Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Efficient extraction of inorganic selenium from water by a Zr metal–organic framework: investigation of volumetric uptake capacity and binding motifs

Riki J. Drout,[a] Ashlee J. Howarth,[b] Ken-ichi Otake,[a] Timur Islamoglu,[a] and Omar K. Farha[a, c, d]*

[a] *Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, United States.*

[b] *Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke St. W. Montreal, Quebec, Canada, H4B 1R6.*

[c] *Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, United States.*

[d] *Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia.*

Abstract

Strict monitoring and control of selenium concentrations in freshwater supplies is critical to safeguarding human health and aquatic life. A handful of previously investigated sorbents exhibit noteworthy gravimetric (mg g^{-1}) Se uptake capacities; however, often display insufficient volumetric (mg cm^{-3}) capacities, thereby requiring large volumes of material for commercial implementation. In pursuit of mitigating this material inefficiency, we investigated the selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) affinity of MOF-808, a Zr-based metal–organic framework with a high density of potential Se oxyanion binding sites. MOF-808 recorded exceptional volumetric and gravimetric Se oxyanion uptake capacities of 133 mg g^{-1} (127 mg cm^{-3}) and 118 mg g^{-1} (112 mg cm^{-3}) for aqueous selenite and selenate, respectively. Single-crystal X-ray diffraction studies revealed that selenite and selenate can bind at the MOF node via two distinct binding motifs, an $\eta_2\mu_2$ motif in which the oxyanion coordinates to two different metal atoms in a single node, and a μ_2 motif in which the oxyanion interacts with only a single metal atom. Furthermore, powder X-ray diffraction (PXRD) patterns and N_2 adsorption/desorption isotherms confirm the retention of bulk crystallinity and porosity after the uptake of Se oxyanions.

Experimental Details

Chemicals. All chemicals were used as received from the supplier. In these experiments, water is Milli-Q (Milli-pore). All gases were Ultra High Purity Grade 5 gases from Airgas Specialty Gases. Fisher Chemical Trace Metal Grade nitric acid was used for all ICP-OES experiments. All ICP standards were purchased from Sigma-Aldrich. As-purchased Se and Na ICP standards were 1000 mg/g in 2% nitric acid, TraceCERT, and the Zr ICP standard was 1000 mg/g in 2% nitric acid and 0.2% hydrofluoric acid.

General Experimental. MOF-808 was prepared solvothermally. In a typical procedure, zirconyl chloride octahydrate (282 mg, 0.875 mmol) and trimesic acid (216 mg, 1.029 mmol) were dissolved in a solution of DMF (40 mL) and formic acid (40 mL) and allowed to react for 48 h in an oven preheated to 120 ºC. The MOF crystals were then washed 3 times with DMF (40 mL) and 3 times with acetone (40 mL). The MOF was soaked overnight in acetone and then dried in an 80 ºC vacuum oven for 2 h. At this point the MOF was soaked in dilute hydrochloric acid (0.1 M, 40 mL) overnight. The MOF was washed 3 times with water (40 mL) and 3 times with acetone (40 mL). Again, the MOF was soaked in acetone (40 mL) overnight before drying in the vacuum oven for 2 h. All native MOF samples were thermally activated under ultra-high vacuum at 120 ºC for 18 h on a Micromeritics Smart VacPrep. Selenium loaded samples were activated using the same technique, but at 80 ºC. Nitrogen adsorption and desorption isotherm measurements were performed on a Micromeritics Tristar II at 77K. Powder X-ray diffraction measurements were collected on a STOE STADI MP equipped with $K\alpha 1$ source and a 1D strip detector over a range of $2° < 2\theta < 45°$. ICP-OES data were obtained using a Thermo iCAP 7600 ICP Spectrometer. ICP-OES standards (0.5 - 20 ppm) were prepared via serial dilution in 2% nitric acid. All uptake experiments were performed in triplicate at a minimum.

Single-Crystal X-Ray Crystallography. Single-crystal X-ray diffraction measurements were performed on a Bruker Kappa APEX II CCD equipped with a Cu $K\alpha$ ($\lambda = 1.54178$ Å) microsource with MX optics. Single crystals of MOF-808(Hf) were immersed in an aqueous sodium selenite or sodium selenate solution (0.1 M) at room temperature for 24 h. A single crystal was mounted on MicroMesh (MiTeGen) with paratone oil. The structure was solved by direct methods (SHELXT-2014/5)[1] and refined by full-matrix least-squares refinement on F^2 (SHELXL-2014/7)[2] using the Yadokari-XG software package.[3] The disordered non-coordinated solvents were removed using the PLATON SQUEEZE program.[4] The selenium site occupancies were determined by structural refinement, and the total selenium content agrees well with data obtained from ICP-OES analysis of digested selenite- and selenate-loaded MOF samples. Refinement results are summarized in Supporting Information Table S1 and Table S2. The associated CIF data file has been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-1843055 and CCDC-1843056. The data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.).

Maximum Uptake Per Node. Initial selenite and selenate uptake experiments were performed by exposing 5 mg (3.8×10^{-6} mol) of MOF-808 to 10 mL of an aqueous sodium selenite or sodium selenate solution in a 15 mL polypropylene centrifuge tube. Selenite and selenate solutions with Se concentrations of 61, 91, 121, 151, 182, and 212 ppm corresponding to 2 – 7 ions per MOF node (Zr_6-cluster) were used. Solutions were centrifuged for 3 min to allow the MOF to settle. A 0.5 mL aliquot of the supernatant was removed after 1 h, 3 h, and 24 h of exposure, and diluted to 7 mL in 2% nitric acid. The concentration of Se, Zr, and

Na in each sample was determined by ICP-OES. These concentrations were compared to the concentrations of an identical analyte solution without MOF to determine the amount of selenium captured per node.

Maximum Uptake Capacity. The maximum amount of selenite and selenate adsorbed per gram of MOF-808 was determined by exposing 5 mg (3.8×10^{-6} mol) of MOF to 10 mL of an aqueous sodium selenite or sodium selenate solution in a 15 mL polypropylene centrifuge tube. Solutions with selenium concentrations of 15, 30, 45, 61, and 76 ppm corresponding to 0.5, 1.0, 1.5, 2.0, and 2.5 selenite or selenate ions per MOF node were used. Each sample was centrifuged for 3 min to allow the MOF to settle. A 0.5 mL aliquot of the supernatant was removed at 5, 10, 15, 30, 60, 90, 120, and 180 min and diluted to 7 mL in 2% nitric acid. The concentration of Se, Zr, and Na in each solution was determined by ICP-OES. These were compared to the concentrations of identical analyte solutions without MOF to determine the amount of selenium adsorbed q in mg/g of MOF-808 where $q = (C_i - C_f) \times V/m$, where $C_i =$ initial concentration (mg/L), $C_f =$ final concentration (mg/L), $V =$ volume of solution exposed to MOF-808 (L), and $m =$ mass of MOF-808 (g). The volumetric uptake capacity of MOF-808 for selenium in the form of selenite and selenate was easily calculated by considering the framework density.

Table S1. Crystallographic data for Hf-MOF-808-SeO_3.

Formula	C18 H6 Hf6 O33.08 Se1.56
Formula Weight	1945.95
Temperature (K)	100(2)
Wavelength (Å)	1.54178
Crystal system	Cubic
Space group	$Fd\bar{3}m$ (no.227)
a (Å)	35.286(9)
b (Å)	35.286(9)
c (Å)	35.286(9)
V ($Å^3$)	43936(34)
Z	16
Calcd Density (g/cm^3)	1.177
μ (mm^{-1})	11.073
F(000)	13821
Crystal size (mm^3)	0.025 ×0.025 ×0.025
θ_{min}, θ_{max} (°)	6.52, 58.49
Total reflection	10188
Unique reflection	1502
Parameter number	68
R_{int}	0.2229
Goodness-of-fit	0.944
R_1 [$I>2\sigma(I)$]	0.0636
wR_2 (all reflection)	0.1722

Table S2. Crystallographic data for Hf-MOF-808-SeO_4.

Formula	C18 H6 Hf6 O34.16 Se1.44
Formula Weight	1953.43
Temperature (K)	100(2)
Wavelength (Å)	1.54178
Crystal system	Cubic
Space group	$Fd\bar{3}m$ (no.227)
a (Å)	35.087(1)
b (Å)	35.087(1)
c (Å)	35.087(1)
V (Å^3)	43196(4)
Z	16
Calcd Density (g/cm^3)	1.201
μ (mm^{-1})	11.228
F(000)	13892
Crystal size (mm^3)	0.03 ×0.03 ×0.03
θ_{min}, θ_{max} (°)	2.18, 58.81
Total reflection	11057
Unique reflection	1515
Parameter number	68
R_{int}	0.0473
Goodness-of-fit	1.125
R_1 [I>2σ(I)]	0.0363
wR_2 (all reflection)	0.1134

Table S3. Selenite adsorption per Zr_6-node of MOF-808 when exposed to aqueous sodium selenite solutions with concentrations of 2 to 7 SeO_3^{2-} ions per node.

Exposure	Time 1 Hr	 3 Hr	 24 Hr
2	1.5	1.5	1.5
3	1.6	1.5	1.6
4	1.5	1.4	1.6
5	1.1	1.2	1.2
6	0.9	1.0	1.1
7	1.2	1.2	1.4

Table S4. Selenate adsorption per Zr_6-node of MOF-808 when exposed to aqueous sodium selenate solutions with concentrations of 2 to 7 SeO_4^{2-} ions per node.

Exposure	Time 1 Hr	 3 Hr	 24 Hr
2	1.1	1.1	1.1
3	1.2	1.2	1.2
4	1.2	1.2	1.2
5	1.1	1.0	1.1
6	1.4	1.3	1.4
7	1.4	1.4	1.3

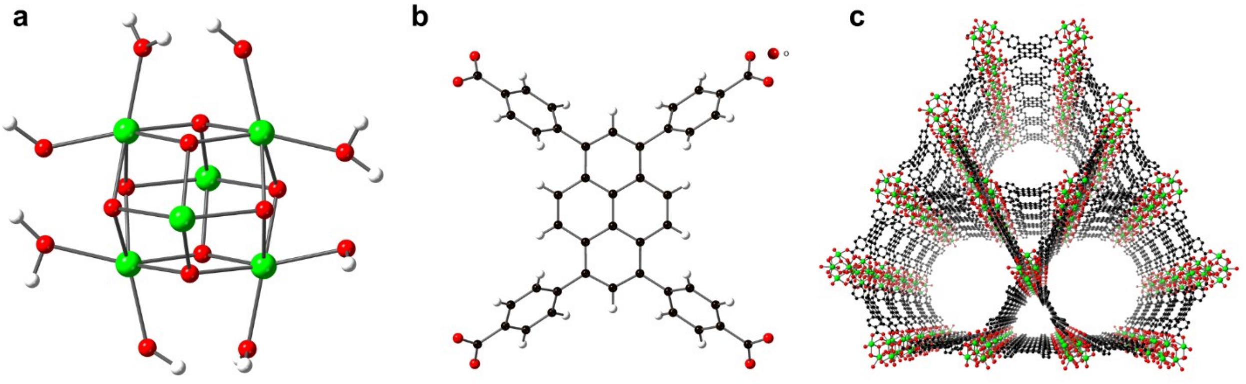


Figure S1. NU-1000 is comprised of a) Zr_6-nodes like MOF-808 and b) tetratopic H_4TBAPy linkers which assemble into the **csq**-topology with ~ 30 Å hexagonal 1D channels and ~ 10 Å triangular pores. The green, black, red, and white spheres represent zirconium, carbon, oxygen, and hydrogen atoms, respectively.

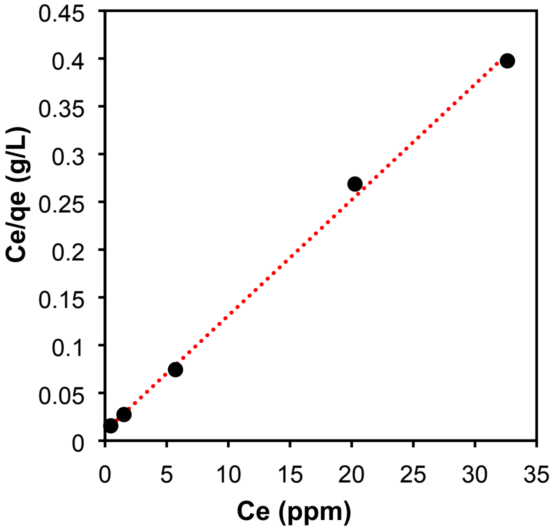


Figure S2. The Type I, linear Langmuir plot of C_e/q_e versus C_e for selenite capture in MOF-808 at various equilibrium concentrations according to eq 1 reproduced below, in Table S5, for convenience.

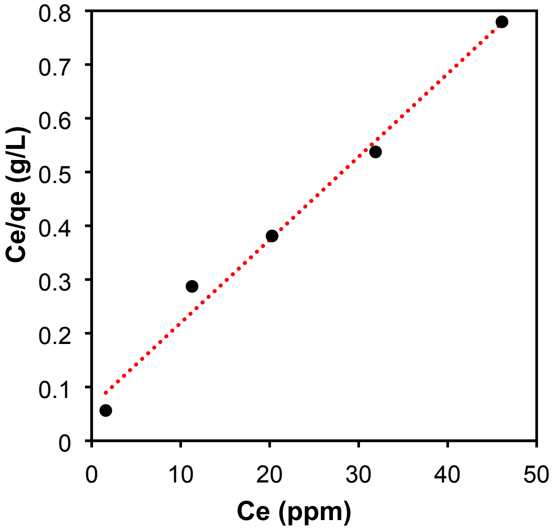


Figure S3. The Type I, linear Langmuir plot of C_e/q_e versus C_e for selenate capture in MOF-808 at various equilibrium concentrations according to equation 1 reproduced below, in Table S5, for convenience.

Table S5. The selenite and selenate uptake isotherms (Figure 2) and the Langmuir equation

$$\frac{C_e}{q_e} = \left(\frac{1}{Q}\right) C_e + \frac{1}{K_L Q}$$

where C_e is the equilibrium concentration (mg/L), q_e is the equilibrium uptake (mg/g), Q is maximum uptake capacity (mg/g), and K_L is the Langmuir constant (L/mg) were employed to determine the maximum selenium uptake capacity of MOF-808 in the form of selenite or selenate as summarized below.

	mg/g	**mg/cm^3**
SeO_3^{2-}	133	127
SeO_4^{2-}	118	112

Table S6. Comparison of the gravimetric and volumetric selenite uptake capacity of MOF-808 and NU-1000. The shaded box indicates the greater capacity.

	mg/g	**mg/cm^3**
MOF-808	133	127
NU-1000	95	45

Table S7. Comparison of the gravimetric and volumetric selenate uptake capacity of MOF-808 and NU-1000. The shaded box indicates the greater capacity.

	mg/g	**mg/cm^3**
MOF-808	118	112
NU-1000	85	40

Table S8. Comparison of gravimetric uptake capacities for selenite and selenate in various materials.

Material	Selenite Gravimetric Uptake Capacity (mg/g)	Selenate Gravimetric Uptake Capacity (mg/g)	Ref.
Al_2O_3 Impregnated Chitosan Beads	11	20	5
Fe(III) on Silica	20	2	6
Al(III) on Silica	33	11	6
NU-1000	62	102	7
MOF-808	133	118	This Work
$Y_2(OH)_5Cl \cdot 1.5H_2O$	150	102	8
$MgAl\text{-}MoS_4\text{-}LDH$	294	85	9
Thiourea-formaldehyde (TUF) Resin	833	526	10
$MgAl_2O_4$ (cLDH)	180	N/A	11
Cu^{2+}/diaminofunctionalized-MCM-41	N/A	83	12
UiO-66-HCl	N/A	86.8	13
Fe^{2+}/diaminofunctionalized-MCM-41	N/A	117	12
H^+/diaminofunctionalized-MCM-41	N/A	123	12

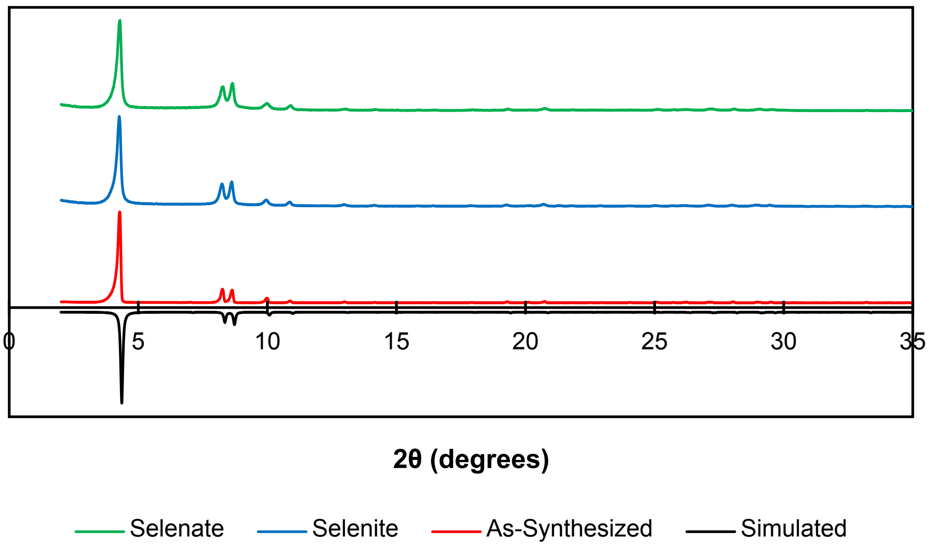
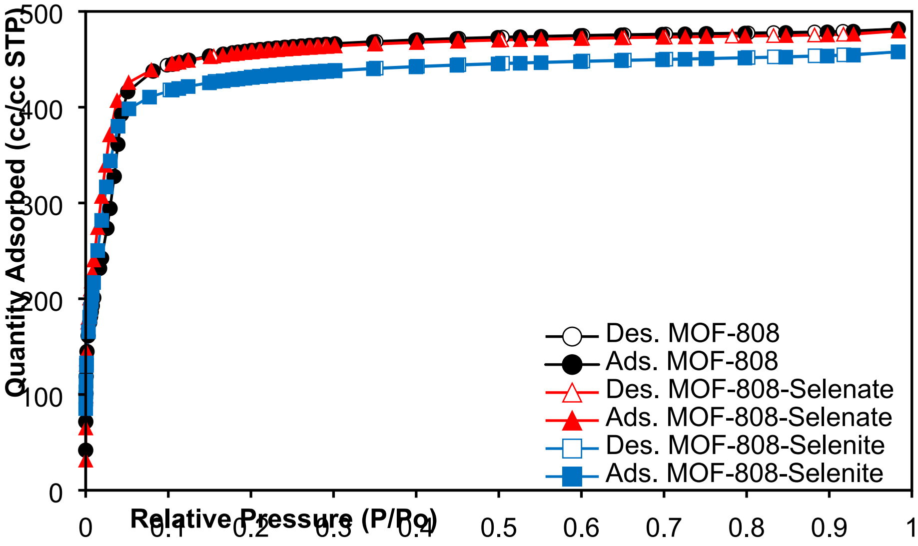


Figure S4. Powder X-ray diffraction (PXRD) patterns of neat MOF-808 and MOF-808 loaded with 1.8 SeO_3^{2-} ions per node or 1.6 SeO_4^{2-} ions per node confirm the retention of bulk crystallinity and purity.

a



b

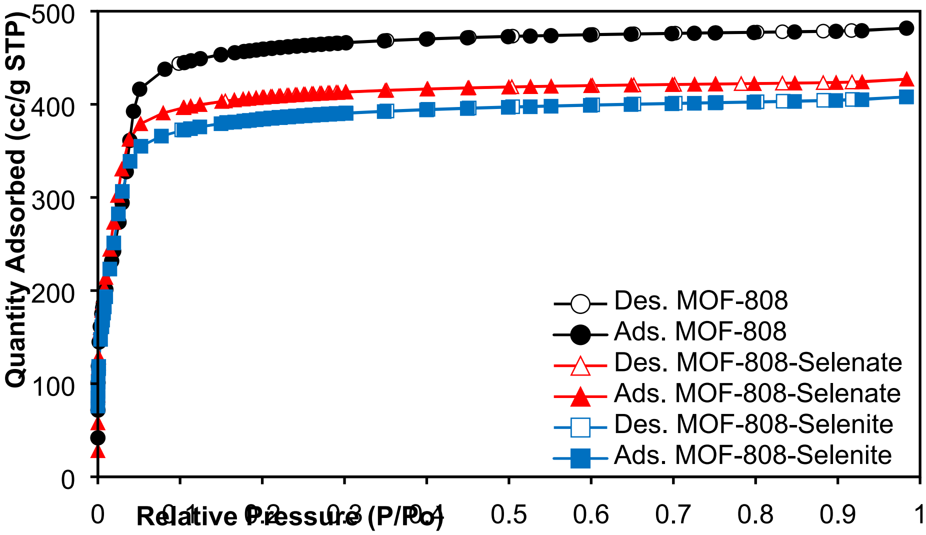


Figure S5. a) Volumetric N_2 adsorption/desorption isotherms of neat MOF-808 and MOF-808 loaded with 1.8 SeO_3^{2-} ions per node or 1.6 SeO_4^{2-} ions per node confirm the retention of porosity throughout the adsorption process. b) The associated gravimetric N_2 adsorption/desorption isotherms show a surface area reduction consistent with the installation of functionality at the MOF node.

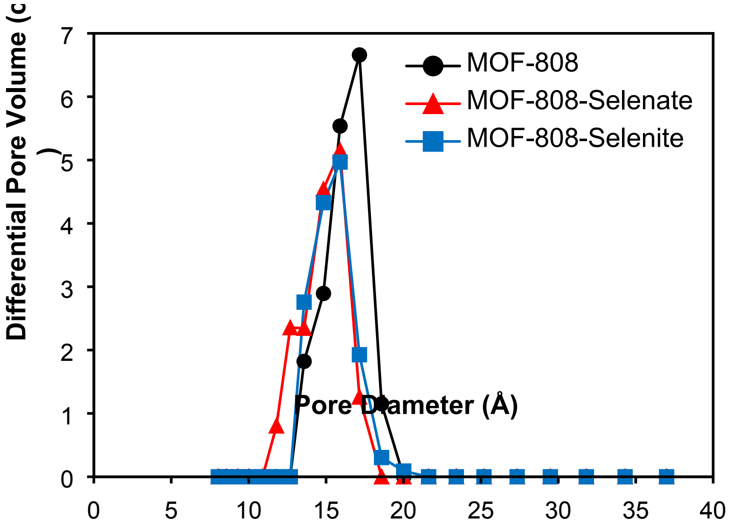


Figure S6. DFT pore size distributions for neat MOF-808 and MOF-808 loaded with 1.8 SeO_3^{2-} ions per node or 1.6 SeO_4^{2-} ions per node reveal a decrease in the pore volume which supports the capture of selenite and selenate within the framework.

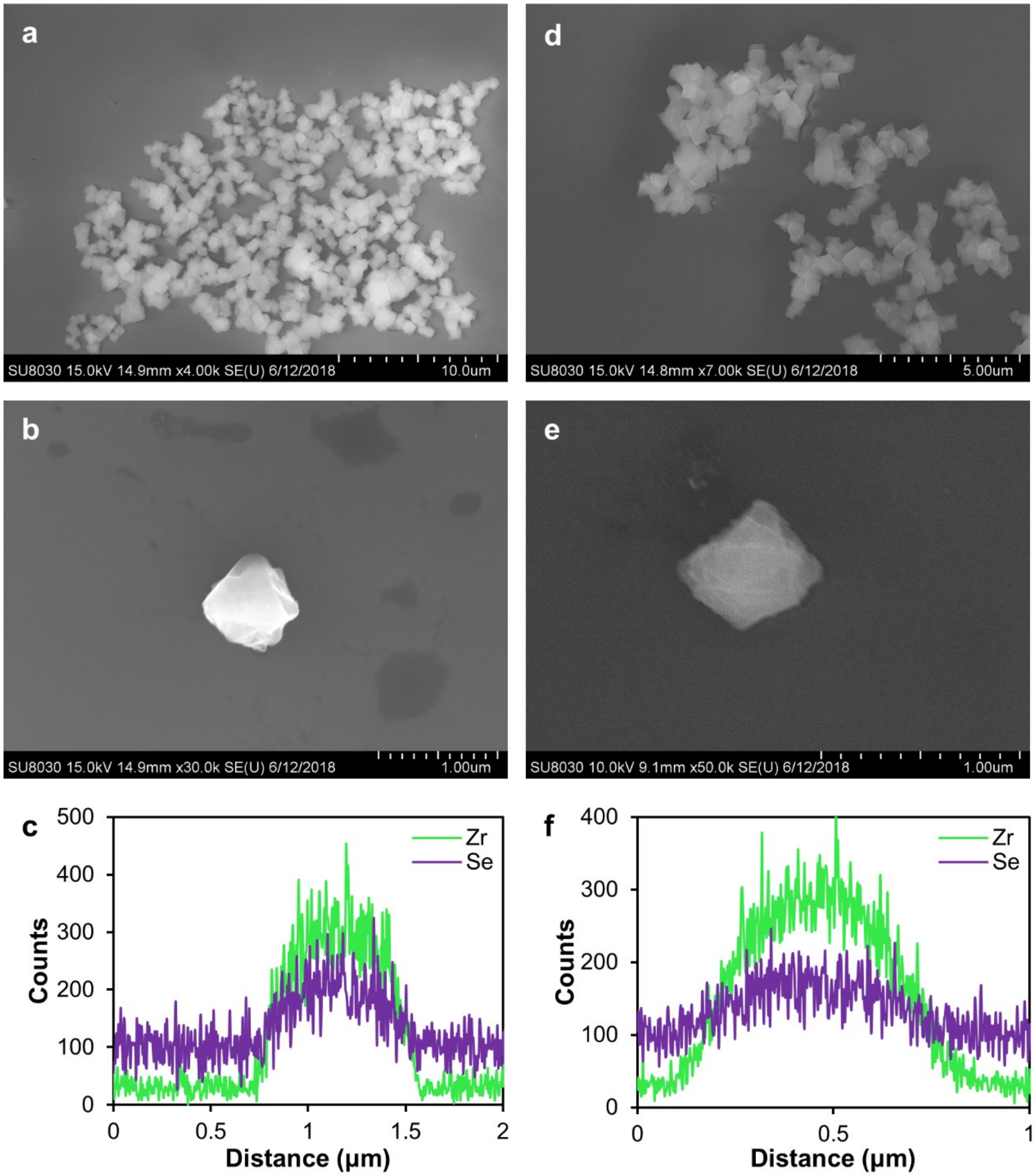


Figure S7. SEM images of a) the bulk sample and b) an individual crystal of MOF-808 loaded with 1.8 SeO_3^{2-} ions per node, and c) the EDS linescan of the crystal in b. SEM images of d) the bulk sample and e) an individual crystal of MOF-808 loaded with 1.6 SeO_4^{2-} ions per node, and f) the EDS linescan of the crystal in e. Both EDS linescans confirm the uniform distribution of selenium throughout the MOF-808 crystals.

References

1. G. M. Sheldrick, *Acta Crystallographica Section A: Foundations and Advances*, 2015, **71**, 3-8.
2. G. M. Sheldrick, *Acta Crystallogr C Struct Chem*, 2015, **71**, 3-8.
3. C. Kabuto, S. Akine, T. Nemoto and E. Kwon, *Nihon Kessho Gakkaishi*, 2010, **51**, 218-224.
4. A. L. Spek, *Acta Crystallogr D Biol Crystallogr*, 2009, **65**, 148-155.
5. J. S. Yamani, A. W. Lounsbury and J. B. Zimmerman, *Water Research*, 2014, **50**, 373-381.

6. Y. T. Chan, W. H. Kuan, T. Y. Chen and M. K. Wang, *Water Research*, 2009, **43**, 4412-4420.
7. A. J. Howarth, M. J. Katz, T. C. Wang, A. E. Platero-Prats, K. W. Chapman, J. T. Hupp and O. K. Farha, *Journal of the American Chemical Society*, 2015, **137**, 7488-7494.
8. 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, *Environmental Science & Technology*, 2017, **51**, 8606-8615.
9. L. Ma, S. M. Islam, C. Xiao, J. Zhao, H. Liu, M. Yuan, G. Sun, H. Li, S. Ma and M. G. Kanatzidis, *Journal of the American Chemical Society*, 2017, **139**, 12745-12757.
10. G. Nisa, G. Mustafa and A. A. Osman, *Journal of Applied Polymer Science*, 2011, **122**, 1134-1141.
11. N. Tian, Z. Zhou, X. Tian, C. Yang and Y. Li, *Separation and Purification Technology*, 2017, **176**, 66-72.
12. Y. Toshiyuki, T. Takashi and Y. Hideaki, *Bulletin of the Chemical Society of Japan*, 2003, **76**, 2225-2232.
13. J. Li, Y. Liu, X. Wang, G. Zhao, Y. Ai, B. Han, T. Wen, T. Hayat, A. Alsaedi and X. Wang, *Chemical Engineering Journal*, 2017, **330**, 1012-1021.