Electronic Supporting Information

Zr⁴⁺-terephthalate MOFs with 6-connected structures, highly efficient As(III/V) sorption and superhydrophobic properties

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Experimental Procedures

Experimental section

Materials. Zirconium chloride (ZrCl₄), 2-aminoterephthalic (NH₂-H₂BDC) and NaBH₄ were purchased from Aldrich. Hexanaldehyde (CH₃(CH₂)₄CHO), heptaldehyde (CH₃(CH₂)₅CHO), octanaldehyde (CH₃(CH₂)6CHO), nonanaldehyde (CH₃(CH₂)₇CHO), and dodecanaldehyde (CH₃(CH₂)₁₀CHO)) were purchased from Alfa Aesar. The solvents were used as received. **Syntheses.**

[1]

Alkylamino-terephthalic acid. Alkylaldehyde ($C_nH_{2n+1}CHO$; n=5-9,12; 27.5 mmol) was added into a stirred suspension of NH₂-H₂BDC (1 g, 5.5 mmol) in MeOH (50 mL), in a 100 mL single-neck round-bottomed flask. Within a few minutes a clear yellow solution was formed. To this solution, solid NaBH₄ (2.08g, 55 mmol) was gradually added. The resulting mixture was stirred for 24 h. A pale-yellow solid was precipitated after the addition of diethyl ether (50 ml), isolated by filtration and dried in the air. The precipitate was dissolved in dH₂O (50ml) and a yellow solid was precipitated after the addition of concentrated hydrochloric acid (pH of solution was adjusted to 3). The product alkylamino-terephthalic acid was isolated by filtration, washed with MeOH and dried in the air. Specifically, we obtained the following ligands:

hexyl-amino-H₂BDC. Yield: 0.955 g; ¹H NMR (400 MHz, D₂O-NaOH): δ (ppm) 7.56 (1H, d, J = 8 Hz, ArH), 7.1 (1H, s, ArH), 6.95 (1H, d, J = 8.1 Hz, ArH), 2.98 (2H, t, J = 6.7 Hz, -CH₂-), 1.44 (2H, m, -CH₂-), 1.21 (2H, m, -CH₂-), 1.1 (4H, m, -(CH₂)₂-), 0.66 (3H, t, J = 6.4 Hz, -CH₃).

heptyl-amino-H₂BDC. Yield: 0.934 g; ¹**H NMR** (400 MHz, D₂O-NaOH): δ (ppm) 7.71 (1H, d, J = 8 Hz, ArH), 7.25 (1H, s, ArH), 7.1 (1H, d, J = 8 Hz, ArH), 3.14 (2H, t, J = 6.8 Hz, -CH₂-), 1.61 (2H, m, -CH₂-), 1.36 (2H, m, -CH₂-), 1.25 (6H, m, -(CH₂)₃-), 0.80 (3H, t, J = 6.7 Hz, -CH₃).

octyl-amino-H₂BDC. Yield: 0.929 g; ¹H NMR (400 MHz, D₂O-NaOH): δ (ppm) 7.7 (1H, d, J = 8 Hz, ArH), 7.25 (1H, s, ArH), 7.1 (1H, d, J = 8 Hz, ArH), 3.14 (2H, t, J = 6.8 Hz, -CH₂-), 1.61 (2H, m, -CH₂-), 1.35 (2H, m, -CH₂-), 1.23 (8H, m, - (CH₂)₄-), 0.79 (3H, t, J = 6.5 Hz, -CH₃).

nonyl-amino-H₂BDC. Yield: 0.944 g; ¹H NMR (400 MHz, D₂O-NaOH): δ (ppm) 7.71 (1H, d, J = 8 Hz, ArH), 7.26 (1H, s, ArH), 7.1 (1H, d, J = 8 Hz, ArH), 3.14 (2H, t, J = 6.8 Hz, -CH₂-), 1.60 (2H, m, -CH₂-), 1.35 (2H, m, -CH₂-), 1.23 (10H, m, -(CH₂)₅-), 0.78 (3H, t, J = 6.4 Hz, -CH₃).

dodecyl-amino-H₂BDC. Yield: 0.952 g; ¹**H NMR** (400 MHz, D₂O-NaOH): δ (ppm) 7.69 (1H, d, J = 8 Hz, ArH), 7.19 (1H, s, ArH), 7.03 (1H, d, J = 8.1 Hz, ArH), 3.1 (2H, t, J = 6.9 Hz, -CH₂-), 1.52 (2H, m, -CH₂-), 1.11 (18H, m, -(CH₂)₉-), 0.76 (3H, t, J = 6.7 Hz, -CH₃).

 $H_{22}[Zr_6O_{20}(NH_2-BDC)_x(RNH-BDC)_{3-x}]$ -solvent (RNH-BDC²=2-alkyl-amine-terephthalate; R=hexyl-, HEX-MOF; R=heptyl-, HEPT-MOF; R=octyl-, OCT-MOF; R=nonyl-, NON-MOF; R=dodecyl-, DOD-MOF): $ZrCl_4$ (0.0625g, 0.27 mmol) and 2-alkyl-amino-terephthalic acid (0.375 mmol) was dissolved in 3.75 mL DMF and 0.5 mL CH₃COOH in a vial. The vial was sealed and placed in an oven operated at 120 °C, remained undisturbed at this temperature for 20 h and then was allowed to cool at room temperature. Pale yellow powder was isolated by filtration, washed with DMF and acetone and dried in the air. To remove any HCl (resulted from hydrolysis of ZrCl₄) or CH₃COOH residuals and thus prevent change of the pH of the solution during the As(III/V) sorption studies, HEX-MOF (0.1 g) was treated with a methanolic solution (4 mL) of Et₃N (0.1mL). This procedure was not followed for the rest of the MOFs. Although we tried different reaction temperatures, modulators etc., unfortunately, we could not isolate single crystals, but only powders.

HEX-MOF (As synthesized). Yield: 0.092 g; ¹**H NMR** (400 MHz, D₂O-NaOH): δ (ppm) 7.58 (1H, d, J = 8 Hz, ArH), 7.13 (1H, s, ArH), 6.98 (1H, d, J = 8 Hz, ArH), 3.02 (2H, t, J = 6.8 Hz, -CH₂-), 1.48 (2H, m, -CH₂-), 1.24 (2H, m, -CH₂-), 1.13 (4H, m, -(CH₂)₂-), 0.69 (3H, t, J = 6.8 Hz, -CH₃).

HEX-MOF (After treatment with MeOH/Et₃N). Yield: 0.091 g; ¹H NMR (400 MHz, D₂O-NaOH): δ (ppm) 7.68 (1H, d, J = 8 Hz, ArH), 7.23 (1H, s, ArH), 7.08 (1H, d, J = 8 Hz, ArH), 3.12 (2H, t, J = 6.8 Hz, -CH₂-), 1.59 (2H, m, -CH₂-), 1.35 (2H, m, -CH₂-), 1.25 (4H, m, -(CH₂)₂-), 0.80 (3H, t, J = 6.8 Hz, -CH₃).

HEPT-MOF. Yield: 0.097 g; ¹**H NMR** (400 MHz, D₂O-NaOH): δ (ppm) 7.69 (1H, d, J = 8 Hz, ArH), 7.24 (1H, s, ArH), 7.09 (1H, d, J = 8 Hz, ArH), 3.14 (2H, t, J = 6.7 Hz, -CH₂-), 1.59 (2H, m, -CH₂-), 1.29 (8H, m, -(CH₂)₄-), 0.79 (3H, t, J = 6.4 Hz, -CH₃).

OCT-MOF. Yield: 0.093 g; ¹H NMR (400 MHz, D₂O-NaOH): δ (ppm) 7.69 (1H, d, J = 8 Hz, ArH), 7.24 (1H, s, ArH), 7.09 (1H, d, J = 8.2 Hz, ArH), 3.14 (2H, t, J = 6.9 Hz, -CH₂-), 1.57 (2H, m, -CH₂-), 1.27 (10H, m, -(CH₂)₅-), 0.79 (3H, t, J = 6.7 Hz, -CH₃).

NON-MOF. Yield: 0.096 g; ¹**H NMR** (400 MHz, D₂O-NaOH): δ (ppm) 7.71 (1H, d, J = 7.8 Hz, ArH), 7.26 (1H, s, ArH), 7.11 (1H, d, J = 8.1 Hz, ArH), 3.15 (2H, t, J = 6.7 Hz, -CH₂-), 1.62 (2H, m, -CH₂-), 1.37 (2H, m, -CH₂-), 1.25 (10H, m, -(CH₂)₅-), 0.79 (3H, t, J = 7.1 Hz, -CH₃).

DODEC-MOF. Yield: 0.092 g; ¹H NMR (400 MHz, D₂O-NaOH): δ (ppm) 7.60 (1H, d, J = 8 Hz, ArH), 7.1 (1H, s, ArH), 6.95 (1H, d, J = 8.1 Hz, ArH), 2.91 (2H, t, J = 7 Hz, -CH₂-), 1.41 (2H, m, -CH₂-), 1.11 (18H, m, -(CH₂)₉-), 0.73 (3H, t, J = 6.4 Hz, -CH₃).

HEX-MOF/calcium alginate beads. The encapsulation of the material with calcium alginate was completed as following: 510 mg of **HEX-MOF** was dispersed in 10 mL of water via ultrasonication, and the resulting suspension was kept under vigorous stirring for 30 min. The next step included the addition of alginic acid sodium salt (60 mg) and the mixture was stirred for 1-2 h. Subsequently, the spherization was performed in a CaCl₂ solution (2% w/v) using a Pasteur pipette. The yellow beads were left in the gelatinization bath for 30 min, isolated via

filtration using a Buchner funnel, washed with excess of water and dried overnight at 60 °C (Yield: 0.514 g). The **HEX-MOF/Alginate** mass ratio used was 8.5. This is the minimum ratio we can use in order to isolate the MOF composite as stable beads. We avoided using more alginate because this will decrease the rate of sorption as the MOF particles would be covered by a thicker calcium alginate shell.

Leaching of organic species after sorption. Prior the ligand leaching studies, **HEX-MOF** was washed with EtOH and dried under vacuum at 100 °C to remove any residual organic solvents. 2.5 mg of **HEX-MOF** was added as a solid to a 2.5 mL solution of $Na_2HAsO_4 \cdot 7H_2O$ (6.67 mM) in D_2O . The mixture was kept under magnetic stirring for 10 min. After centrifugation the supernatant was analyzed via ¹H NMR.

Immobilization of HEX-MOF on cotton fabric (HEX-MOF@cotton fabric). The immobilization of **HEX-MOF** on cotton fabric was conducted in two separate steps. The first step consists of the creation of the polydopamine coating onto the fabric. The second step describes the immobilization of **HEX-MOF** onto the **PDA@cotton fabric** substrate via a solvothermal reaction.

A typical procedure for the immobilization of **HEX-MOF** is the following:

1st step. One piece of cotton fabric with dimensions of 7×7 cm and weighing a total of 727 mg, was washed three consecutive times with 5 mL of MeOH and then dried at 80 °C for 2 h. Afterwards 145.4 mg or 0.766 mmol of dopamine hydrochloride was placed in a conical flask containing 73 mL of aqueous Trizma base solution (10 mM). The mixture was then ultrasonicated for 5 min and the cotton fabrics were immersed in the solution. The flask was sealed with parafilm and kept under stirring at room temperature for 4h. Eventually the PDA@Fabric was first rinsed several times with deionized water in order to remove the excess of PDA and then with acetone. Polydopamine-coated substrates were isolated after drying at 80 °C for 12 h.

2nd **step.** PDA@cotton fabric (727 mg), ZrCl₄ (0.252 g, 1.08 mmol) and **hexyl-amino-H₂BDC** (0.398 g, 1.5 mmol) were added into a mixture of 15 mL DMF/2 mL CH₃COOH in a glass vial. The vial was then ultrasonicated for 5 min. The reaction container was then sealed and allowed to react in an oven operated at 120 °C for 24 h. The next day the mixture was cooled at room temperature and the modified fabric was primarily washed multiple times with deionized H₂O in order to remove the **HEX-MOF** that has not been incorporated into the substrate and additionally with acetone. The final product was dried at 80 °C for 6 h. The immobilization process was repeated twice so we can increase the amount of the incorporated metal-organic material. The amount of **HEX-MOF** immobilized on the fabric was determined by the net difference in the weight of the fabric before and after each synthesis. The results revealed that 145 mg of **HEX-MOF** were immobilized on the fabric after two cycles.

Analytical and characterization techniques

Characterization

PXRD measurements. Powder X-ray diffraction measurements were performed on a Bruker D2-Phaser X-ray diffractometer (CuKa radiation source, wavelength = 1.54184 Å). High quality diffraction data, suitable to be used for Rietveld refinement, were obtained using a step of 0.01° and scan rate of 1.2 second/ 0.01° (overall measurement time was approximately 172 min).

IR spectroscopy. IR spectra were recorded on KBr pellets in the 4000-400 cm⁻¹ range using an Agilent Cary 630 FTIR.

Thermal analyses. Thermogravimetric analyses (TGA) were performed on a DTG-60 Shimadzu Simultaneous DTA-DTG Apparatus from 25 to 700 °C in air atmosphere (100 mL min⁻¹ flow rate) with a heating rate of 10 °C min⁻¹. **¹HNMR.**¹H NMR spectra were measured with Bruker 400 MHz spectrometer.

Energy dispersive spectroscopy (EDS) analyses. These measurements were performed on a JEOL JSM-6390LV scanning electron microscope (SEM) equipped with an Oxford INCA PentaFET-x3 energy dispersive X-ray spectroscopy (EDS) detector. Data acquisition was performed with an accelerating voltage of 20 kV and 120s accumulation time.

SEM. Scanning electron microscopy (SEM) images were taken with a JEOL JSM-6390LV electron microscope operating at 15 kV accelerated voltage. The samples were sputter-coated with a 5-10 nm Au film to reduce charging.

Energy dispersive spectroscopy (EDS) analyses. These measurements were performed on a JEOL JSM-6390LV scanning electron microscope (SEM) equipped with an Oxford INCA PentaFET-x3 energy dispersive X-ray spectroscopy (EDS) detector. Data acquisition was performed with an accelerating voltage of 20 kV and 120s accumulation time.

Gas sorption measurements. N₂ adsorption-desorption isotherms were measured at 77 K on a Quantachrome Nova 3200e sorption analyzer. Before analysis, all samples were EtOH exchanged, activated via supercritical CO₂ drying and then, degassed at 150 °C under vacuum (<10⁻⁵ Torr) for 12 h. The specific surface areas were calculated by applying the Brumauer-Emmett-Teller (BET) method to the absorption branch of isotherms in the 0.04–0.23 relative pressure (P/P_o) range.

Zeta potential measurement. Zeta potential was measured with a Malvern Zetasizer Nano ZS (Malvern Panalytical, Worcestershire, UK) in a two-electrode capillary cell using the Laser Doppler Micro-electrophoresis technique.

XPS measurements. XPS measurements were performed on a SPECS spectrometer using a Phoibos 100 1D-DLD electron analyzer and an A1 K α radiation as the energy source (1486.6 eV). Binding energy values were corrected for charging by assigning a binding energy of 284.8 eV to the C 1s signal of adventitious carbon.

Atomic absorption spectroscopy. As(III/V) was determined by electrothermal atomic absorption spectrometry (ETAAS) in a Shimadzu AA-6800 atomic absorption spectrophotometer (Shimadzu Corp., Kyoto, Japan) with a hollow cathode lamp operating at 12 mA. Measurements were performed at 242.8 nm with D_2 background correction.

Contact angle measurements. Water contact angles were determined using the drop shape analysis utility of the ImageJ software, and specifically the Low- Bond Axisymmetric Drop Shape Analysis (LBADSA) method.^{1,2}

Stability studies with HEX-MOF

Chemical Stability. 10 mg of **HEX-MOF** was added in 10 mL of strongly acidic (HCl 1M) or alkaline (pH=12) solution, in ambient conditions and kept under stirring for 12 h. The resultant mixtures were centrifuged, washed with deionized water and dried in air prior to PXRD analysis.

Thermal Stability. 50 mg of **HEX-MOF** was treated under vacuum at 150 and 200 °C respectively for 3h. The solids were allowed to cool down at room temperature and then studied via PXRD.

Sorption studies

Batch sorption studies. A typical sorption experiment of HEX-MOF with As(V) anions is the following: In a solution of Na₂HAsO₄·7H₂O (6.67 mM) in deionized water (10 mL, pH≥ 6.5), compound HEX-MOF (10 mg ~ 0.005 mmol) was immersed as a solid. The mixture was kept under vigorous magnetic stirring for approximately 10 min. The metal-organic material was isolated by centrifugation, washed a few times with water and acetone and dried at 80 °C for at least 6 h (Yield: 8.5 mg). The isolation of the HEX-MOF/As(III) was done similarly as that of the As(V)-loaded material, with the exception that $NaAsO_2(10 \text{ mM}, 10 \text{ mL}, pH = 7)$ aqueous solution was used instead of that of Na₂HAsO₄·7H₂O. The uptake of the As species from solutions of various concentrations was studied by the batch method at V:m ~ 1000 mL/g, room temperature and 10 min contact. These experimental data were used for the determination of the respective sorption isotherms. The competitive and variable pH sorption experiments were also carried out with the batch method at V:m ratio ~ 1000 mL/g, room temperature and 10 min contact. The batch sorption experiments with the bottled water solutions were also conducted with V:m ratio ~ 1000 mL/g, room temperature and 10 min contact. For the determination of the sorption kinetics, experiments of different reaction times (1-30 min) have been performed. For each experiment a 10 mL sample of As(V) or As(III) solution (initial As concentration of 1 ppm) was added to each vial (containing 10 mg of HEX-MOF) and the mixtures were kept under magnetic stirring for the designated reaction times. The suspensions from the various reactions were filtrated and the resulting solutions were analyzed for their As content with atomic absorption spectroscopy. Each sorption experiment has been done at least twice and the reported sorption data represent the average of sorption results from the distinct sorption experiments. The difference between the concentrations of As(V) determined for the different sorption experiments was < 2%.

Regeneration/reusability study. 0.1g of **HEX-MOF/As(III)** were immersed in 100 mL HCl 4 M and kept under stirring for 1h in order to release As(III) from the loaded sorbent. The regenerated material, isolated by filtration, was treated for 2h with a methanolic solution (4 mL) of Et_3N (0.1mL), to remove the excess of HCl. The regenerated **HEX-MOF** was reused for the treatment of an As(III) solution (1000 ppm). The same procedure was followed for the regeneration and the reuse of **HEX-MOF** for As(V) sorption.

Column As(III) sorption studies. Several samples of bottled water solution intentionally contaminated with As(III) (total volume = 2500mL, initial concentration = 20 ppb) were passed through a column filled with **HEX-MOF/calcium alginate beads** (700mg; 0.7 cm ID column) and collected at the bottom in glass tubes. The solutions were analyzed with atomic absorption spectroscopy. Similar sorption experiments with calcium alginate showed no arsenic sorption capacity.

As(V) Sorption under Continuous Flow Conditions. As(V) removal experiments under continuous flow conditions were carried out utilizing several circular shaped **HEX-MOF@cotton fabrics** (1.5 cm diameter) containing approximately 270 mg of the sorbent. The modified fabrics were packed inside a 10 mL syringe (Fig. S31a) and washed with deionized water (3×15 mL). Then the excess of water was carefully removed from the fibers using filter paper and they were relocated inside the syringe. Nearly 3500 mL of the As(V) contaminated bottled water solution (sample 1, concentration = 93 ppb) were passed through the experimental setup in small portions (10 mL) and collected at the bottom in glass tubes. The concentration of the effluents was determined via atomic absorption spectroscopy. Similar sorption experiment conducted with PDA@cotton fabrics showed no arsenic sorption capacity.

HEPT-MOF OCT-MOF

Results and Discussion

Figure S 1. Representation of the structures of **HEPT-**, **OCT-**, **NON-**, and **DODEC-MOF**. Color code: Zr, cyan; N, blue; O, red; C, grey. H atoms and solvent molecules were omitted for clarity.



Figure S 2. Representation of the structure of **HEX-MOF** showing the guest water molecules (shown as red balls). H atoms were omitted for clarity.



Figure S 3. N₂ sorption isotherms (77 K) for HEPT-, OCT-, NON-, and DODEC-MOF.

MOF	BET(m ² /g)/experimental	BET(m ² /g)/calculated with poreblazer
HEX-MOF	911	909
HEPT-MOF	792	744
OCT-MOF	733	735
NON-MOF	471	571
DODEC-MOF	394	541

Table S1. Experimental and calculated (via poreblazer) surface areas for the MOFs.

Thermal analyses data



Figure S 4. The TGA and DTG (first derivative) data for **HEX-MOF** measured in air.



Figure S 5. The TGA and DTG (first derivative) data for **HEPT-MOF** measured in air.



Figure S 6. The TGA and DTG (first derivative) data for **OCT-MOF** measured in air.



Figure S 7. The TGA and DTG (first derivative) data for **NON-MOF** measured in air.



Figure S 8. The TGA and DTG (first derivative) data for **DODEC-MOF** measured in air.

The TGA and DTG data revealed two main steps of weight losses: One ending at 250.58, 255.56, 255.33, 265 and 255.33 $^{\circ}$ C for **HEX-MOF**, **HEPT-MOF**, **OCT-MOF**, **NON-MOF** and **DODEC-MOF** respectively, assigned to the removal of lattice solvents and a second completed at ~600 $^{\circ}$ C which is due to the release of organic ligands. Therefore, at 250-265 $^{\circ}$ C the MOFs contain no lattice solvents and at 600 $^{\circ}$ C the MOFs were converted to ZrO₂. In order to identify the number of linkers for the MOFs, we are comparing the experimental % Zr content (calculated based on ZrO₂) of the MOFs containing no lattice solvents with the values calculated for the MOFs (also with no lattice solvents) with four (8-c framework) and three (6-c framework) linkers (Table S1). From this comparison, it is clear that the MOFs contain 3 linkers per formula unit.

Calculated Difference Difference Calculated Zr(%) for 4 Zr(%) for 3 (calc.-(calc.-MOF Found Zr(%) linkers (8-c linkers (6-c exp.)/8-c exp.)/6-c framework) framework) **HEX-MOF** 29.6 32.9 31.5 1.9 -1.4 **HEPT-MOF** 28.7 32.1 30.5 1.8 -1.6 **OCT-MOF** 27.9 31.3 31.9 4 0.6 **NON-MOF** 27.2 30.6 30.1 2.9 0.5

31.0

5.8

2.3

Table S2 Experimental Zr(%) of MOFs (with no lattice solvents) vs. calculated values of MOFs with no lattice solvents and 4 or 3 linkers.

X-ray powder diffraction studies and other characterization data for the reported MOFs

28.7

Details of the structural refinement

25.2

DODEC-MOF

The PXRD pattern of the **HEX-MOF** (MOF treated with MeOH/Et₃N, see Experimental Section) was indexed successfully in the hexagonal/trigonal crystal system and *R3* space group using TOPAS.³ Then, structureless (Le Bail) refinement was performed and the results of such refinement were satisfactory confirming the accuracy of indexing results, as shown below:



Figure S 9. Le Bail plot of **HEX-MOF.** Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions.

The initial structural model for the six-connected framework was derived from the structure of the corresponding 12-connected framework (in *R3* space group), by removing 6 linkers (i.e. one of the two crystallographically unique linkers) in the second structure, as shown below:



Figure S 10. A 6-c framework derived from a 12-C framework via removal of 6 linkers.

The initial 6-c structural model was optimized with simulating annealing methods, allowing (a) the torsion angles related to the alkyl-chain group on the terephthalate moiety to rotate, (b) water lattice solvents to move freely in the cell and (c) the bond distances and angles of the terminal oxygen atoms of the Zr_6 clusters to change. The optimized model was used as starting point for the Rietveld refinement. The coordinates of the non-hydrogen atoms of the alkyl-chain groups and terminal O atoms were refined. The occupancies for the atoms of the alkyl-chain groups and terminal O atoms were refined. The occupancies for the atoms of the alkyl-chain groups were fixed to 0.94, based on ¹H NMR data (Fig. S19) indicating that ~6% of the alkyl-amino-BDC ligands were decomposed to (non-alkylated) amino-BDC. The rest of the framework atoms were kept fixed as this part of the structure is identical to the well-known Zr^{4+} -terephthalate structure. The occupancies and coordinates of water molecules were also refined. Attempts to refine thermal parameters were unsuccessful as unusual values were found for several atoms. Thus, we decided to keep the thermal parameters fixed to a value of 0.05.

Prior the inclusion of solvent molecules in the pores of the **HEX-MOF**, the refinement results were the following:



Figure S 11. Rietveld plot of **HEX-MOF/solvent – free model**. Violet crosses: experimental points; red line: calculated pattern; black line: difference pattern (exp-calc); and green bars: Bragg positions. Inset: magnification of the 2 ϑ region 30– 60°.

From the above data, it is apparent that the residual peak intensities are relatively high, see for example the residual peak intensity for the third peak (at \sim 12 deg.).

However, after inclusion of the water solvents (with their positions initially found via simulating annealing methods) and refinement of coordinates and occupancies of the non-hydrogen atoms, the residual peak intensities became much lower and there was substantial improvement of the R_{wp} , R_p values from 8.48, 5.59 % (for the solvent-free model) to 6.04, 4.61% respectively, as shown below:



Figure S 12. Rietveld plot of **HEX-MOF**. Violet crosses: experimental points; red line: calculated pattern; black line: difference pattern (exp-calc); and green bars: Bragg positions. Inset: magnification of the 2ϑ region $30-60^\circ$.

We have also attempted Rietveld refinement using structural models where acetate anions have replaced some of the terminal ligands of the cluster, taking into account that ¹H NMR data of **HEX-MOF** digested in D₂O/NaOH indicated some amounts of CH₃COO⁻ species (Fig. S19). However, Rietveld refinements with such models yielded considerably higher R_{wp} , R_p values (2-4 % higher) than the corresponding values for the model with no acetate groups. Therefore, we believe that acetate or acetic acid groups are bound to the Zr⁴⁺ ions on the external surface of the particles and not to the Zr₆ clusters in the interior of the framework.

Similar procedures were followed for the Rietveld refinements of the other MOFs (HEPT, OCT, NON, DODEC-MOFs) and As(III)/As(V)-loaded HEX-MOF. We should, however, note that the solvent molecules included in HEPT, OCT, NON, DODEC-MOFs were DMF, since the MOFs measured were as synthesized (no treatment with MeOH/Et₃N was applied for these MOFs). In addition, it should be mentioned that (prior the optimization of the structure of As(III)-loaded HEX-MOF via simulating annealing methods) H₃AsO₃ species were initially placed in random positions in the pores of the MOF. However, after the optimization procedure, one of the O atoms of the H₃AsO₃ species was found close to Zr atoms (in a distance of ~ 2.3 Å). Thus, we decided to build a structural model with As(III) species as monodentate ligands in the Zr₆ clusters (see Fig.4b in main text) and the results of Rietveld refinement with such structural model was satisfactory (see Fig. S33). In addition, R_{wp}, R_p values for Rietveld refinement using models with As(III) species ligated as bridging ligands to Zr₆ clusters were significantly higher (0.5-1% higher) than the corresponding ones for the refinement using a model with monodentate As(III)

species. All above support a monodentate coordination of As(III) species. Finally, considering that **HEX-MOF** a) absorbs 3 moles of As(V) per formula unit, b) As(V) exists as a mixture of $H_2AsO_4^-$ and $HAsO_4^{2-}$ at pH =7 and c) the hard Zr^{4+} will prefer coordination with the divalent $HAsO_4^{2-}$, the only possible As(V) coordination mode involves bidentate (bridging) ligation of $HAsO_4^{2-}$ species to the Zr_6 clusters (see main text).

CCDC 2176057-2176063 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <u>www.ccdc.cam.ac.uk/data_request/cif</u>.



Figure S 13. Rietveld and Le Bail plots of **HEPT-MOF.** Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2ϑ region $30 - 60^{\circ}$.



Figure S 14. Rietveld and Le Bail plots of **OCT-MOF.** Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2ϑ region $30 - 60^{\circ}$.



Figure S 15. Rietveld and Le Bail plots of **NON-MOF.** Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2ϑ region $30 - 60^{\circ}$.



Figure S 16. Rietveld and Le Bail plots of **DODEC-MOF.** Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2ϑ region $30 - 60^{\circ}$.



Figure S 17. Representation of the pcu-net (with point symbol {4 12 .6 3}) of **HEX-, HEPT-, OCT-, NON-**, and **DODEC- MOFs**. The topological analysis was performed with TOPOSPRO.⁴



Figure S 18. Le Bail plots of a) **HEX-MOF/1M HCI** and b) **HEX-MOF/pH=12**. Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions. Unit cell parameters: a) a=14.696 (3) Å, b=35.991 (8) Å, V=6732 (3)Å³; b) a=14.68 (2) Å, b=35.99 (5) Å, V=6718 (20)Å³. c) Comparative PXRD data for **HEX-MOF** as synthesized and **HEX-MOF** after treatment with acidic (HCl 1M) or alkaline (pH=12) aqueous solutions.



Figure S 19. Le Bail plots of **HEX-MOF** after thermal treatment at 150 and 200 °C under vacuum for 3 hours. Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions. Refined unit cell parameters: **HEX-MOF** heated at 150 °C (a= 14.668(5) Å, c= 35.95(1) Å and V= 6699(5) Å³) and **HEX-MOF** heated at 200 °C (a= 14.64(7) Å, c= 35.9 (2) Å and V= 6664(76) Å³).



Figure S 20. Comparative PXRD data for **HEX-MOF** as synthesized and **HEX-MOF** after thermal treatment at 150 and 200 °C under vacuum.



Figure S 21. ¹H NMR spectra of a) as synthesized **HEX-MOF**, and b) **HEX-MOF** treated with MeOH/Et₃N after digestion in $D_2O/NaOH$ solution.

The ¹H NMR data revealed an average HEX-NH₂-BDC/NH₂-BDC ratio of 1/0.06 (see enlarged view of the region 7-7.7 ppm).

In the ¹H NMR spectra of the as synthesized material several peaks are attributed to solvent impurities such as DMF, Acetic Acid and the base hydrolysis products of DMF, i.e. HCOOH and $(CH_3)_2NH$. On the other hand, the material after its treatment with a mixture of MeOH/Et₃N does not exhibit signals that are assigned to HCOOH and DMF and the intensities for the $(CH_3)_2NH$ and CH_3COOH peaks are substantially decreased.



Figure S 22. FT-IR spectra of HEX-NH-BDCH₂ ligand and HEX-MOF.



Figure S 23. FT-IR spectra of HEPT-NH-BDCH₂ ligand and HEPT-MOF.



Figure S 24. FT-IR spectra of OCT-NH-BDCH₂ ligand and OCT-MOF.



Figure S 25. FT-IR spectra of NON-NH-BDCH₂ ligand and **NON-MOF**.



Figure S 26. FT-IR spectra of DODEC-NH-BDCH₂ ligand and **DODEC-MOF**.



Figure S 27. SEM images of **HEX-MOF** with a) x2500, b) x10000, and c) x20000 magnification.

As(III)/(V) Sorption data



Figure S 28. Fitting of the kinetics data with the Ho and Mckay's pseudo-second-order equation for the sorption of a) As(III) and b) As(V) by **HEX-MOF** (initial concentration = 1 ppm, $pH^{\sim}7$).

Lagergren's First-order equation and Ho and Mckay's pseudo-second-order equation were used to fit the kinetics data. The expressions of these equations are the following:

Lagergren's First-order equation:

$$q_t = q_e [1 - \exp(-K_L t)]$$

where q_e = the amount (mg g⁻¹) of ion sorbed in equilibrium, K_L = the Lagergren or first-order rate constant.⁵

Ho and Mckay's pseudo-second-order equation:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$

where q_t = the amount (mg/g) of ion sorbed at different reaction times (t), q_e = the amount (mg/g) of ion sorbed in equilibrium, and where k_2 is the second-order rate constant [g/(mg·min)].⁵

Table S3. The parameters of Lagergren's first-order equation and Ho-Mckay's second-order equation, found after the fitting of kinetics data for the sorption of As(III) and As(V) by **HEX-MOF**.

	Lagergren's Firs	t-Order Equation	Ho-Mckay's Second - Order Equation			
	q₌ mg g⁻¹	g ⁻¹ K _L R ²		q₀ mg g⁻¹	K₂ g (mg min) ⁻¹	R ²
As(V)	0.995 ± 0.001	3.55 ± 0.12	0.89	1.00 ± 8.27 10-4	28.83 ± 1.85	0.97
As(III)	0.997 ± 0.001	3.53 ± 0.11	0.89	1.00 ± 7.03 10-4	28.10 ± 1.50	0.98

Table S4. The fitting parameters found after the fitting of the isotherm sorption data of As(III) and As(V) for the **HEX- MOF**.

As(III)	Langmuir							
STEP 1	q₌ (mg/g)	b (L/mg)	R ²	R ²				
0121 1	134±27	0.008±0.004	0.9	0.93				
	Langmuir-Freundlich							
STEP 2	q₌ (mg/g)	b (L/mg)	n	R²				
	198±5	0.003±8.0 10 ⁻⁵	0.21±0.04	0.98				
As(V)	Langmuir							
	q₌ (mg/g)	R ²						
	104±8	0.008±0.002	0.95					

Langmuir, and Langmuir-Freundlich isotherms were used to fit the sorption equilibrium data. The expressions of the three model equations are the following:

$$q = q_m \frac{bC_e}{1 + bC_e}$$

a) Langmuir

$$q = q_m \frac{(bC_e)^{\frac{1}{n}}}{1 + (bC_e)^{\frac{1}{n}}}$$

b) Langmuir-Freundlich

where q (mg/g) is the amount of the ion sorbed at the equilibrium concentration C_e (ppm), q_m is the maximum sorption capacity of the sorbent, b (L/mg) is the Langmuir constant related to the free energy of the sorption, K_F and 1/n are the Freundlich constants.^{6,7}



Figure S 29. Reusability study for **HEX-MOF** towards As(V) and As(III).



Figure S 30. a) Comparative PXRD data of **HEX-MOF/As(V)** and **HEX-MOF/As(III)** after the 1st and 4th cycle of regeneration/sorption. b) Le Bail plots of **HEX-MOF/As(V)** and **HEX-MOF/As(III)** after four cycles of regeneration/sorption. Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions. Refined unit cell parameters: **HEX-MOF/As(V)** (a= 14.7(1) Å, c= 35.9(2) Å and V= 6738(115) Å³) and **HEX-MOF/As(III)** (a= 14.7(2) Å, c= 35.8(4) Å and V= 6652(153) Å³).



Figure S 31. Percentage (%) sorption of a) As(III) and b) As(V) by **HEX-MOF** in the pH range of 1-12.



Figure S 32. a) As(III) and b) As(V) and sorption data for **HEX-MOF** in the presence of various competitive anions. The initial total As concentration was 1 ppm in all sorption experiments.

	Total Hardness (CaCO _{3,} mg/L)	рН	NO₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	SO4 ²⁻ (mg/L)	HCO₃ ⁻ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na⁺ (mg/L)	K ⁺ (mg/L)
Bottled water (1)	223.5	7.8	0.83	5.02	7.71	241.5	80.7	5.34	2.24	0.6
Bottled water (2)	94.6	8	0.72	1.23	2.75	102.2	34.6	1.98	1.53	0.18

Table S 5. Physicochemical characteristics of bottled water samples.

Characterization of the HEX-MOF@cotton fabric



Figure S 33. a) FT-IR spectrum, b) PXRD pattern, and c) SEM image of **HEX-MOF@cotton fabric**. For comparison IR spectrum and PXRD pattern of **HEX-MOF** in powder form are also shown.



Figure S 34. Experimental setups for the continuous flow experiments. a) **HEX-MOF@cotton fabric** and b) **HEX-MOF/calcium alginate beads** as stationary phase in column sorption experiments.



Figure S 35. SEM image of a **HEX-MOF/calcium alginate bead**.

Table S 6. Comparison of the As(V) sorption properties of **HEX-MOF** with other state-of-the-art As(V) MOF-based sorbents. In the data provided in the table, the As content corresponds to the quantity of total As and not that of the oxoanionic species.

MOF-based Sorbent	Capacity mg As/g	Equilibrium time	Working pH range	Selectivity vs.	Reusability	Sorption under flow conditions	Ref.
Fe-BTC	6.6 (pH=4)	10 min	2-10	NA	NA	NA	8
MIL-53(Fe)	11.4 (pH=5)	90 min	3-10	NA	NA	NA	9
ZIF-8 (nps)	32.1 (pH=7)	7 h	6-9	NO3 ⁻ , SO4 ²⁻	NA	NA	10
ED-ZIF-8	44.7 (pH=7)	6 h	3-9	Cl ⁻ , HCO ₃ ⁻ , SO4 ²⁻ and mixture of various ions in genuine water samples	NA	NA	11
iMOF-1C	45.5 (pH=7)	15 h	NA	Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻	Reusable	NA	12
AUBM-1	55.2 (pH=7.6)	3 h	7-8	CO32-	Reusable	NA	13
MIL-53(AI)	56.5 (pH=8)	24 h	6-8	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	NA	NA	14
MIL-100(Fe)	62.1 (pH=7)	NA	NA	Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻	NA	NA	15
MIL-100(AI)	68.5 (pH=7)	NA	NA	Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻	NA	NA	15
Al-MOF-1	71.9 (pH=7)	1 min	3-7	Cl ⁻ , HCO ₃ ⁻ , SO4 ²⁻ , NO3 ⁻ , HPO4 ²⁻ and mixture of various ions in genuine water samples	Not reusable but recyclable	Performed	16
MIL-88A	77.6 (pH=5)	20 min	3-7	NA	NA	NA	17
UiO-66	162.3 (рН=2) 79.1 (рН=7)	48 h	1-10	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ (pH = 2)	NA	NA	18
HP-UiO-66-40%	133.2 (pH=6)	5h	2-10	Cl ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , CO ₃ ²⁻	Reusable	NA	19
Fe-Co-MOF-74	156.3 (pH=3)	12 h	2-5	CO3 ²⁻ , SO4 ²⁻ and mixture of various ions in genuine water samples	Reusable	NA	20
Fe/Mg-MIL-88B	162.1 (pH=7)	30 min	4-10	Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Reusable	NA	21
Zn-MOF-74	173.9 (pH=7)	150 min	3-9	Cl⁻, NO₃⁻	Reusable	NA	22
HEX-MOF	104 (pH=7)	4 min	1-12	Cl ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , HPO ₄ ²⁻ and mixture of various ions in genuine water samples	Reusable	Performed	This Study

Table S 7. Comparison of the As(III) sorption properties of **HEX-MOF** with other state-of-the-art As(III) MOF-based sorbents. In the data provided in the table, the As content corresponds to the quantity of total As and not that of the oxoanionic species.

MOF-based Sorbent	Capacity mg As/g	Equilibrium time	Working pH range	Selectivity vs.	Reusability	Sorption under flow conditions	Ref.
2D-ZIF-L	43.7 (pH=10)	3 h	9-10	NA	Reusable	NA	23
ZIF-8 (nps)	49.5 (pH=7)	10 h	7-9	NO3 ⁻ , SO4 ²⁻	NA	NA	10
Fe ₃ O ₄ @ZIF-8	100 (pH=8)	5 h	5-10	Cl ⁻ , NO ₃ ⁻ , SO4 ²⁻	Reusable	NA	24
Fe₃O₄@MIL- 101(Cr)	121.5 (рН=7) 110.8 (рН=9)	24 h	7-10	Mixture of various ions in genuine water samples	NA	NA	25
Dodecahedral ZIFs	117.5 (pH=8.5)	10 h	8-10	Cl ⁻ , SO4 ²⁻	Reusable	NA	26
β-MnO₂@ZIF-8	140.3 (pH=7)	24 h	NA	NA	NA	NA	27
UiO-66	205 (pH=9.2)	20 min	9-11	Cl ⁻ , Br ⁻ , CO ₃ ²⁻ , NO ₃ ⁻ , SO ₄ ²⁻	Reusable	Performed	28
Zn-MOF-74	211 (pH=12)	90 min	11-12	Cl ⁻ , NO ₃ -	Reusable	NA	22
Fe-Co-MOF-74	266.5 (pH=7)	12 h	4-10	Mixture of various ions in genuine water samples	Reusable	NA	20
ZrMOF@SF _d	1800 (pH=7)	2 h	6-7	Cl ⁻ , HCO ₃ ⁻ , CO ₃ ²⁻ SO ₄ ²⁻ , NO ₃ ⁻ ,	NA	NA	29
HEX-MOF	198 (pH=7)	4 min	1-12	Mixture of various ions in genuine water samples	Reusable	Performed	This Study

Characterization of the As(III)/(V) loaded materials and mechanism of ion sorption



Figure S 36. ¹H NMR spectra of the supernatant solution, after treatment of **HEX-MOF** with a deuterium oxide solution of Na_2HAsO_4 ·7H₂O (6.67 mM) for 10 minutes. This result shows no release of organic ligand in the solution during As sorption.



Figure S 37. Rietveld plots of a) **HEX-MOF/As(III)** and b) **HEX-MOF/As(V)**. Violet crosses: experimental points; Red line: calculated pattern; Black line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2ϑ region $30 - 60^{\circ}$.



Figure S 38. The charges of atoms in a) H_3AsO_3 and b) H_2O calculated via natural bond orbital (NBO) analysis at the B3LYP/6-311++G(d,p) level of theory in aqueous solution using the Gaussian 09, version D.01 program suite.²⁹



Figure S 39. High resolution As 2p and As 3d core-level photoelectron spectra of a) **HEX-MOF/As(V)**, b) **HEX-MOF/As(III)** and c) **HEX-MOF/As(V)**, d) **HEX-MOF/As(III)** respectively. The peaks appeared at 1327.2 and 45.1 eV for As $2p_{3/2}$ and As 3d lines are consistent with As(V), whereas the corresponding values at 1326.1 eV and 44.1 are consistent with As(III).



Figure S 40. FT-IR spectra of a) **HEX-MOF/As(III)**, and b) **HEX-MOF/As(V)** with indication of characteristic peaks assigned to As species.



Figure S 41. N₂ sorption isotherms (77 K) for a) HEX-MOF/As(III), and b) HEX-MOF/As(V).



Figure S 42. EDS spectra of a) HEX-MOF/As(III) and b) HEX-MOF/As(V).



Study of the hydrophobicity/superhydrophobicity of the MOFs

Figure S 43. Water contact angle data for **HEPT-**, **OCT-**, **NON-**, and **DODEC-MOF** (in powder form) recorded with various types of water media (left column) and at various pH values (right column).



Figure S 44. Water contact angles for MOFs in powder form as determined using ImageJ.



Figure S 45. a) Dispersion of **DODEC-** and **HEX-MOF** in an immiscible diethyl ether/water system, b) **DODEC-MOF** in powder form floats in the surface of water, whereas a powder sample of **HEX-MOF** sinks to the bottom, c) **DODEC-MOF@cotton fabric** floats in the surface of water, whereas **HEX-MOF@cotton fabric** sinks to the bottom.



Figure S 46. Water contact angle data for **HEPT**-, **OCT**-, **NON**-, and **DODEC-MOF@cotton fabric** recorded with various types of water media (left column) and at various pH values (right column).



HEPT-MOF@cotton fabric

OCT-MOF@cotton fabric



NON-MOF@cotton fabric DODEC-MOF@cotton fabric

Figure S 47. Water contact angles for MOFs immobilized in cotton fabric as determined using ImageJ.



Figure S 48. Removal of oil from water under flow using **DODEC-MOF@cotton fabric** (see also supplementarly video).

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