Electronic Supporting Information

Zr\textsuperscript{4+}-terephthalate MOFs with 6-connected structures, highly efficient As(III/V) sorption and superhydrophobic properties

Anastasia D. Pournara,\textsuperscript{a} Sofia Rizogianni,\textsuperscript{a} Dimitrios A. Evangelou,\textsuperscript{a} Evangelos K. Andreou,\textsuperscript{b} Gerasimos S. Armatas,\textsuperscript{b} and Manolis J. Manos\textsuperscript{*a,c}

\textsuperscript{a}Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece. Email: emanos@uoi.gr
\textsuperscript{b}Department of Materials Science and Technology, University of Crete, GR-71003 Heraklion, Greece.
\textsuperscript{c}Institute of Materials Science and Computing, University Research Center of Ioannina, GR-45110, Ioannina, Greece.

Table of Contents

Experimental Procedures ..........................................................................................................1
Experimental section ..................................................................................................................1
Analytical and characterization techniques.............................................................................3
Characterization ........................................................................................................................3
Stability Studies with HEX-MOF...............................................................................................4
Sorption studies.........................................................................................................................4
Results and Discussion.............................................................................................................5
Thermal analyses data .............................................................................................................7
X-ray powder diffraction studies and other characterization data for the reported MOFs ....10
Details of the structural refinement........................................................................................10
As(III)/(V) Sorption data...........................................................................................................21
Characterization of the HEX-MOF@cotton fabric .................................................................26
Characterization of the As(III)/(V) loaded materials and mechanism of ion sorption..........30
Study of the hydrophobicity/superhydrophobicity of the MOFs ............................................34
References...............................................................................................................................38

Experimental Procedures

Experimental section

Materials. Zirconium chloride (ZrCl\textsubscript{4}), 2-aminoterephthalic (NH\textsubscript{2}-H\textsubscript{2}BDC) and NaBH\textsubscript{4} were purchased from Aldrich. Hexanaldehyde \((\text{CH}_3\text{CH}_2\text{CHO})\), heptaldehyde \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO})\), octanaldehyde \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO})\), nonanaldehyde \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO})\), and dodecanaldehyde \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO})\) were purchased from Alfa Aesar. The solvents were used as received.

Syntheses.
Alkylamino-terephthalic acid. Alkylaldehyde (C₇H₄nCHO; n=5,9,12; 27.5 mmol) was added into a stirred suspension of NH₂-H-BDC (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), 2.98 (2H, t, J = 6.7 Hz, -CH₂), 1.21 (2H, m, -CH₂), 1.11 (4H, m, -(CH₂)₄), 0.66 (3H, t, J = 6.4 Hz, -CH₃).

heptyl-amino-H₂BDC. Yield: 0.934 g; ¹H NMR (400 MHz, D₂O-NaOH): δ (ppm) 7.11 (1H, d, J = 8 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)₆), 0.79 (3H, t, J = 6.8 Hz, -CH₃).

dodecyl-amino-H₂BDC. Yield: 0.952 g; ¹H NMR (400 MHz, D₂O-NaOH): δ (ppm) 7.68 (1H, d, J = 8 Hz, ArH), 7.19 (1H, s, ArH), 7.03 (1H, d, J = 8 Hz, ArH), 3.12 (2H, t, J = 6.8 Hz, -CH₂), 1.52 (2H, m, -CH₂), 1.11 (18H, m, -(CH₂)₁₈), 0.76 (3H, t, J = 6.7 Hz, -CH₃).

H₂(ZrO)₂(NH₂-BDC)₃(RNH-BDC)₄·solvent (RNH·BDC=2-alkylamine-terephthalate); R=hexyl-, HEX-MOF; R=heptyl-, HEPT-MOF; R=octyl-, OCT-MOF; R=nonyl-, NON-MOF; R=dodecyl-, DOD-MOF: ZrCl₄ (0.0625g, 0.27 mmol) and 2-alkyl-aminoterephthalic acid (0.375 mmol) was dissolved in 3.75 mL DMF and 0.5 mL CH₂Cl₂. A suspension of NH₄Cl (0.0625g, 0.27 mmol) 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 Na₂HAsO₄·7H₂O (6.67 mM) in D₂O. 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:

1**st 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.

2**nd 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.

**¹H NMR.** 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.
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. N\textsubscript{2} 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 CO\textsubscript{2} 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\textsubscript{o}) range.

Zeta potential measurement. Zeta potential was measured with a Malvern Zetasiser 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\alpha 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\textsubscript{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.\textsuperscript{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 Na\textsubscript{2}HAsO\textsubscript{4}·7H\textsubscript{2}O (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\textsubscript{2} (10 mM, 10 mL, pH = 7) aqueous solution was used instead of that of Na\textsubscript{2}HAsO\textsubscript{4}·7H\textsubscript{2}O. 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$_3$N (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.

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. N$_2$ sorption isotherms (77 K) for HEPT-, OCT-, NON-, and DODEC-MOF.
Table S1. Experimental and calculated (via poreblazer) surface areas for the MOFs.

<table>
<thead>
<tr>
<th>MOF</th>
<th>BET(m$^2$/g)/experimental</th>
<th>BET(m$^2$/g)/calculated with poreblazer</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX-MOF</td>
<td>911</td>
<td>909</td>
</tr>
<tr>
<td>HEPT-MOF</td>
<td>792</td>
<td>744</td>
</tr>
<tr>
<td>OCT-MOF</td>
<td>733</td>
<td>735</td>
</tr>
<tr>
<td>NON-MOF</td>
<td>471</td>
<td>571</td>
</tr>
<tr>
<td>DODEC-MOF</td>
<td>394</td>
<td>541</td>
</tr>
</tbody>
</table>

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 °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 °C which is due to the release of organic ligands. Therefore, at 250-265 °C the MOFs contain no lattice solvents and at 600 °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.

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

<table>
<thead>
<tr>
<th>MOF</th>
<th>Calculated Zr(%) for 4 linkers (8-c framework)</th>
<th>Calculated Zr(%) for 3 linkers (6-c framework)</th>
<th>Found Zr(%)</th>
<th>Difference (calc.-exp.)/8-c</th>
<th>Difference (calc.-exp.)/6-c</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEX-MOF</td>
<td>29.6</td>
<td>32.9</td>
<td>31.5</td>
<td>1.9</td>
<td>-1.4</td>
</tr>
<tr>
<td>HEPT-MOF</td>
<td>28.7</td>
<td>32.1</td>
<td>30.5</td>
<td>1.8</td>
<td>-1.6</td>
</tr>
<tr>
<td>OCT-MOF</td>
<td>27.9</td>
<td>31.3</td>
<td>31.9</td>
<td>4</td>
<td>0.6</td>
</tr>
<tr>
<td>NON-MOF</td>
<td>27.2</td>
<td>30.6</td>
<td>30.1</td>
<td>2.9</td>
<td>0.5</td>
</tr>
<tr>
<td>DODEC-MOF</td>
<td>25.2</td>
<td>28.7</td>
<td>31.0</td>
<td>5.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>

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

Details of the structural refinement

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.® 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 Zr₆ 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 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 Zr⁴⁺-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 2θ 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 ~ 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°.](image)

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 $^1$H NMR data of HEX-MOF digested in D$_2$O/NaOH indicated some amounts of CH$_3$COO$^-$ 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 Zr$^{4+}$ ions on the external surface of the particles and not to the Zr$_6$ 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/Et$_3$N 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) H$_3$AsO$_3$ 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 H$_3$AsO$_3$ 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 Zr$_6$ 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 Zr$_6$ 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 H₂AsO₄⁻ and HAsO₄²⁻ at pH =7 and c) the hard Zr⁴⁺ will prefer coordination with the divalent HAsO₄²⁻, the only possible As(V) coordination mode involves bidentate (bridging) ligation of HAsO₄²⁻ species to the Z₆ clusters (see main text).

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

**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°.

**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°.
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 $2\theta$ 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 $2\theta$ 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 TOPOS PRO.4

Figure S 18. Le Bail plots of a) HEX-MOF/1M HCl 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) \(a=14.696\ (3) \text{ Å}, \ b=35.991\ (8) \text{ Å}, \ V=6732\ (3)\text{Å}^3\); b) \(a=14.68\ (2) \text{Å}, \ b=35.99\ (5) \text{Å}, \ V=6718\ (20)\text{Å}^3\). 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. $^1$H NMR spectra of a) as synthesized HEX-MOF, and b) HEX-MOF treated with MeOH/Et$_3$N after digestion in D$_2$O/NaOH solution.

The $^1$H NMR data revealed an average HEX-NH$_2$-BDC/NH$_2$-BDC ratio of 1/0.06 (see enlarged view of the region 7-7.7 ppm).

In the $^1$H 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$_3$)$_2$NH. On the other hand, the material after its treatment with a mixture of MeOH/Et$_3$N does not exhibit signals that are assigned to HCOOH and DMF and the intensities for the (CH$_3$)$_2$NH and CH$_3$COOH peaks are substantially decreased.
Figure S 22. FT-IR spectra of HEX-NH-BDCH$_2$ ligand and HEX-MOF.

Figure S 23. FT-IR spectra of HEPT-NH-BDCH$_2$ ligand and HEPT-MOF.
Figure S 24. FT-IR spectra of OCT-NH-BDCH$_2$ ligand and OCT-MOF.

Figure S 25. FT-IR spectra of NON-NH-BDCH$_2$ ligand and NON-MOF.
Figure S 26. FT-IR spectra of DODEC-NH-BDCH$_2$ 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 S28. 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~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 \( q_e \) is the amount (mg g\(^{-1}\)) of ion sorbed in equilibrium, \( K_L \) is 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 \( q_t \) is the amount (mg/g) of ion sorbed at different reaction times (t), \( q_e \) is 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.

<table>
<thead>
<tr>
<th></th>
<th>Lagergren’s First-Order Equation</th>
<th>Ho-Mckay’s Second-Order Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_e ) mg g(^{-1})</td>
<td>( K_L ) g (mg min(^{-1}))</td>
</tr>
<tr>
<td>As(V)</td>
<td>0.995 ± 0.001</td>
<td>3.55 ± 0.12</td>
</tr>
<tr>
<td>As(III)</td>
<td>0.997 ± 0.001</td>
<td>3.53 ± 0.11</td>
</tr>
</tbody>
</table>
Table S4. The fitting parameters found after the fitting of the isotherm sorption data of As(III) and As(V) for the HEX-MOF.

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Langmuir-Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>As(III)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>STEP 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>134±27</td>
<td>198±5</td>
</tr>
<tr>
<td>$b$ (L/mg)</td>
<td>0.008±0.004</td>
<td>0.003±8.0 $10^{-5}$</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.93</td>
<td>0.21±0.04</td>
</tr>
<tr>
<td><strong>As(V)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>STEP 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>104±8</td>
<td></td>
</tr>
<tr>
<td>$b$ (L/mg)</td>
<td>0.008±0.002</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.95</td>
<td></td>
</tr>
</tbody>
</table>

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

a) Langmuir

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

b) Langmuir-Freundlich

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

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) \((a= 14.7(1) \, \text{Å}, \ c= 35.9(2) \, \text{Å} \text{and} \ V= 6738(115) \, \text{Å}^3)\) and HEX-MOF/As(III) \((a= 14.7(2) \, \text{Å}, \ c= 35.8(4) \, \text{Å} \text{and} \ V= 6652(153) \, \text{Å}^3)\).
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.

Table S 5. Physicochemical characteristics of bottled water samples.

<table>
<thead>
<tr>
<th></th>
<th>Total Hardness (CaCO₃, mg/L)</th>
<th>pH</th>
<th>NO₃⁻ (mg/L)</th>
<th>Cl⁻ (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
<th>HCO₃⁻ (mg/L)</th>
<th>Ca²⁺ (mg/L)</th>
<th>Mg²⁺ (mg/L)</th>
<th>Na⁺ (mg/L)</th>
<th>K⁺ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottled water (1)</td>
<td>223.5</td>
<td>7.8</td>
<td>0.83</td>
<td>5.02</td>
<td>7.71</td>
<td>241.5</td>
<td>80.7</td>
<td>5.34</td>
<td>2.24</td>
<td>0.6</td>
</tr>
<tr>
<td>Bottled water (2)</td>
<td>94.6</td>
<td>8</td>
<td>0.72</td>
<td>1.23</td>
<td>2.75</td>
<td>102.2</td>
<td>34.6</td>
<td>1.98</td>
<td>1.53</td>
<td>0.18</td>
</tr>
</tbody>
</table>

[25]
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.

<table>
<thead>
<tr>
<th>MOF-based Sorbent</th>
<th>Capacity mg As/g</th>
<th>Equilibrium time</th>
<th>Working pH range</th>
<th>Selectivity vs.</th>
<th>Reusability</th>
<th>Sorption under flow conditions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-BTC</td>
<td>6.6 (pH=4)</td>
<td>10 min</td>
<td>2-10</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>8</td>
</tr>
<tr>
<td>MIL-53(Fe)</td>
<td>11.4 (pH=5)</td>
<td>90 min</td>
<td>3-10</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>9</td>
</tr>
<tr>
<td>ZIF-8 (nps)</td>
<td>32.1 (pH=7)</td>
<td>7 h</td>
<td>6-9</td>
<td>NO₃⁻, SO₄²⁻</td>
<td>NA</td>
<td>NA</td>
<td>10</td>
</tr>
<tr>
<td>ED-ZIF-8</td>
<td>44.7 (pH=7)</td>
<td>6 h</td>
<td>3-9</td>
<td>Cl⁻, HCO₃⁻, NO₃⁻, SO₄²⁻, and mixture of various ions in genuine water samples</td>
<td>NA</td>
<td>NA</td>
<td>11</td>
</tr>
<tr>
<td>iMOF-1C</td>
<td>45.5 (pH=7)</td>
<td>15 h</td>
<td>NA</td>
<td>Cl⁻, NO₃⁻, HCO₃⁻, SO₄²⁻</td>
<td>Reusable</td>
<td>NA</td>
<td>12</td>
</tr>
<tr>
<td>AUBM-1</td>
<td>55.2 (pH=7.6)</td>
<td>3 h</td>
<td>7-8</td>
<td>CO₃²⁻</td>
<td>Reusable</td>
<td>NA</td>
<td>13</td>
</tr>
<tr>
<td>MIL-53(Al)</td>
<td>56.5 (pH=8)</td>
<td>24 h</td>
<td>6-8</td>
<td>Cl⁻, NO₃⁻, SO₄²⁻</td>
<td>NA</td>
<td>NA</td>
<td>14</td>
</tr>
<tr>
<td>MIL-100(Fe)</td>
<td>62.1 (pH=7)</td>
<td>NA</td>
<td>NA</td>
<td>Cl⁻, NO₃⁻, HCO₃⁻, SO₄²⁻</td>
<td>NA</td>
<td>NA</td>
<td>15</td>
</tr>
<tr>
<td>MIL-100(Al)</td>
<td>68.5 (pH=7)</td>
<td>NA</td>
<td>NA</td>
<td>Cl⁻, NO₃⁻, HCO₃⁻, SO₄²⁻</td>
<td>NA</td>
<td>NA</td>
<td>15</td>
</tr>
<tr>
<td>Al-MOF-1</td>
<td>71.9 (pH=7)</td>
<td>1 min</td>
<td>3-7</td>
<td>Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻ and mixture of various ions in genuine water samples</td>
<td>Not reusable but recyclable</td>
<td>Performed</td>
<td>16</td>
</tr>
<tr>
<td>MIL-88A</td>
<td>77.6 (pH=5)</td>
<td>20 min</td>
<td>3-7</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>17</td>
</tr>
<tr>
<td>UiO-66</td>
<td>162.3 (pH=2)</td>
<td>48 h</td>
<td>1-10</td>
<td>Cl⁻, NO₃⁻, SO₄²⁻ (pH = 2)</td>
<td>NA</td>
<td>NA</td>
<td>18</td>
</tr>
<tr>
<td>HP-Uio-66-40%</td>
<td>133.2 (pH=6)</td>
<td>5h</td>
<td>2-10</td>
<td>Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, CO₃²⁻</td>
<td>Reusable</td>
<td>NA</td>
<td>19</td>
</tr>
<tr>
<td>Fe-Co-MOF-74</td>
<td>156.3 (pH=3)</td>
<td>12 h</td>
<td>2-5</td>
<td>CO₃²⁻, SO₄²⁻ and mixture of various ions in genuine water samples</td>
<td>Reusable</td>
<td>NA</td>
<td>20</td>
</tr>
<tr>
<td>Fe/Mg-MIL-88B</td>
<td>162.1 (pH=7)</td>
<td>30 min</td>
<td>4-10</td>
<td>Cl⁻, NO₃⁻, SO₄²⁻</td>
<td>Reusable</td>
<td>NA</td>
<td>21</td>
</tr>
<tr>
<td>Zn-MOF-74</td>
<td>173.9 (pH=7)</td>
<td>150 min</td>
<td>3-9</td>
<td>Cl⁻, NO₃⁻</td>
<td>Reusable</td>
<td>NA</td>
<td>22</td>
</tr>
<tr>
<td>HEX-MOF</td>
<td>104 (pH=7)</td>
<td>4 min</td>
<td>1-12</td>
<td>Cl⁻, HCO₃⁻, SO₄²⁻, NO₃⁻, HPO₄²⁻ and mixture of various ions in genuine water samples</td>
<td>Reusable</td>
<td>Performed</td>
<td>This Study</td>
</tr>
</tbody>
</table>
Table S7. 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.

<table>
<thead>
<tr>
<th>MOF-based Sorbent</th>
<th>Capacity mg As/g</th>
<th>Equilibrium time</th>
<th>Working pH range</th>
<th>Selectivity vs.</th>
<th>Reusability</th>
<th>Sorption under flow conditions</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2D-ZIF-L</td>
<td>43.7 (pH=10)</td>
<td>3 h</td>
<td>9-10</td>
<td>NA</td>
<td>Reusable</td>
<td>NA</td>
<td>23</td>
</tr>
<tr>
<td>ZIF-8 (nps)</td>
<td>49.5 (pH=7)</td>
<td>10 h</td>
<td>7-9</td>
<td>NO$_3^-$, SO$_4^{2-}$</td>
<td>NA</td>
<td>NA</td>
<td>10</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@ZIF-8</td>
<td>100 (pH=8)</td>
<td>5 h</td>
<td>5-10</td>
<td>Cl$^-$, NO$_3^-$, SO$_4^{2-}$</td>
<td>Reusable</td>
<td>NA</td>
<td>24</td>
</tr>
<tr>
<td>Fe$_3$O$_4$@MIL-101(Cr)</td>
<td>121.5 (pH=7)</td>
<td>24 h</td>
<td>7-10</td>
<td>Mix of various ions in genuine water samples</td>
<td>NA</td>
<td>NA</td>
<td>25</td>
</tr>
<tr>
<td>Dodecahedral ZIFs</td>
<td>117.5 (pH=8.5)</td>
<td>10 h</td>
<td>8-10</td>
<td>Cl$^-$, SO$_4^{2-}$</td>
<td>Reusable</td>
<td>NA</td>
<td>26</td>
</tr>
<tr>
<td>β-MnO$_2$@ZIF-8</td>
<td>140.3 (pH=7)</td>
<td>24 h</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>NA</td>
<td>27</td>
</tr>
<tr>
<td>UiO-66</td>
<td>205 (pH=9.2)</td>
<td>20 min</td>
<td>9-11</td>
<td>Cl$^-$, Br$^-$, CO$_3^{2-}$, NO$_3^-$, SO$_4^{2-}$</td>
<td>Reusable</td>
<td>Performed</td>
<td>28</td>
</tr>
<tr>
<td>Zn-MOF-74</td>
<td>211 (pH=12)</td>
<td>90 min</td>
<td>11-12</td>
<td>Cl$^-$, NO$_3^-$</td>
<td>Reusable</td>
<td>NA</td>
<td>22</td>
</tr>
<tr>
<td>Fe-Co-MOF-74</td>
<td>266.5 (pH=7)</td>
<td>12 h</td>
<td>4-10</td>
<td>Mix of various ions in genuine water samples</td>
<td>Reusable</td>
<td>NA</td>
<td>20</td>
</tr>
<tr>
<td>ZrMOF@SF$_d$</td>
<td>1800 (pH=7)</td>
<td>2 h</td>
<td>6-7</td>
<td>Cl$^-$, HCO$_3^-$, CO$_3^{2-}$, SO$_4^{2-}$, NO$_3^-$</td>
<td>NA</td>
<td>NA</td>
<td>29</td>
</tr>
<tr>
<td>HEX-MOF</td>
<td>198 (pH=7)</td>
<td>4 min</td>
<td>1-12</td>
<td>Mix of various ions in genuine water samples</td>
<td>Reusable</td>
<td>Performed</td>
<td>This Study</td>
</tr>
</tbody>
</table>

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

[29]
Figure S 36. $^1$H NMR spectra of the supernatant solution, after treatment of HEX-MOF with a deuterium oxide solution of $\text{Na}_2\text{HAsO}_4\cdot7\text{H}_2\text{O}$ (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 $2\theta$ region 30 – 60°.
Figure S 38. The charges of atoms in a) $\text{H}_3\text{AsO}_3$ and b) $\text{H}_2\text{O}$ 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. 

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. N$_2$ 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).
Figure S47. 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 supplementary video).

References


18 C. Wang, X. Liu, J. P. Chen and K. Li, Sci. Rep., DOI:10.1038/srep16613.