# **Electronic Supplementary Information (ESI)**

# Alkylamino-Terephthalate Ligands Stabilize 8-Connected Zr<sup>4+</sup> MOFs with Highly Efficient Sorption for Toxic Se Species

Anastasia D. Pournara<sup>a</sup>, Sofia Rapti<sup>a</sup>, Alexandros Valmas<sup>b</sup>, Irene Margiolaki<sup>b</sup>, Euaggelos Andreou<sup>c</sup>, Gerasimos S. Armatas<sup>c</sup>, Athanassios C. Tsipis<sup>a</sup>, John C. Plakatouras<sup>a,d</sup>, Dimosthenis L. Giokas<sup>a,d</sup> and Manolis J. Manos<sup>\*a,d</sup>

<sup>a</sup>Department of Chemistry, University of Ioannina, GR-45110 Ioannina, Greece

<sup>b</sup> Department of Biology, Section of Genetics, Cell Biology and Development, University of Patras, GR-26500 Patras, Greece

<sup>c</sup> Department of Materials Science and Technology, University of Crete, GR-71003 Heraklion, Greece

<sup>d</sup> Institute of Materials Science and Computing, University Research Center of Ioannina, GR-45110, Ioannina, Greece

# **Table of Contents**

Table of Contents	1
Experimental Procedures	2
Results and Discussion	4
i. Thermal analyses data	4
ii. X-ray powder diffraction studies and other characterization data for the reported MOFs	7
iii. Ion sorption data and characterization of ion-loaded materials	20
iv. Theoretical calculations	31
References	33

# **Experimental Procedures**

#### **Experimental Section**

**Materials.** Zirconium chloride (ZrCl<sub>4</sub>), 2-aminoterephthalic (NH<sub>2</sub>-H<sub>2</sub>BDC) and NaBH<sub>4</sub> were purchased from Aldrich. Acetylaldehyde (CH<sub>3</sub>CHO), propionaldehyde (CH<sub>3</sub>CH<sub>2</sub>CHO), isobutyraldehyde ((CH<sub>3</sub>)<sub>2</sub>CHCHO) and butyraldehyde (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHO) were purchased from Alfa Aesar. The solvents were used as received.

# **Syntheses**

**Alkylamino-terephthalic acid.** Alkylaldehyde ( $C_nH_{2n+1}CHO$ ; n=2-4; 27.5 mmol) was added into a stirred suspension of NH<sub>2</sub>-H<sub>2</sub>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 NaBH<sub>4</sub> (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 distilled H<sub>2</sub>O (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:

ethyl-amino-H<sub>2</sub>BDC: Yield: 0.955 g; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O-NaOH): δ (ppm) 7.44 (1H, d, J = 5 Hz, , -CH-), 6.96 (1H, s, J = 7 Hz, -CH-), 6.86 (1H, d, J = 4 Hz, -CH-), 2.87 (2H, f, J = 7.1 Hz, -CH<sub>2</sub> -), 0.92 (3H, t, J = 14 Hz, -CH<sub>3</sub> -).

**propyl-amino-H<sub>2</sub>BDC**: Yield: 0.915 g; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O-NaOH):  $\delta$  (ppm) 7.46 (1H, d, J = 4 Hz, , -CH-), 6.97 (1H, s, J = 5 Hz, -CH-), 6.85 (1H, d, J = 3.2 Hz, -CH-), 2.81 (2H, t, J = 6.8 Hz, -CH<sub>2</sub>-), 1.61 (2H, f, J = 5 Hz, -CH<sub>2</sub>-), 0.63 (3H, t, J = 11 Hz, -CH<sub>3</sub>-).

**isobutyl-amino-H<sub>2</sub>BDC**: Yield: 0.965 g; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O-NaOH): δ (ppm) 7.67(1H, d, J = 1.8 Hz, -CH-), 7.19 (1H, s, J = 2 Hz, -CH-), 7.03 (1H, d, J = 1.2 Hz, -CH-), 2.93 (2H, t, J = 3 Hz, -CH<sub>2</sub>-), 1.84 (1H, f, J = 1 Hz, -CH-), 0.90 (6H, t, J = 10 Hz, -CH<sub>3</sub>-).

**n-butyl-amino-H<sub>2</sub>BDC**: Yield: 0.945 g; <sup>1</sup>**H NMR** (400 MHz, D<sub>2</sub>O-NaOH):  $\delta$  (ppm) 7.66 (1H, d, J = 2 Hz, , -CH-), 7.20 (1H, s, J = 2.5 Hz, -CH-), 7.07 (1H, d, J = 1.8 Hz, -CH-), 3.10 (2H, t, J = 3 Hz, -CH<sub>2</sub>-), 1.54 (2H, f, J = 2.1 Hz, -CH<sub>2</sub>-), 1.34 (2H, f, J = 2 Hz, -CH<sub>2</sub>-), 0.83 (3H, t, J = 6 Hz, -CH<sub>3</sub>-).

 $H_{16}[Zr_6O_{16}(RNH-BDC)_4]$ -solvent (RNH-BDC<sup>2</sup>=2-alkyl-amine-terephthalate; R=ethyl-, ET-MOF; R=propyl-, PROP-MOF; R=isobutyl-, SBUT-MOF; R=n-butyl, BUT-MOF): ZrCl<sub>4</sub> (0.0625g, 0.27 mmol) and 2-alkyl-amino-terephthalic acid (0.375 mmol) was dissolved in 3.75 mL DMF and 0.25 mL HNO<sub>3</sub> 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 ZrCl<sub>4</sub>) or HNO<sub>3</sub> residuals, the MOFs (0.1g) were treated with a methanolic solution (4 mL) of Et<sub>3</sub>N (0.1mL). Then, the MOFs were characterized via <sup>1</sup>H NMR, TGA and PXRD.

**ET-MOF:** Yield: 0.092 g. <sup>1</sup>**H NMR** (400 MHz, D<sub>2</sub>O-NaOH):  $\delta$  (ppm) 7.44 (1H, d, J = 3.1 Hz, , -CH-), 6.96 (1H, s, J = 5 Hz, -CH-), 6.83 (1H, d, J = 3 Hz, -CH-), 2.88 (2H, f, J = 5.2 Hz, -CH<sub>2</sub>-), 0.93 (3H, t, J =10 Hz, -CH<sub>3</sub>-).

**PROP-MOF:** Yield: 0.095 g. <sup>1</sup>**H NMR** (400 MHz, D<sub>2</sub>O-NaOH):  $\delta$  (ppm) 7.41 (1H, d, J = 4 Hz, , -CH-), 6.98 (1H, s, J = 5.2 Hz, -CH-), 6.85 (1H, d, J = 3 Hz, -CH-), 2.84 (2H, f, J = 7 Hz, -CH<sub>2</sub>-), 1.33 (2H, f, J = 5 Hz, -CH<sub>2</sub>-), 0.67 (3H, t, J = 13 Hz, -CH<sub>3</sub>-).

**SBUT-MOF:** Yield: 0.096 g. <sup>1</sup>**H NMR** (400 MHz, D<sub>2</sub>O-NaOH): δ (ppm) 7.66 (1H, d, J = 4 Hz, -CH-), 7.19 (1H, s, J = 5 Hz, -CH-), 7.05 (1H, d, J = 3 Hz, -CH-), 2.93 (2H, f, J = 7 Hz, -CH<sub>2</sub>-), 1.85 (1H, f, J = 3 Hz, -CH-), 0.90 (6H, t, J = 13 Hz, -CH<sub>3</sub>-).

**BUT-MOF:** Yield: 0.099 g. <sup>1</sup>**H NMR** (400 MHz, D<sub>2</sub>O-NaOH):  $\delta$  (ppm) 7.42 (1H, d, J = 3 Hz, , -CH-), 6.95 (1H, s, J = 4 Hz, -CH-), 6.81 (1H, d, J = 2 Hz, -CH-), 2.84 (2H, t, J = 4.5 Hz, -CH<sub>2</sub>-), 1.28 (2H, f, J = 3.8 Hz, -CH<sub>2</sub>-), 1.05 (2H, f, J = 3.5 Hz, -CH<sub>2</sub>-), 0.58 (3H, t, J = 9 Hz, -CH<sub>3</sub>-).

**Protonated MOFs.** Prior the sorption studies, the MOFs were treated with 4 M HCl solution to afford the protonated materials. EDS analysis of the acid-treated MOFs revealed only a small amount of Cl (Zr:Cl atomic ratio was ~ 6:1), which is due to HCl molecules bound to the surface of particles (see main text). The content of lattice water solvents for the various protonated MOFs were determined by TGA analysis:

H<sub>16</sub>[Zr<sub>6</sub>O<sub>16</sub>(RNH-BDC)<sub>4</sub>]·xH<sub>2</sub>O (R=ethyl-, x=22; R=propyl-, x=32; R=isobutyl-, x=17; R=n-butyl, x=33),

We have also performed Rietveld refinement for the HCI-treated **BUT-MOF** (see below). The water content determined from the Rietveld refinement (32  $H_2O$  per formula of acid-treated **BUT-MOF**) is in very good agreement with that found from TGA data. In addition, we have done Rietveld refinement for the BUT-MOF after its treatment with a basic (pH = 11) aqueous solution (see below).

**BUT-MOF/HA composite.** 0.100 g of sodium alginate (SA) was dissolved in 200 mL of water. A fine suspension of **BUT-MOF-SA** was formed by adding 1 g of **BUT-MOF** to ~ 20 ml of the SA solution. To this suspension, HCl solution (final concentration ~ 4 M) was then added with continuous stirring. The composite **BUT-MOF/HA** immediately precipitated and was isolated by filtration. The product was further treated with 4M HCl acid to ensure complete protonation of the functional groups of the material. Yield: 0.915 g. PXRD data

revealed that **BUT-MOF/HA** is highly crystalline and we have been able to perform Rietveld refinement, which indicated that the composite is isostructural to the pristine **BUT-MOF** material (Fig.S17, Table S3).

#### Analytical and characterization techniques

#### Lab PXRD measurements

The powder X-ray diffraction (PXRD) measurements were performed at room temperature on a Malvern Panalytical X'Pert PRO diffractometer with focusing  $K\alpha_1$  geometry. Polycrystalline samples were loaded in 1mm borosilicate glass capillaries while the X-ray tube operated at 45kV and 40mA. The incident-beam side (CuK $\alpha_1$  radiation,  $\lambda = 1.54056$ Å) is equipped with a focusing X-ray mirror, a 0.5° fixed divergence slit, 0.5° anti-scatter slits and 0.04 rad Soller slits, while on the diffracted-beam side the system was configured with 0.04 rad Soller slits and a PIXcel<sup>1D</sup> detector with anti-scatter shielding. Four scans were performed in Debye-Scherrer mode, with a step size of 0.0066° on a spinning stage (~300 rpm), within a 2 $\theta$  range of 4.0–90.0°. No radiation damage was observed even after 5 h of measurement, therefore all scans were merged together to increase counting statistics.

#### Synchrotron PXRD measurements

Data of enhanced angular resolution were collected under ambient conditions at the high-resolution powder diffraction beamline, ID22 <sup>1,2</sup> of the European Synchrotron Radiation Facility (ESRF) in Grenoble. Polycrystalline samples were loaded in borosilicate glass capillaries, of 1.0 mm inner diameter, which were later wax sealed and mounted on a translating fast capillary spinner (1000 rpm) on the axis of the diffractometer. Patterns were measured with a period of 9.0 min using a beam size of 1.0 mm<sup>2</sup> (photon flux on sample  $\sim$ 3 X 10<sup>12</sup> photons s<sup>-1</sup>). Spinning in combination with the rapid data collection performance of this beamline guaranteed enhanced diffracting particle statistics. The detector is equipped with nine analyzer silicon (111) crystals, considerably enhancing angular resolution. Approximately 6 scans were collected per sample (two scans per position followed by sample translation of 1.3 mm), at room temperature and a wavelength of 1.30003(3) Å (March 2018) or 1.30017(2) Å (September 2018), within a range of 4.0–90.0° (10°/minute). In those samples where no radiation damage was observed (e.g. intensity damping, peak shifts), all scans were summed together to increase counting statistics, while, in samples suffering from radiation damage effects, only first-scans -collected from fresh parts of the samples- were summed together.

IR spectroscopy. IR spectra were recorded on KBr pellets in the 4000-400 cm<sup>-1</sup> 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<sup>-1</sup> flow rate) with a heating rate of 10 °C min<sup>-1</sup>.

<sup>1</sup>HNMR.<sup>1</sup>H 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.

**FE-SEM.** Scanning electron microscopy (SEM) images were taken with a field emission JEOL JSM 7000F electron microscope operating at 15 kV accelerated voltage. The samples were sputter-coated with a 5-10 nm Au film to reduce charging.

**Gas sorption measurements.** N<sub>2</sub> 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<sub>2</sub> drying and then, degassed at 120 °C under vacuum (<10<sup>-5</sup> 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<sub>o</sub>) range. CO<sub>2</sub> adsorption isotherms were measured at 273 K using an IGA-003 gravimetric sorption analyzer (Hiden Isochema, UK). The activation of the materials was done as with the N<sub>2</sub> sorption experiments. The pore size distribution plot was obtained from the CO<sub>2</sub> adsorption data using the density functional theory (DFT) method.

**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.

Atomic absorption spectroscopy. Se(IV/VI) and SeCN<sup>-</sup> were 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.

#### SORPTION STUDIES

**Preparation of the column.** 50 mg of **BUT-MOF-HA** composite and 5 g of sand (50-70 mesh SiO<sub>2</sub>) was mixed in a mortar and pestle and filled in a glass column (0.7 cm ID column). Prior the ion exchange studies, the column was washed with ~ 7 mL HCl (4 M) solution and deionized water.

**Batch sorption studies.** A typical sorption experiment of **BUT-MOF** with Se(IV) anions is the following: In a solution of Na<sub>2</sub>SeO<sub>3</sub> (0.4 mmol) in water (10 mL, pH ~ 7), compound **BUT-MOF** (100 mg, ~ 0.04 mmol of **BUT-MOF**) was added as a solid. The mixture was kept under magnetic stirring for ~10 min. The polycrystalline material was isolated by filtration, washed several times with water and acetone and dried in the air. The isolation of the Se(VI) and SeCN-loaded products was done similarly as that of the Se(IV)-loaded material, with the exception that Na<sub>2</sub>SeO<sub>4</sub> and KSeCN was used instead of Na<sub>2</sub>SeO<sub>3</sub>. The uptake of all selenium species from solutions of various concentrations was studied by the batch method at V:m ~ 1000 mL/g, room temperature and 1 h contact. These data were used for the determination of selenium sorption isotherms. The competitive and variable pH ion exchange experiments were also carried out with the batch method at V: m ratio ~ 1000 mL/g, room temperature and 1 h contact. For the determination of the sorption kinetics, selenium ion-exchange experiments of various reaction times (1-60 min) have been performed. For each experiment, a 10 mL sample of Se(IV), Se(VI) or SeCN<sup>-</sup> solution (initial total Se concentration = 1 ppm, pH~7) was added to

each vial (containing 10 mg of **BUT-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 Se 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 different sorption experiments. The difference between the concentrations of Se determined for the different sorption experiments was <2%.

**Column sorption studies.** Several bed volumes of the solution were passed through the column and collected at the bottom in glass vials. The solutions were analyzed with atomic absorption spectroscopy. The regeneration of the column was performed by its treatment with ~ 7 mL of HCl acid (4 M) solution. Then, the column is washed with enough water to remove excess acid. Column containing only sand as stationary phase showed no selenium sorption capacity.

# **Results and Discussion**

i. Thermal analyses data



Figure S1. The TGA and DTG (first derivative) data for ET-MOF measured in air.



Figure S2. The TGA and DTG (first derivative) data for PROP-MOF measured in air.



Figure S3. The TGA and DTG (first derivative) data for SBUT-MOF measured in air.



Figure S4. The TGA and DTG (first derivative) data for BUT-MOF measured in air.

The TGA and DTG data revealed two main steps of weight losses: One ending at ~200  $^{\circ}$ C assigned to the removal of lattice solvents and a second completed at ~800  $^{\circ}$ C which is due to the release of organic ligands. Therefore, at ~200  $^{\circ}$ C the MOFs contain no lattice solvents and at 800  $^{\circ}$ C the MOFs were converted to ZrO<sub>2</sub>. In order to identify the number of linkers for the MOFs, we are comparing the experimental % Zr content (calculated based on ZrO<sub>2</sub>) 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 six (12-c framework) linkers (Table S1). From this comparison, it is clear that the MOFs contain 4 linkers per formula unit.

Table S1. Experimental Zr(%) of MOFs (with no lattice solvents) vs. calculated values of MOFs with no lattice solvents and 4 or 6 linkers.

MOF	Calculated Zr(%) for 4 linkers (8-c framework)	Calculated Zr(%) for 6 linkers (12-c framework)	Found Zr(%)
ET-MOF	33.2	28.5	33.7
PROP-MOF	32.1	27.3	33.0
SBUT-MOF	31.1	26.2	32.1
BUT-MOF	31.1	26.2	30.1

In addition, TGA data can be used for calculation of the number of lattice solvents. According to Rietveld data, the pores of the MOFs are filled with DMF and water molecules. Based on the comparison of experimental % Zr content (calculated based on ZrO<sub>2</sub>) of solvated MOFs with those calculated for MOFs with different solvent content, we have been able to determine the DMF and water content of the MOFs (Table S2). Note that the determined DMF and water contents of the MOFs are in agreement with those found from the Rietveld refinements.

Table S2. Experimental Zr(%) for the solvated MOFs vs. calculated Zr(%) for MOFs with different solvent content. The theoretical values closer to the experimental ones are shown with bold characters.

MOF	Found Zr(%)	calculated Zr(%) for MOF·4DMF·H₂O	calculated Zr(%) for MOF·3DMF·H <sub>2</sub> O	calculated Zr(%) for MOF·5DMF·H₂O
ET-MOF	28.90	27.95	29.03	26.94
PROP-MOF	27.72	27.17	28.19	26.22
SBUT-MOF	27.32	26.43	27.40	25.53
BUT-MOF	25.55	26.43	27.40	25.53

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

Cell indexing, Le Bail and Rietveld refinements were performed using EXPO2014.<sup>3</sup> For the pristine MOFs, the occupancies of the Zr, µ<sub>3</sub>-O, terminal O and dicarboxylate ligand atoms were assigned according to the *I4/m* space group demands. For the anion-loaded MOFs, the occupancies of Zr,  $\mu_3$ –O and dicarboxylate ligands were also adjusted based on the demands of *I4/m* space group; however, the occupancies of Se anions and terminal O atoms were fixed according to analytical data. Specifically, due to the restrictions of the space group (14/m), Se(VI) anions are placed in four positions in each Zr<sub>6</sub> cluster and each of the Se(VI) anion is positionally disordered over two positions. To take into account the analytical data (indicating 2 Se(VI) per cluster), the occupancy of the Se atoms and the O atoms that are not connected to Zr4+ metal ions were fixed to 0.25. However, the occupancies of the O atoms of selenate anions connected to the Zr4+ centers were fixed to 0.5, as these O atoms represent not only Se(VI) oxygen groups but also O atoms of terminal H<sub>2</sub>O/OH ligands that have not been replaced by the Se(VI) species. In the case of Se(IV)-loaded MOF, Se and O atoms that are not bonded to Zr4+ are disordered over two positions and their occupancies were fixed to 0.5 (to take into account the analytical data indicating 4 Se(IV) per cluster), whereas no disorder exists for the Se(IV) oxygen atoms connected to Zr4+ metal ions and thus, their occupancies were kept full. In the case of SeCN-loaded MOF, the N atom of SeCN- and terminal O atoms were placed in split positions and the occupancy each of them was fixed to 0.5 (to take into account the analytical data indicating four SeCN per cluster). The occupancies of solvent atoms were either refined or fixed according to analytical data. The final formulas used for the pristine and anion-loaded MOFs, the corresponding % Rp and % Rwp values for Le Bail and Rietveld refinements and cell parameters derived from the Rietveld refinements are shown in Table S3. CCDC 2017777-2017786 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 S5. Le Bail and Rietveld plots of ET-MOF. Blue crosses: experimental points; Red line: calculated pattern; Violet line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2θ region 30 – 90 °.



Figure S7. Le Bail and Rietveld plots of SBUT-MOF. Blue crosses: experimental points; Red line: calculated pattern; Violet line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2θ region 30 – 90 °.



Figure S8. Le Bail plot of BUT-MOF. Blue crosses: experimental points; red line: calculated pattern; violet line: difference pattern (exp. – calc.); green bars: Bragg positions.

Table S3.	Selected	data from t	he refinemen	t of PXRD	data for the	compounds r	eported in	this work
10010 00.	00100100	auta nonn			data for the	oompoundo i	opontou in	

Formula⁺	R <sub>p</sub> /R <sub>wp</sub> (%) Le Bail	R <sub>p</sub> /R <sub>wp</sub> (%) Rietveld	Cell parameters a, c (Å)/ V(ų)
$H_{16}[Zr_{6}O_{16}(C_{4}H_{9}NHC_{8}O_{4}H_{3})_{4}]\cdot 5(C_{3}NH_{7}O)\cdot H_{2}O (\textbf{BUT-MOF})$	5.23/7.29	5.77/8.09	14.683, 20.768/4477.4
$H_{16}[Zr_6O_{16}(C_4H_9NHC_8O_4H_3)_4]$ ·32 $H_2O$ ( <b>BUT-MOF/ACID</b> )	4.54/6.20	6.11/8.11	14.664, 20.760/4464.2
$H_{16}[Zr_6O_{16}(C_4H_9NHC_8O_4H_3)_4]$ ·32 $H_2O$ ( <b>BUT-MOF/HA</b> )	4.51/5.86	5.15/6.48	14.654, 20.743/4454.6
$H_{16}[Zr_6O_{16}(C_4H_9NHC_8O_4H_3)_4]$ ·32 $H_2O$ ( <b>BUT-MOF/BASE</b> )	5.13/6.70	6.11/7.80	14.646, 20.747/4450.4
$H_{16}[Zr_{6}O_{16}(C_{4}H_{9}NHC_{8}O_{4}H_{3})_{4}]\cdot 3(C_{3}NH_{7}O)\cdot H_{2}O \text{ (SBUT-MOF)}$	5.15/7.30	6.01/8.41	14.679, 20.760/4473.5
$H_{16}[Zr_{6}O_{16}(C_{3}H_{7}NHC_{8}O_{4}H_{3})_{4}]\cdot 3(C_{3}NH_{7}O)\cdot H_{2}O (\textbf{PROP-MOF})$	4.19/5.75	5.77/8.09	14.692, 20.778/4485.3
$H_{16}[Zr_6O_{16}(C_2H_5NHC_8O_4H_3)_4] \cdot 3(C_3NH_7O) \cdot H_2O \text{ (ET-MOF)}$	4.27/5.53	5.15/6.47	14.699, 20.735/4480.3
$H_{12}[Zr_6O_{12}(SeO_4)_2(C_4H_9NHC_8O_4H_3)_4]$ ·16 $H_2O$ ( <b>BUT-MOF/SeO_4</b> <sup>2</sup> ·)	2.85/3.64	4.12/5.63	14.646, 20.708/4442.2
$H_4[Zr_6O_8(HSeO_3)_4(C_4H_9NHC_8O_4H_3)_4] \cdot 16H_2O (\textbf{BUT-MOF/HSeO_3^{-}})$	4.07/5.17	5.13/6.93	14.567, 20.675/4387.3
H <sub>12</sub> [Zr <sub>6</sub> O <sub>12</sub> (SeCN) <sub>4</sub> (C <sub>4</sub> H <sub>9</sub> NHC <sub>8</sub> O <sub>4</sub> H <sub>3</sub> ) <sub>4</sub> ]·10.24H <sub>2</sub> O ( <b>BUT-MOF/SeCN·</b> )	3.97/5.70	7.53/11.17	14.643, 20.706/4439.6

\*The formulas reported in the Table include all H atoms. However, the hydrogen atoms of water molecules,  $HSeO_3$ , bridged OH and terminal OH/H<sub>2</sub>O ligands of the Zr<sub>6</sub>O<sub>16</sub> unit were not included in the refinement. In addition, due to the positional disorder of alkyl-amino groups, one of the 3 H atoms of the phenyl group cannot be included in the refinement. The remaining H atoms (i.e. those of ligands and DMF) were placed in calculated positions.



Figure S9. Structure of ET-MOF viewed down the c-axis. Color code: Zr, cyan; N, blue; O, red; C, grey.



Figure S10. Structure of PROP-MOF viewed down the c-axis. Color code: Zr, cyan; N, blue; O, red; C, grey.



Figure S11. Structure of SBUT-MOF viewed down the c-axis. Color code: Zr, cyan; N, blue; O, red; C, grey.



Figure S12. Representation of the structure of BUT-MOF viewed down the c-axis, also showing the guest DMF and water molecules. Color code: Zr, cyan; N, blue; O, red; C, grey.



Figure S13. Particle size distribution-profile of BUT-MOF nanoparticles as found from FE-SEM using ImageJ Software.<sup>4</sup> The profile was constructed based on measurements of >70 particles.



Figure S14. FT-IR spectra of R-NH-BDCH<sub>2</sub> ligands and alkyl-amino-MOFs.



Figure S15. CO<sub>2</sub> adsorption isotherms at 273 K for ET-, PROP-, SBUT- and BUT-MOF.



Figure S16. DFT micropore size distribution for ET-, PROP-, SBUT- and BUT-MOF. The DFT analysis of the adsorption data indicates microporous structure with pore sizes of 5.5-8.5 Å.



Figure S17. Le Bail and Rietveld plots of BUT-MOF/ACID, BUT-MOF/BASE and BUT-MOF/HA. Blue crosses: experimental points; Red line: calculated pattern; Violet line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2θ region 30 – 90 °.



Figure S18. Representation of the structure of BUT-MOF/ACID viewed down the c-axis, showing also the guest water molecules. Color code: Zr, cyan; N, blue; O, red; C, grey.



Figure S19. Fitting of the kinetics data with the Lagergren's first-order equation for the sorption of HSeO<sub>3</sub><sup>-</sup> by BUT-MOF (initial concentration = 1.2 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<sub>e</sub> = the amount (mg g<sup>-1</sup>) of ion sorbed in equilibrium, K<sub>L</sub> = the Lagergren or first-order rate constant.<sup>5</sup>

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)].<sup>5</sup>

Table S4. 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 HSeO<sub>3</sub><sup>-</sup> by BUT-MOF.

Lagergren's F	irst-Order Equation	Ho-Mckay's Second - Order Equation					
q₌ mg g¹	K⊥ g (mg min) <sup>-1</sup>	R <sup>2</sup>	q₀ mg g⁻¹	K₂ g (mg min)⁻¹	R <sup>2</sup>		
1.62 ± 3.93 10 <sup>-5</sup>	6.85 ± 0.07	0.96	1.62 ± 9.52 10 <sup>-5</sup>	529 ± 68	0.87		



Figure S20. Se(VI) Isotherm sorption data for ET-MOF, PROP-MOF, SBUT-MOF and BUT-MOF with their fitting with the various models. Red: Langmuir model; Green: Langmuir-Freundlich model; Blue: Freundlich model.

Table S5. The parameters of Langmuir, Freundlich and Langmuir-Freundlich isotherms,	found after the fitting of the isotherm sorption data of Se(VI) for the reported
Zr <sup>4+</sup> MOFs. The fitting data with the best R <sup>2</sup> values are highlighted with bold characters.	

Se(VI) STEP 1		Langmuir			Freundlich			Langmuir -Freur	ndlich	
MOF	q <sub>e</sub>	b	R <sup>2</sup>	K <sub>F</sub>	n	R <sup>2</sup>	q <sub>e</sub>	b	n	R <sup>2</sup>
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)		
ET-MOF	94±3	0.27±0.12	0.63	62±7	13.8±4	0.75	NA	NA	NA	NA
PROP-MOF	108±2	0.23±0.05	0.93	63±6	10±1.9	0.91	118±2.1	0.32±0.17	1.9±2.1	0.91
SBUT-MOF	115±4	0.12±0.04	0.77	NA	NA	NA	NA	NA	NA	NA
BUT-MOF	115±3	0.45±0.08	0.99	26±7	4±0.8	0.91	121±9	0.04±0.10	1.2±0.3*	0.99
STEP 2		Langmuir			Freundlich			Langmuir-Freun	dlich	
MOF	q <sub>e</sub>	b	R <sup>2</sup>	K <sub>F</sub>	n	R <sup>2</sup>	q <sub>e</sub>	b	n	R <sup>2</sup>
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)		
ET-MOF	NA	NA	NA	2±1	1.4±0.2	0.86	283±10	0.002±5.68 10 <sup>-5</sup>	0.3±0.04	0.98
PROP-MOF	NA	NA	NA	6±2	1.9±0.2	0.96	290±31	0.002±2.04 10 <sup>-4</sup>	0.5±0.2	0.97
SBUT-MOF	NA	NA	NA	NA	NA	NA	244±5	0.002±4.65 10 <sup>-5</sup>	0.3±0.03	0.98
BUT-MOF	NA	NA	NA	NA	NA	NA	226±4	0.002±3.78 10⁵	0.2±0.03	0.98

\*Since n parameter is close to 1, Langmuir and Langmuir-Freundlich equations are equivalent. In this case, independently of R<sup>2</sup> values, fitting of the data with the Langmuir equation is that preferred.



Figure S21. SeCN: isotherm sorption data for ET-MOF, PROP-MOF and SBUT-MOF with their fitting with the various models. Red: Langmuir model; Green: Langmuir-Freundlich model; Blue: Freundlich model.

Table S6. The parameters of Langmuir, Freundlich and Langmuir-Freundlich isotherm	s, found after the fitting of the isotherm sorption data of SeCN <sup>-</sup> for the reported
Zr4+ MOFs. The fitting data with the best R2 values are highlighted with bold character	S.

SeCN <sup>.</sup> STEP 1		Langmuir		Freundlich			Freundlich Langmuir-Freundlich			
MOF	q <sub>e</sub>	b	R <sup>2</sup>	K <sub>F</sub>	n	R <sup>2</sup>	q <sub>e</sub>	b	n	R <sup>2</sup>
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)		
ET-MOF	133±3	0.06±0.04	0.69	29±19	3.4±1.8	0.53	114±5	0.07±0.003	0.2±0.05	0.96
PROP-MOF	156±6	0.04±0.01	0.98	22±6	2.84±0.44	0.96	NA	NA	NA	NA
SBUT-MOF	114±12	0.04±0.01	0.93	21±6	3.21±0.68	0.94	NA	NA	NA	NA
BUT-MOF	147±7	0.10±0.03	0.93	NA	NA	NA	NA	NA	NA	NA
STEP 2		Langmuir		F	reundlich			Langmuir-Freu	ndlich	
MOF	q <sub>e</sub>	b	R <sup>2</sup>	K <sub>F</sub>	n	R <sup>2</sup>	q <sub>e</sub>	b	n	R <sup>2</sup>
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)		
ET-MOF	NA	NA	NA	NA	NA	NA	312±15	0.006±3.3 10-4	0.2±0.1	0.89
PROP-MOF	NA	NA	NA	NA	NA	NA	361±89	0.003±8.3 10⁴	0.5±0.2	0.91
SBUT-MOF	NA	NA	NA	NA	NA	NA	341±28	0.003±2.7 10 <sup>-4</sup>	0.3±0.1	0.94
BUT-MOF	NA	NA	NA	0.076±0.22	0.781±0.28	0.64	316±13	0.002±5.8 10⁵	0.1±0.03	0.96



Figure S22. HSeO<sub>3</sub><sup>-</sup> isotherm sorption data for ET-MOF, PROP-MOF and SBUT-MOF with their fitting with the various models. Red: Langmuir model; Green: Langmuir-Freundlich model; Blue: Freundlich model.

**Table S7.** The parameters of Langmuir, Freundlich and Langmuir-Freundlich isotherms, found after the fitting of the isotherm sorption data of Se(IV) for the reported  $Zr^{4+}$  MOFs. The fitting data with the best R<sup>2</sup> values are highlighted with bold characters.

Se(IV)		Langmuir			Freundlich			Langmuir -Fre	eundlich	
MOF	q <sub>e</sub>	b	$\mathbb{R}^2$	K <sub>F</sub>	n	R <sup>2</sup>	q <sub>e</sub>	b	n	R <sup>2</sup>
	(mg/g)	(L/mg)		(L/g)			(mg/g)	(L/mg)		
ET-MOF	236±14	0.04±0.02	0.73	77±7	6.2±0.5	0.97	NA	NA	NA	NA
PROP-MOF	261±14	0.02±0.01	0.78	85±0.1	6.3±0.006	0.99	NA	NA	NA	NA
SBUT-MOF	202±4	0.89±0.20	0.92	121±12	12.2±2.4	0.79	212±3	0.73±0.11	1.7±0.2	0.98
BUT-MOF	272±22	0.02±0.01	0.92	42±10	3.5±0.5	0.94	240±22	0.11±0.14	0.6±0.9	0.71

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

a) Langmuir

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

 $q = K_F C_e^{\overline{n}}$ 

q

b) Freundlich

c) 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.<sup>6,7</sup>



Figure S23. Percentage (%) sorption of Se(IV), Se(VI) and SeCN<sup>-</sup> by BUT-MOF in the pH range of 1-10.



Figure S24. Se(IV) sorption isotherms for BUT-MOF at pH~9.5. The solid line in the Se(IV) sorption isotherm represents the fitting of the data with the Langmuir model. Fitting data:  $q_m$ =118±3 mg SeO<sub>3</sub><sup>2-</sup>/g, b=0.026±0.0036 L/mg, R<sup>2</sup>=0.99.

Table S8. Se(IV), Se(VI) and SeCN<sup>-</sup> sorption data from experiments with bottled water samples intentionally contaminated with traces of Se (initial Se concentration = 1 ppm).

	% Removal						
MOF	Se(IV)	Se(VI)	SeCN <sup>-</sup>				
ET-MOF	90.11	-	-				
PROP-MOF	94.81	-	-				
SBUT-MOF	82.13	-	-				



Figure S25. Column sorption data with an aqueous Se(IV) solution (flow rate ~1.0 mL min<sup>-1</sup> and stationary phase BUT-MOF/silica sand 0.05 g : 5 g). The initial concentration of Se (total Se) was 1 ppm.  $V_{eff}$  and  $C_{eff}$  are the volume (mL) and Se concentration (ppb) of the solution passed through the column (i.e. effluent) respectively.

Table S9, Compar	ison of the Se(IV)	and Se(VI) sorption	capacities of BUT-MOE a	and analogues with the	ose of other MOEs
		ana 00(11) 001paon			

Target	MOF-based sorbent	Capacity* mg/g	Equilibrium time	pH range	Selectivity	Reusability	Ref.
Se( <i>IV</i> )	NU-1000	102	<1min	6	NA	NA	8
	UiO-66 UiO-66-NH <sub>2</sub>	59.9 26.8	90mn	6-8	vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	Reusable	9
	MOF-808	133	5min	NA	NA	NA	10
	CAU-17	255.3	6h	4-11	vs. various anions	NA	11
	BUT-MOF ET-MOF PROP-MOF SBUT-MOF	270 234 259 210	3min - - -	1-10 - - -	$ \begin{array}{c} \text{vs. NO}_3, \text{ Cl}, \text{ SO}_4^{2}, \\ \text{HCO}_3^{-} \\ \text{vs. NO}_3, \text{ Cl}, \text{ SO}_4^{2}, \\ \text{HCO}_3^{-} \\ \text{vs. NO}_3, \text{ Cl}, \text{ SO}_4^{2}, \\ \text{HCO}_3^{-} \\ \text{vs. NO}_3, \text{ Cl}, \text{ SO}_4^{2}, \\ \text{HCO}_3^{-} \\ \text{vs. NO}_3, \text{ Cl}, \text{ SO}_4^{2}, \\ \text{HCO}_3^{-} \\ \end{array} $	Reusable - - -	this work
	NU-1000	62	<1min	6	NA	NA	8
Se(VI)	UiO-66 UiO-66-HCl UiO-66-Ac UiO-66-36Dif UiO-66-12Trif UiO-66-36Trif NU-1000 MOF-808	34.3 86.8 45.6 55.1 62.9 70.8 78.8 60.5	>10h 5h 10h 10h 5h 10h <3h 5h	6.8 3-7 6.8 6.8 6.8 6.8 6.8 6.8 6.8 6.8	- vs. NO <sub>3</sub> · - - - - -	NA	12
	UiO-66 UiO-66-NH <sub>2</sub>	37.3 11.9	90mn	3-5	vs. Cl <sup>-</sup>	Reusable	9
	MOF-808	118	5min	NA	NA	NA	10
	iMOF-1C	100	60min	NA	vs. various anions	reusable	13
	CAU-17	20.3	6h	NA	Not selective	NA	11
	BUT-MOF ET-MOF PROP-MOF SBUT-MOF	226 283 290 244	<1min - - -	1-10 - - -	vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO4 <sup>2-</sup> - - -	Reusable - - -	this work

\*The maximum sorption capacity for Se(IV) and Se(VI) is expressed as mg SeO<sub>3</sub><sup>2-/</sup>g and mg SeO<sub>4</sub><sup>2-/</sup>g respectively. In the main text, the Se(IV) sorption capacities of our materials at pH-7 are expressed as mg HSeO<sub>3</sub><sup>-/</sup>g, taking into account that at neutral solution Se(IV) is present in the form of HSeO<sub>3</sub><sup>-</sup>. Nevertheless, in order to perform comparison with the Se(IV) sorption capacities of known materials, expressed as mg SeO<sub>3</sub><sup>2-/</sup>g, in Table S9 the sorption capacities of our materials are also calculated as mg SeO<sub>3</sub><sup>2-/</sup>g.

NOFs).							
Target	Sorbent	Capacity* mg/g	Equilibrium time	pH range	Selectivity	Reusability	Ref.
Se(IV)	MgAl-MoS₄-LDH	294	24h	6-9	NA	NA	14
	Thiourea-formaldehyde (TUF) Resin	833.3	78h	< 1	NA	NA	15
	HMBA incorporated into mesoporous inorganic silica	93.56	40min	1.5	vs. various anions	reusable	16
	Mg–Al–CO <sub>3</sub> layered double hydroxide	160	NA	5-8.5	NA	NA	17
	Y₂(OH)₅CI·1.5H₂O	207	5h	7-9	vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , HPO <sub>4</sub> <sup>2-</sup>	reusable	18
	BUT-MOF ET-MOF PROP-MOF SBUT-MOF	270 234 259 210	3min - - -	1-10 - - -	vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>-2</sup> , HCO <sub>3</sub> <sup>-</sup> vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>-2</sup> , HCO <sub>3</sub> <sup>-</sup> vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>-2</sup> , HCO <sub>3</sub> <sup>-</sup> vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>-2</sup> , HCO <sub>3</sub> <sup>-</sup>	Reusable - - -	this work
Se(VI)	Thiourea-formaldehyde (TUF) Resin	526.3	78h	< 0	NA	NA	15
	H <sup>+</sup> -diaminofunctionalized MCM- 41	123	10h	6.5	vs. NO <sub>3</sub> -, Cl-, SO <sub>4</sub> <sup>2-</sup>	NA	19
	Fe <sup>3+</sup> - diamino-functionalized MCM-41	117	10h	6.5	vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	NA	19
	Mg–Al–CO <sub>3</sub> layered double hydroxide	90	NA	5-8.5	NA	NA	17
	Polyamine-type Ion Exchange Resin (Eporasu K-6)	243	3h	3-12	vs. Cl-	NA	20
	Y₂(OH)₅CI·1.5H₂O	124	5h	7-9	vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , SO <sub>4</sub> <sup>2-</sup> , HPO <sub>4</sub> <sup>2-</sup>	reusable	18
	BUT-MOF ET-MOF PROP-MOF SBUT-MOF	226 283 290 244	<1min - - -	1-10 - - -	vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> - -	Reusable - - -	this work
SeCN <sup>.</sup>	BUT-MOF ET-MOF PROP-MOF SBUT-MOF	316 312 361 341	3min - - -	1-10	vs. NO <sub>3</sub> <sup>-</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> - - -	Reusable - - -	this work
	Smopex®-269 Smopex®-103	126 178	2min	3-10	vs. SO <sub>4</sub> <sup>2-</sup>	Reusable	21

 Table S10. Comparison of the Se(IV), Se(VI) and SeCN<sup>-</sup> sorption capacities of BUT-MOF and analogues with those of other state-of-the-art sorbents (besides MOFs).

\*The maximum sorption capacity for Se(IV) and Se(VI) is expressed as mg SeO<sub>3</sub><sup>2-/</sup>g and mg SeO<sub>4</sub><sup>2-/</sup>g respectively. In the main text, the Se(IV) sorption capacities of our materials at pH~7 are expressed as mg HSeO<sub>3</sub><sup>-/</sup>g, taking into account that at neutral solution Se(IV) is present in the form of HSeO<sub>3</sub><sup>-</sup>. Nevertheless, in order to perform comparison with the Se(IV) sorption capacities of known materials, expressed as mg SeO<sub>3</sub><sup>2-/</sup>g, in Table S10 the sorption capacities of our materials are also calculated as mg SeO<sub>3</sub><sup>2-/</sup>g.



Figure S26. The IR spectra (KBr pellets) of ion-loaded BUT-MOF. The arrows point to characteristic ion IR peaks found in the ion-loaded materials. The CN stretching IR peak for BUT-MOF/SeCN<sup>-</sup> was found at 2065 cm<sup>-1</sup>. This value suggests the coordination mode Se-C-N-Metal ion.<sup>22</sup>



Figure S27. N2 sorption isotherms (77 K) for BUT-MOF/Se(IV), BUT-MOF/Se(VI) and BUT-MOF/SeCN:



Figure S28. Le Bail and Rietveld plots of BUT-MOF/HSeO<sub>4</sub><sup>2</sup>. Blue crosses: experimental points; Red line: calculated pattern; Violet line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2θ region 30 – 90 °.







**Figure S30.** Le Bail and Rietveld plots of **BUT-SeCN**<sup>-</sup> Blue crosses: experimental points; Red line: calculated pattern; Violet line: difference pattern (exp. – calc.); Green bars: Bragg positions. Inset: Magnification of the 2*θ* region 30 – 90 °.

### iv. Theoretical calculations



Figure S31. Natural atomic charges on the benzenaminium, SeCN<sup>-</sup>, HSeO<sub>3</sub><sup>-</sup>, SeO<sub>4</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> species<sup>-</sup> calculated at the B3LYP/6-31+G(d)/PCM level of theory in aqueous solution.



Figure S32. Equilibrium geometries of the possible MOF@SeCN<sup>-</sup>, MOF@HSeO<sub>3</sub><sup>-</sup>, MOF@SeO<sub>4</sub><sup>2-</sup>, MOF@SO<sub>4</sub><sup>2-</sup> and MOF@HCO<sub>3</sub><sup>-</sup> weak associations optimized at the B3LYP/6-31+G(d)/PCM level of theory in aqueous solution.

### References

- 1 A. N. Fitch, in Journal of Research of the National Institute of Standards and Technology, 2004, vol. 109, pp. 133–142.
- 2 C. Dejoie, M. Coduri, S. Petitdemange, C. Giacobbe, E. Covacci, O. Grimaldi, P. O. Autran, M. W. Mogodi, D. Š. Jung and A. N. Fitch, *J. Appl. Crystallogr.*, 2018, **51**, 1721–1733.
- 3 A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, J. Appl. Crystallogr., 2013, 46, 1231–1235.
- 4 W. Burger and M. J. Burge, *ImageJ*, 2015.
- 5 A. Benhammou, A. Yaacoubi, L. Nibou and B. Tanouti, J. Colloid Interface Sci., 2005, 282, 320–326.
- 6 M. J. Manos and M. G. Kanatzidis, Chem. A Eur. J., 2009, 15, 4779–4784.
- 7 M. J. Manos, N. Ding and M. G. Kanatzidis, Proc. Natl. Acad. Sci. U. S. A., 2008, 105, 3696–3699.
- 8 A. J. Howarth, M. J. Katz, T. C. Wang, A. E. Platero-Prats, K. W. Chapman, J. T. Hupp and O. K. Farha, J. Am. Chem. Soc., 2015, 137, 7488–7494.
- 9 J. Wei, W. Zhang, W. Pan, C. Li and W. Sun, *Environ. Sci. Nano*, 2018, 5, 1441–1453.
- 10 R. J. Drout, A. J. Howarth, K. I. Otake, T. Islamoglu and O. K. Farha, *CrystEngComm*, 2018, **20**, 6140–6145.
- 11 H. Ouyang, N. Chen, G. Chang, X. Zhao, Y. Sun, S. Chen, H. Zhang and D. Yang, Angew. Chemie Int. Ed., 2018, 57, 13197–13201.
- 12 J. Li, Y. Liu, X. Wang, G. Zhao, Y. Ai, B. Han, T. Wen, T. Hayat, A. Alsaedi and X. Wang, Chem. Eng. J., 2017, 330, 1012–1021.
- 13 S. Sharma, A. V. Desai, B. Joarder and S. K. Ghosh, *Angew. Chemie Int. Ed.*, 2020, **59**, 7788–7792.
- 14 L. Ma, S. M. Islam, C. Xiao, J. Zhao, H. Liu, M. Yuan, G. Sun, H. Li, S. Ma and M. G. Kanatzidis, J. Am. Chem. Soc., 2017, 139, 12745–12757.
- 15 N. Gezer, M. Gülfen and A. O. Aydín, *J. Appl. Polym. Sci.*, 2011, **122**, 1134–1141.
- 16 M. R. Awual, M. M. Hasan and M. A. Khaleque, Sensors Actuators, B Chem., 2015, 209, 194–202.
- 17 N. Chubar, J. Mater. Chem. A, ,2014, 2, 15995-16007.
- 18 L. Zhu, L. Zhang, J. Li, D. Zhang, L. Chen, D. Sheng, S. Yang, C. Xiao, J. Wang, Z. Chai, T. E. Albrecht-Schmitt and S. Wang, *Environ. Sci. Technol.*, 2017, **51**, 8606–8615.
- 19 T. Yokoi, T. Tatsumi and H. Yoshitake, *Bull. Chem. Soc. Jpn.*, 2003, **76**, 2225–2232.
- 20 T. Nishimura, H. Hashimoto and M. Nakayama, Sep. Sci. Technol., 2007, 42, 3155-3167.
- 21 C. Mac Namara, J. Torroba and A. Deacon, Johnson Matthey Technol. Rev., 2015, 59, 334–352.
- 22 A. Manceau and D. L. Gallup, *Environ. Sci. Technol.*, 1997, **31**, 968-976.