# **Supporting Information**

# Functionalized Porous Aromatic Framework for Efficient Uranium Adsorption from Aqueous Solutions

Baiyan Li,<sup>†</sup> Qi Sun,<sup>†</sup> Yiming Zhang,<sup>†</sup> Carter W. Abney,<sup> $\ddagger$ ,§</sup> Briana Aguila,<sup>†</sup> Wenbin Lin,<sup> $\ddagger$ </sup> and Shenggian  $Ma^{\dagger,*}$ 

<sup>†</sup> Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, FL 33620, USA.

<sup>‡</sup> Department of Chemistry, University of Chicago, 929 East 57th St, Chicago, IL 60637, USA.

<sup>§</sup> Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge,

TN 37831, USA.

Email: <u>sqma@usf.edu</u>

# **Characterizations:**

The gas adsorption isotherms were collected on a surface area analyzer, ASAP 2020. The N<sub>2</sub> sorption isotherms were measured at 77 K using a liquid N<sub>2</sub> bath. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer. ICP-OES was performed on a Perkin-Elmer Elan DRC II Quadrupole. ICP-MS was performed on a Perkin-Elmer Elan DRC II Quadrupole Inductively Coupled Plasma Mass Spectrometer. <sup>13</sup>C (100.5 MHz) cross-polarization magic-angle spinning (CP-MAS) was recorded on a Varian infinity plus 400 spectrometer equipped with a magic-angle spin probe in a 4-mm ZrO<sub>2</sub> rotor. CHN elemental analyses were performed on a Perkin-Elmer series II CHN analyzer 2400.



Figure S1. Pore size distributions of PAF-1 and PAF-1-CH<sub>2</sub>AO.



**Figure S2.** The kinetics of  $UO_2^{2+}$  recovery from simulated seawater by PAF-1-CH<sub>2</sub>AO. Conditions: U simulated sea water solution (200 mL, 7.05 ppm), PAF-1-CH<sub>2</sub>-AO (5 mg).

### **XAFS Experimental Details and Analysis:**

# Preparation of XAFS Samples

The mass of uranium needed to achieve a 1-2.5 absorption length edge step was calculated for PAF-1-CH<sub>2</sub>AO based on the elemental composition and mass absorption coefficient for each element. Samples were blended with sugar to achieve the appropriate concentration. Approximately 20-25 mg of sample (after diluting) was enclosed within a nylon washer of 4.953 mm inner diameter (area of 0.193 cm<sup>2</sup>), sealed on one side with Kapton film held in place with Kapton tape. The sample was pressed thoroughly by hand to form a firm, uniform pellet, then sealed on the open side with a second piece of Kapton film secured with Kapton tape. The entire sample was placed into a baggie formed of Kapton tape which had been folded in half to prevent any contact with the adhesive. Small pieces of Kapton tape were used to seal the three open edges of the Kapton baggie. This method was approved in advance by the APS Radiation Safety Review Board for achieving the double containment necessary for analysis of radioactive samples.

## Data Collection:

The X-ray absorption data were collected at Beamline 10BM-B at the Advanced Photon Source (APS) at Argonne National Laboratory.<sup>1</sup> Spectra were collected at the uranium L<sub>3</sub>-edge (17166 eV) in transmission mode. The X-ray white beam was monochromatized by a Si(111) monochromator and detuned by 50% to reduce the contribution of higher-order harmonics to below the level of noise. The K-edge of an yttrium foil (17038 eV) was used as the reference for energy calibration and measured simultaneously for all samples. The incident beam intensity (I<sub>0</sub>), transmitted beam intensity (I<sub>t</sub>), and reference (I<sub>r</sub>) were all measured by 20 cm ionization chambers with gas compositions of 80% N<sub>2</sub> and 20% Ar, 95% Ar and 5% N<sub>2</sub>, and 100% N<sub>2</sub>, respectively. All spectra were collected at room temperature.

Samples were centered on the beam and adjusted to find the most homogeneous location in the sample for data collection. The beam was reduced to dimensions of  $400 \times 3100$  mm for all data collection. Data were collected over six regions: -250 to -30 eV (10 eV step size, dwell time of 0.25 seconds), -30 to -5 eV (5 eV step size, dwell time of 0.5 seconds), -5 to 30 eV (1 eV step size), 3 Å-1 to 6 Å-1 (0.05 Å-1 step size, dwell time of 2 seconds), 6 Å-1 to 9 Å-1 (0.05 Å-1 step size, dwell time of 4 seconds), and 9 Å-1 to 15 Å-1 (0.05 Å-1 step size, dwell time of 8 seconds). Three scans were collected at room temperature (~25 °C) for each sample.

The data were processed and analyzed using the Athena and Artemis programs of the IFEFFIT package based on FEFF 6.<sup>2,3</sup> Reference foil data were aligned to the first zero-crossing of the second derivative of the normalized  $\mu(E)$  data, which was subsequently calibrated to the literature  $E_0$  for the yttrium K-edge (17038 eV). Spectra were averaged in  $\mu(E)$  prior to normalization. The background was removed and the data were assigned an Rbkg value of 0.8, slightly less than one-half the value of the half-path length for the nearest scattering element, prior to normalizing to obtain a unit edge step.

All data were initially fit with k-weighting of 1,2, and 3, then finalized with k<sup>3</sup>-weighting in R-space. Structural parameters that were determined by the fits include the degeneracy of the scattering path (N<sub>degen</sub>), the change in R<sub>eff</sub> ( $\Delta$ R<sub>i</sub>), the relative mean square displacement of the scattering element ( $\sigma$ <sub>i</sub><sup>2</sup>), and the energy shift of the photoelectron, ( $\Delta$ E<sub>0</sub>). The passive electron reduction factor (S<sub>0</sub><sup>2</sup>) was fixed at 1. For each fit, the fit range ( $\Delta$ R), data range ( $\Delta$ k), number of independent points ( $N_{idp}$ ), number of variables ( $N_{var}$ ), degress of freedom (v), reduced chi-squared value ( $\chi_v^2$ ), and R-factor (R) are in Table S1. For each fit, the number of independent points was not permitted to exceed 2/3 the number of variables, in keeping with the Nyquist criterion.<sup>4</sup>

 Table S1.
 Data range and goodness-of-fit parameters for Uranium L<sub>III</sub>-edge EXAFS

ΔR	1 - 4.5
Δk	2.5 - 13
N <sub>idp</sub>	23
N <sub>var</sub>	14
ν	9
Xv <sup>2</sup>	34.5
R	1.37 %

Spectrum of PAF-1-CH<sub>2</sub>AO.

#### EXAFS Fitting:

Scattering paths used in the fit of PAF-1-CH<sub>2</sub>AO were taken from previously reported single crystal structures for UO<sub>2</sub>(Benzamidoxime)<sub>2</sub>·2 MeOH and uranyl acetate. The best-fit model contains two axial oxygen on uranyl (O<sub>yl</sub>) and direct scattering paths from first shell oxygen (O) and nitrogen (N), and second shell carbon (C). Coordination numbers were varied by scaling S<sub>0</sub><sup>2</sup> by a free variable. Scattering paths for the amidoxime ligand, carbonate, and free solvent were all included. To ensure reasonable coordination numbers were obtained, the sum of all equatorial scattering elements was restrained between 4 and 6. Multiple scattering paths from the axial oxygen contributed to the fits significantly, which can be attributed to strong uranyl binding as well as the linear orientation of O<sub>yl</sub>-U-O<sub>yl</sub>. Additional multiple scattering feature and their R<sub>eff</sub> was < 4.5 Å. The degeneracy of O<sub>yl</sub> was fixed at two, while the coordination number of O, N, and C were allowed to vary. Change in scattering half-path length ( $\Delta$ R) and mean squared relative deviation ( $\sigma^2$ ) were free parameters for all direct scattering paths. Errors for multiple scattering pathways were obtained by standard propagation of error from their

constituent single scattering pathways. Figure S3 displays the single crystal structures used to construct the EXAFS structure model.

Scattering Path	Ndegen	<b>R</b> (Å)	ΔR (Å)	$\sigma^2$ (Å <sup>2</sup> )	
U→O <sub>yl</sub>	2	1.796	$\Delta R-O_{yl}$	$\sigma^2$ -O <sub>yl</sub>	
U→O <sub>AO</sub>	1	2.352	$\Delta R$ -O <sub>AO</sub>	σ <sup>2</sup> -Ο	
$U \rightarrow O_{solv.}$	1	2.419	$\Delta R$ -O <sub>solv</sub>	σ <sup>2</sup> -Ο	
U→N	1	2.438	$\Delta R-N$	$\sigma^2$ -N	
U→C <sub>CO2</sub>	1	2.876	$\Delta R$ -C <sub>CO2</sub>	σ <sup>2</sup> -C	
U→C <sub>AO</sub>	1	3.572	$\Delta R$ -C <sub>AO</sub>	σ <sup>2</sup> -C	
$U \rightarrow O_{yl(1)} \rightarrow O_{AO}$	4	3.580	$0.5  imes \Delta R$ -O <sub>yl</sub> +	$0.5\times\sigma^2\text{-}O_{yl}$	
			$0.5  imes \Delta R$ -O <sub>AO</sub>	$+0.5 \times \sigma^2$ -O	
$U \rightarrow O_{yl(1)} \rightarrow O_{yl(2)}$	2	3.593	$2 \times \Delta R$ -O <sub>yl</sub>	$2\times\sigma^2\text{-}O_{yl}$	
$U \rightarrow O_{yl(1)} \rightarrow U \rightarrow O_{yl(2)}$	2	3.593	$2 \times \Delta R$ -O <sub>yl</sub>	$2\times\sigma^2\text{-}O_{yl}$	
$U \rightarrow O_{yl(1)} \rightarrow U \rightarrow O_{yl(1)}$	2	3.593	$2 \times \Delta R$ -O <sub>yl</sub>	$2\times\sigma^2\text{-}O_{yl}$	
U→N→C <sub>AO</sub>	2	3.651	$0.5 \times \Delta R-N +$	$0.5 \times \sigma^2$ -N +	
			$0.5 \times \Delta R$ -C <sub>AO</sub>	$0.5 \times \sigma^2$ -C	

**Table S2.** Paths, Initial Path Lengths, Initial Degeneracy, and Parameters for Fitting PAF-1

CH<sub>2</sub>AO.

**Table S3.**Best-Fit Values for PAF-1-CH2AO.

Scattering Path	Ndegen	Error	<b>R</b> (Å)	Error	$\sigma^2 (\times 10^{-3} \text{ \AA}^2)$	Error
U→O <sub>yl</sub>	2		1.791	0.005	2.1	0.3
U→O <sub>AO</sub>	1.4	0.3	2.495	0.029	2.0	0.3
U→O <sub>solv.</sub>	2.1	0.8	2.368	0.015	2.0	0.3
U→N	1.4	0.3	2.286	0.034	2.0	0.3
$U \rightarrow C_{CO2}$	0.5	0.3	2.898	0.054	2.0	0.3
U→C <sub>AO</sub>	1.4	0.3	3.432	0.056	2.0	0.3
U→N→C <sub>AO</sub>	2.4	0.3	3.505	0.066	2.0	0.3
$U \rightarrow O_{yl(1)} \rightarrow O_{yl(2)}$	2		3.582	0.010	4.2	0.3
$U \rightarrow O_{yl(1)} \rightarrow U \rightarrow O_{yl(2)}$	2		3.582	0.010	4.2	0.3
$U \rightarrow O_{yl(1)} \rightarrow U \rightarrow O_{yl(1)}$	2		3.582	0.010	4.2	0.3
$U \rightarrow O_{yl(1)} \rightarrow O_{AO}$	2.8	0.3	3.611	0.029	2.1	0.3
$\Delta E = 8.6 \pm 1.3 \text{ eV}$						



Figure S3. Crystal structures used to prepare the EXAFS structure model. (Left) [UO<sub>2</sub>(Acetamidoxime)<sub>2</sub>]·2MeOH.<sup>5</sup> (Right) Uranyl acetate, UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O. The atomic positions used to calculate EXAFS scattering paths are enclosed in a circle for each structure. Note that for the scattering paths included in the structure model, the acetate ligand is indistinguishable from carbonate or carboxylic acid.

# **References:**

- Kropf, A. J.; Katsoudas, J.; Chattopadhyay, S.; Shibata, T.; Lang, E. A.; Zyryanov, V. N.; Ravel, B.; McIvor, K.; Kemner, K. M.; Scheckel, K. G.; Bare, S. R.; Terry, J.; Kelly, S. D.; Bunker B. A.; Segre, C. U. The new MRCAT (Sector 10) bending magnet beamline at the advanced photon source. *AIP Conf. Proc.* **2010**, *1234*, 299-302.
- 2. Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12*, 537-541.
- 3. Rehr, J. J.; Albers, R. C. Theoretical approaches to x-ray absorption fine structure. *Rev. Mod. Phys.* **2000**, *72*, 621-654.
- 4. Calvin, S. XAFS for Everyone, CRC Press, Boca Raton, FL, 2013.
- Vukovic, S.; Watson, L. A.; Kang, S. O.; Custelcean R.; Hay, B. P. How amidoximate binds the uranyl cation. *Inorg. Chem.* 2012, *51*, 3855-3859.