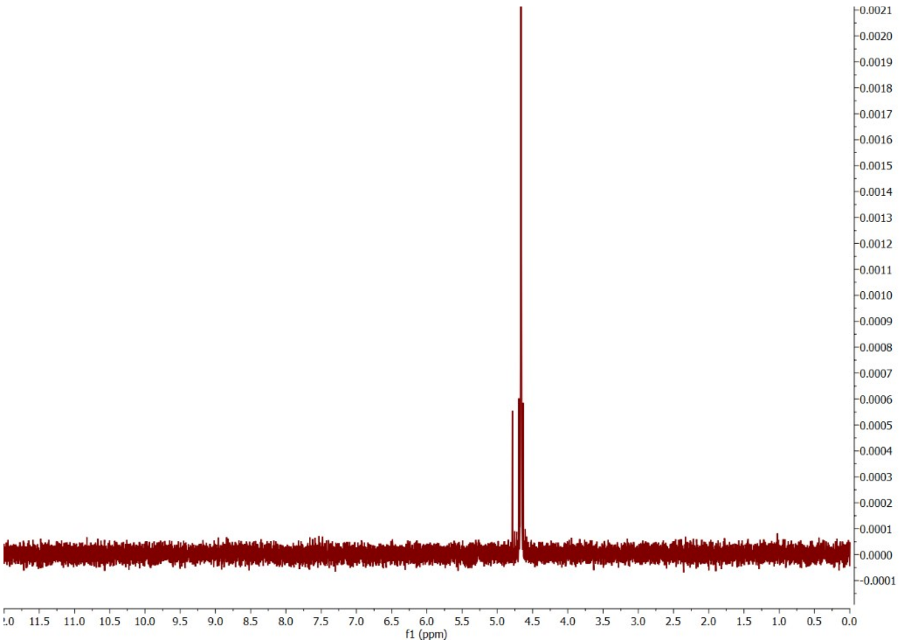


Figure S17. Full ^{1}H-NMR spectrum of the supernatant when 2 mg of MIP-202-NO_3 were dispersed in 200 mL of D_2O for 1 h.

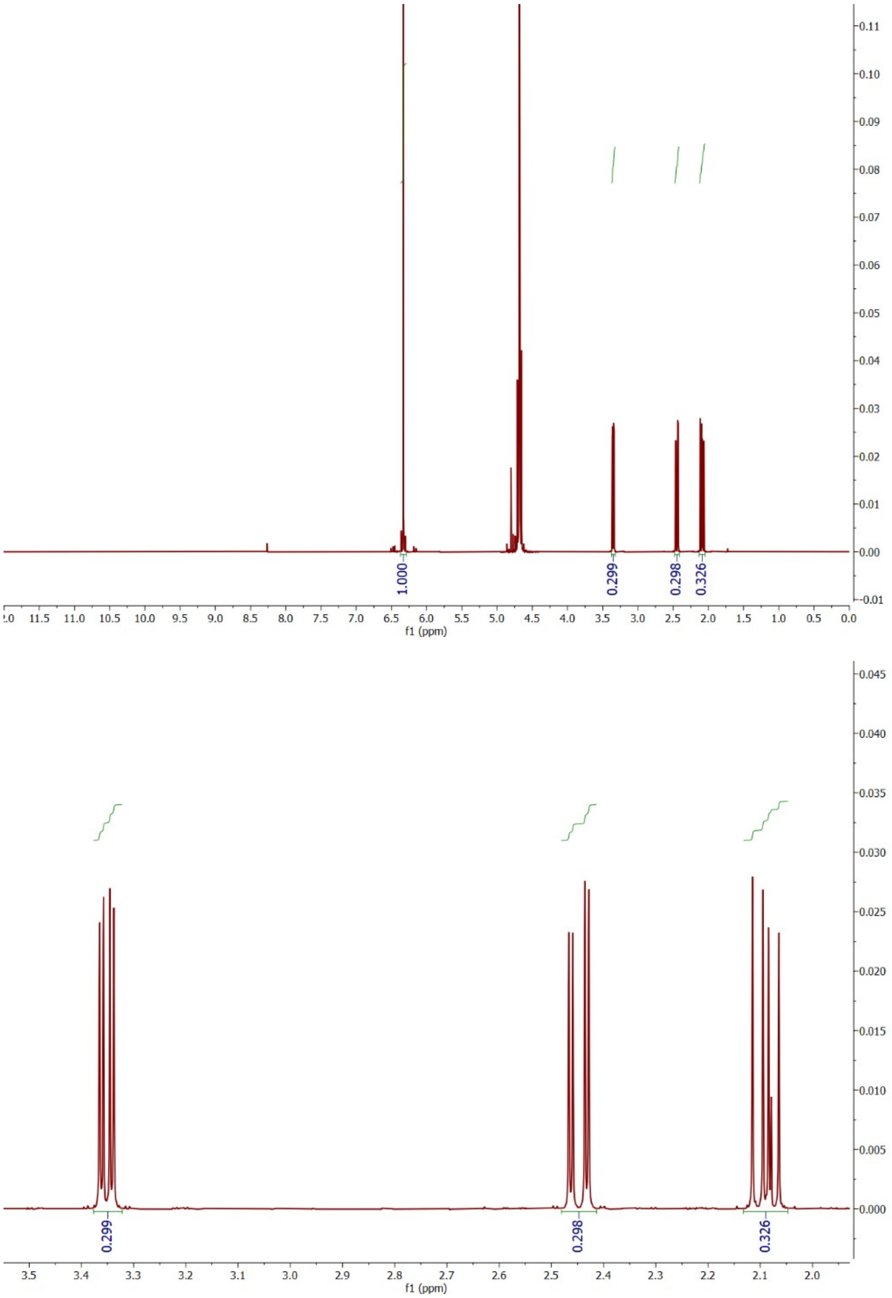


Figure S18. Full ^{1}H-NMR spectrum (top) and zoom on the region where the signals of Asp appear (bottom) of a 19.0 mg sample of dry MIP-202-NO$_3$ after five washing cycles in water (200 mg of MOF in 200 mL of water). The solid was digested in 1 mL of 1 M NaOH in D$_2$O in the presence of 0.110 M fumaric acid. Each signal of Asp accounts for one proton. The signal at 2.1 ppm is superimposed with a singlet, probably due to acetone, used to wash the solid, therefore its integral (0.326) is higher than that of the two other signals at 2.45 and 3.35 ppm (0.298 and 0.298, respectively). The average integral for Asp, derived from the two latter signals, is 0299. The signal of fumaric acid accounts for two protons. The integral of fumaric acid is 1.000, which is normalised to 0.500. The concentration of Asp is derived to be 0.0658 M, corresponding to 8.62 mg of Asp in the original solid (45.4 wt%).

Table S4. CHN elemental analysis results for MIP-202-NO_3 after five washing cycles in water (200 mg of MOF in 200 mL of water).

%C	%H	%N	C/N molar ratio
14.01	3.39	3.78	4.32

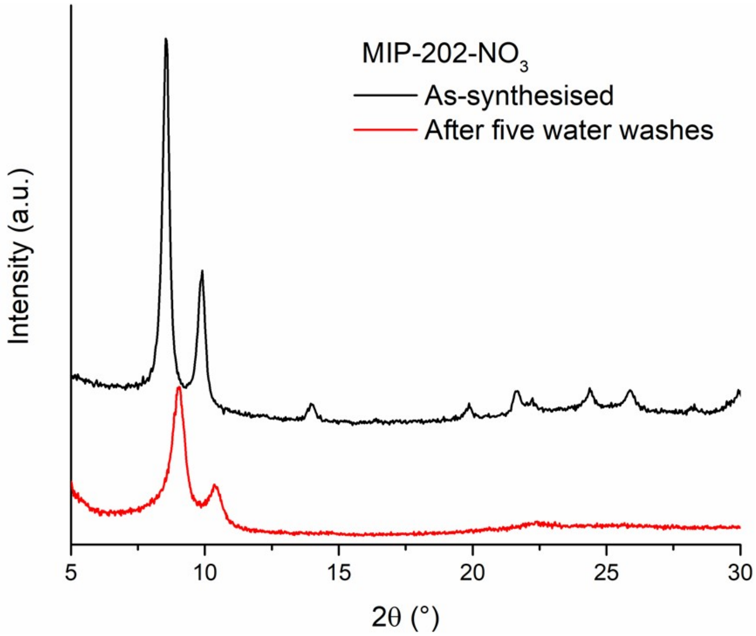


Figure S19. PXRD patterns of MIP-202-NO_3 as synthesised (black) and after five washes in water (200 mg of MOF in 200 mL H_2O, red). The shift of the Bragg reflections to higher angles is a symptom of a decrease in the lattice parameter, which we speculate could be due to a contraction of the structure upon removal of the extraframework anions. Given its aliphatic nature, the aspartate linker possesses a few degrees of freedom in terms of conformation, even though there are only two carbon atoms between the carboxylic groups. Such limited flexibility could be enough to allow a rearrangement of the linker to a more compact conformation, thus leading to a decrease of the unit cell volume.

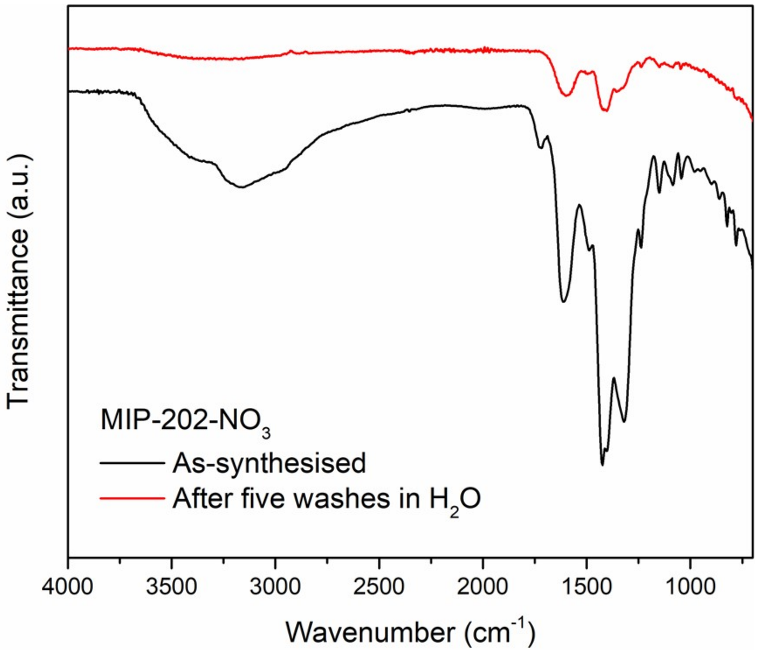


Figure S20. ATR-IR spectra of MIP-202-NO$_3$ as synthesised (black) and after five water washes (red).

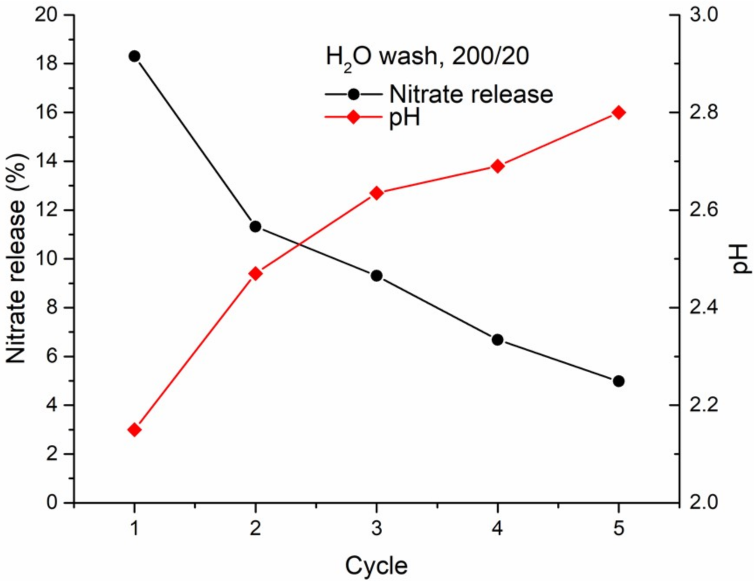


Figure S21. Nitrate release (black) and pH of the supernatant (red) during five cycles of washing of 200 mg of MIP-202-NO$_3$ in 20 mL water.