Uranium MOFs

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Design and Synthesis of a Water-Stable Anionic Uranium-Based Metal–Organic Framework (MOF) with Ultra Large Pores

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Abstract: *Ionic metal–organic frameworks (MOFs) are a subclass of porous materials that have the ability to incorporate different charged species in confined nanospace by ion-exchange. To date, however, very few examples combining mesoporosity and water stability have been realized in ionic MOF chemistry. Herein, we report the rational design and synthesis of a water-stable anionic mesoporous MOF based on uranium and featuring tbo-type topology. The resulting tbo MOF exhibits exceptionally large open cavities (3.9 nm) exceeding those of all known anionic MOFs. By supercritical* CO_2 *activation, a record-high Brunauer-Emmett-Teller (BET) surface area (2100* $m^2 g^{-1}$*) for actinide-based MOFs has been obtained. Most importantly, however, this new uranium-based MOF is water-stable and able to absorb positively charged ions selectively over negatively charged ones, enabling the efficient separation of organic dyes and biomolecules.*

The massive scope of the structural components—that is, many organic linkers of different constitutions and types of metal/metal oxide nodes—which can be used to prepare metal-organic frameworks[1,2] (MOFs), have given chemists the unique ability to engineer solid materials with function-driven properties. These properties include high porosity, water stability, acid and base robustness, conductivity, flexibility, different pore diameters, Lewis acidity, and inclusion of chromophores, all of which have enabled the use of MOFs for the storage,[3,4] sensing,[5] and separation[6] of small ions,[7] gases,[8] and larger organic[9] and inorganic molecules. This privileged class of materials has seen a significant expansion in structural scope through the ever increasing variety of metal nodes and organic linkers used in their preparation. Charged MOFs, however, in particular those with anionic character are underexplored.[10]

Our goal was to create a MOF with 1) low density and a non-interpenetrated 2) anionic framework with 3) large pores and apertures (>2 nm) that is 4) stable to water. A framework which meets all of these design criteria would be an ideal candidate for aqueous-phase separation of charged organic small molecules (e.g., dyes and amino acids) and macro-molecules, for example, peptides, proteins, and nucleotide-based biomolecules.[10,11] Paramount to this feature, however, is the aqueous stability of the MOF.

The well-understood *tbo* net is an attractive target as it topologically precludes interpenetration,[12] while allowing the formation of large cages, cavities and apertures.[13] Traditionally, the 3,4-connected *tbo* topology, illustrated (Scheme S1 in the Supporting Information) by the HKUST-1[14] framework, consists of a four-fold symmetric node (i.e., a copper carboxylate paddlewheel), connected to a three-fold symmetric organic linker, that is, 1,3,5-benzenetricarboxylic acid. By switching the geometry of these components—moving to a three-fold symmetric node and four-fold symmetric linker—we are able to explore many more combinations of linkers and nodes to achieve our desired goal.

A common uranium(VI) structure is that of the negatively charged uranyl carboxylates, $[UO_2(RCOO)_3]^-$. Uranyl carboxylates have been well studied in actinide coordination chemistry[15] and consist of three bidentate carboxylate ligands which lie in an equatorial plane and orthogonally oriented apical uranyl oxygen atoms (Figure 1 a) to form a hexagonal bipyramidal geometry. The total formal charge of this unit is −1 and forms the basis of the anionic MOF. Polycarboxylates have been employed as ligands for uranyl organic frameworks[16] owing to the strong affinity of uranyl ions for oxygen donors. The high strength[17] of uranium carboxylate oxygen bonds[18] has been shown[19] to impart structural stability under a wide pH range in aqueous environments. Connecting planar uranyl carboxylates though a nonplanar organic linker allows the building of a 3D water-stable anionic uranium-based MOF. Ideally, the combination of the pseudo-four fold symmetry of 4,4′,4′′,4′′′-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid (H_4TBAPy), with four benzoic acid groups oriented perpendicularly to a large pyrene core, and the D_{3h} symmetry of anionic uranyl(VI), with the ability to bind three in-plane carboxylates (Figure 1 a), should lead to the formation of the desired 4,3-connected uranium MOF with *tbo* topology.[20]

Reaction of square-like linker H_4TBAPy with UCl_4[21] in a solution of *N*,*N*-dimethylformamide (DMF) and trifluoroacetic acid (TFA) at 130 °C for 24 h yielded light yellow polyhedral crystals of NU-1300. Using single-crystal X-ray diffraction (XRD), elemental and thermogravimetric analysis (TGA), the structure was determined to be $[(CH_3)_2NH_2]_4[(UO_2)_4(TBAPy)_3]$ with associated solvent molecules. NU-1300 crystallizes in the space group of *Fm3m* and has, the

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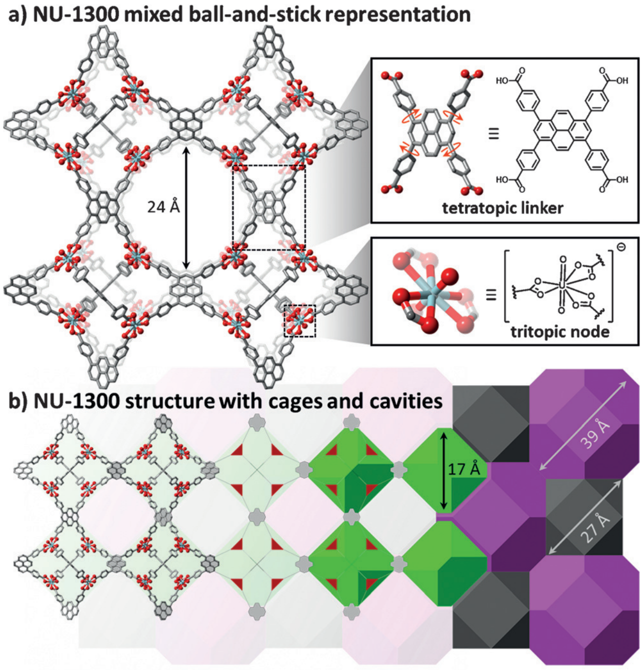


Figure 1. Schematic depiction of the *tbo* topology of NU-1300. a) Ball-and-stick representation of the MOF indicating the 24 Å aperture and highlighting the tetratopic pyrene-based linker with carboxylates twisted perpendicular to the plane of the pyrene and the tritopic uranyl nodes with all three carboxylate ligands in the same plane. C gray; O red; U teal. b) Graphical representation illustrating the cages (green) with 17 Å diameter and the large (39 Å) and small (27 Å) interconnected cavities (purple and gray), respectively.

predicted, *tbo* topology. The crystal structure consists of $[UO_2(RCOO)_3]^-$ units interconnected with $TBAPy^{4-}$ linkers. Each $[UO_2(RCOO)_3]^-$ shows almost ideal hexagonal bipyramidal coordination geometry (Figure 1 b) with an average U−O distance of 2.48 Å in the equatorial plane and U=O bond of 1.69 Å in the axial direction. These values are similar to those of known uranium–organic frameworks[15] (Table S1 and S2). Notably, the benzoic carboxylates of $TBAPy^{4-}$ are perfectly perpendicular to the plane of the pyrene core. As a result, the triangular planes of $[UO_2(RCOO)_3]^-$ are at 90° to the edge of the square-like $TBAPy^{4-}$ linkers, a characteristic feature of the 4,3-connected *tbo* topology. Although the cage structures of NU-1300 are uniformly 17 Å in diameter, the near square geometry (16.7 by 15.3 Å from uranium center to uranium center) of the $TBAPy^{4-}$ results in the formation of two kinds of cavities inside NU-1300. A smaller cavity (Figure 1 b) with 27 Å diameter and a much larger one with a 39 Å diameter. To our knowledge, this cavity is the largest among all reported[10,22] anionic MOFs. The aperture between the cavities is nearly 24 Å (Figure 1 a). The calculated void space[23] in NU-1300 (without counterions) is approximately 91 %. TGA analysis (Figure S1) reveals that a large amount of solvent, which can be removed, resides (ca. 50 % weight loss from 90–210 °C) in the pores of as-synthesized NU-1300. The anionic framework is thermally stable up to 400 °C under N_2.

To activate the NU-1300 samples, the residual solvent (DMF and H_2O) of the as-synthesized NU-1300 was exchanged sequentially with fresh DMF and finally anhydrous EtOH. Supercritical CO_2 drying[2,4,24] was employed to evacuate the NU-1300 structure. See Supporting Information for details. Nitrogen adsorption experiments, performed on an optimally activated sample of NU-1300, exhibits a type IV isotherm consistent with mesoporosity (Figure 2). From the first plateau (ca. 800 $cm^3 g^{-1}$) and following the consistency criteria,[25] we calculated a Brunauer-Emmett-Teller (BET) surface area of 2100 $m^2 g^{-1}$ (Figure S2 and Table S3). The second rise in the isotherm (P/P_0 between 0.21–0.40) indicates filling of the mesopores. We calculated a maximum pore volume of 2.8 $cm^3 g^{-1}$ based on the saturation N_2 uptake (ca. 1800 $cm^3 g^{-1}$) at 1 atm. Both the surface area and pore volume of NU-1300 are among the highest of all actinide-based MOFs described to date.[19,26]

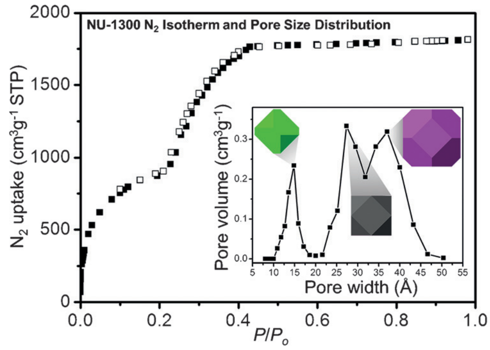


Figure 2. N_2 isotherm at 77 K. Inset: DFT pores size distribution of NU-1300. The peaks of 15, 27, and 36 Å correspond to the small cage and two interconnected cavities, respectively.

To probe the charge of the pore surface within NU-1300, three cationic organic dyes, methylene blue (MEB), Janus Green B (JB), ethyl violet (EV), and an anionic organic dye, resorufin sodium salt (RS), were chosen as diagnostic agents. Their dimensions (molecular size < 2.4 nm) are suitable for pore permeation and their large UV/Vis absorption extinction coefficients facilitate detection and quantification of their uptake by the uranium MOF. Identical amounts (5 mg) of 100 μm-diameter NU-1300 crystals were soaked in different DMF solutions containing each of the dyes. The initial dye concentrations were 1 M and the UV/Vis absorbances were monitored after 0, 1, 3, 7, 16, 24, and 42 h. As evidenced by changes (or not) in the absorbance (λ_{max}) of the supernatant solutions, only the cationic dyes were absorbed by NU-1300; the anionic dye is denied access to the MOF interior and thus is not depleted from the solution (Figure 3 and Figure S3). To demonstrate the selectivity of ion-exchange based on the dye-uptake by NU-1300, a competition experiment using JB and RS was carried out. Mixing equimolar amounts of JB and RS in solution results in a purple mixture, which is then transferred to a vial containing NU-1300 solid. Assessment after 2 days, shows that the color of the mixture changes from purple to pink while the NU-1300 solid turns from its original light yellow to dark blue, qualitatively indicating selective adsorption of the anionic dye JB (Figure S3–4). Given the smaller size of RS compared to that of JB, the possibility of size-based adsorption selectivity can be excluded. Encour-

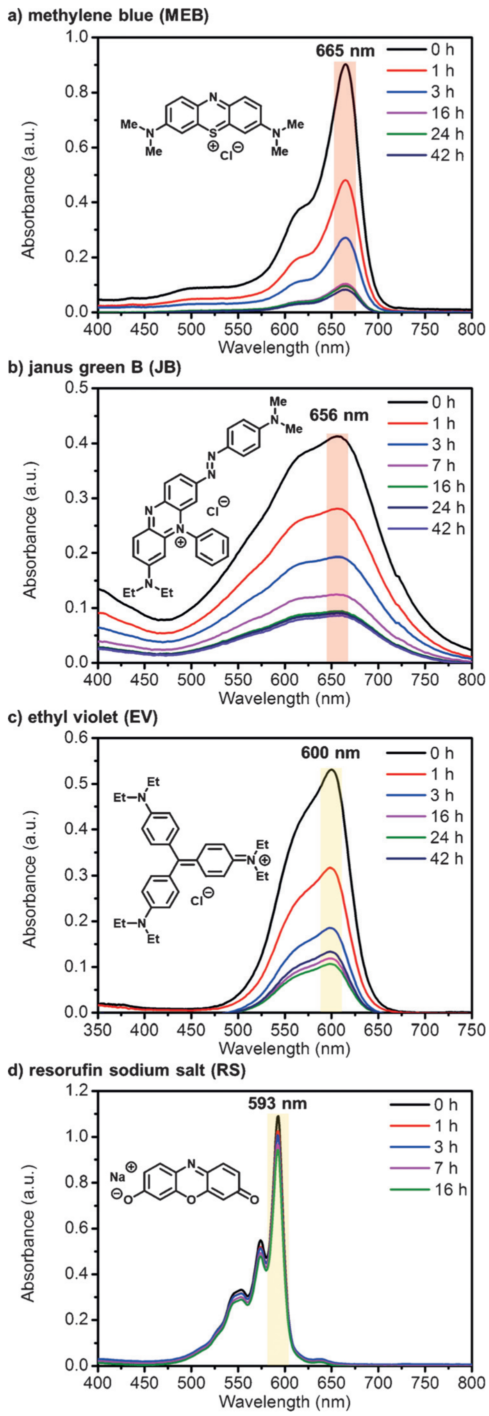


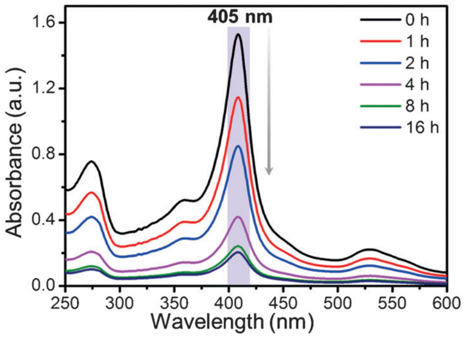
Figure 3. UV/Vis spectra of solutions of dyes a) MEB, b) JB, c) EV, and d) RS in DMF in the presence of NU-1300 with time. Peak maximum highlighted.

aged by these results, we decided to test the ability of NU-1300, with its mesoporous structure, to discriminate between large anionic and cationic proteins in an aqueous solution. To assess the aqueous stability of NU-1300, samples were soaked in aqueous solutions with pH ranging from 1 to 10. Powder X-ray diffraction (PXRD), N_2 isotherms, and optical microscopy (Figure S5–7) of NU-1300 indicate that it is structurally stable and maintains its crystallinity under both acidic conditions (pH down to 1) and weakly basic conditions (pH up to 8).

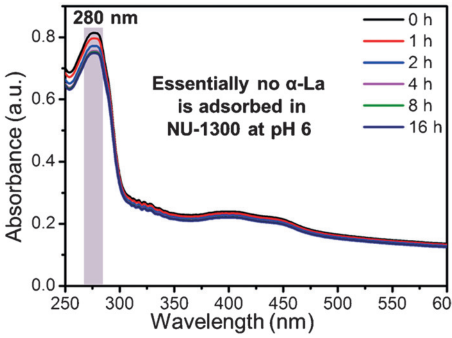
Before protein selectivity experiments were performed, the zeta potential of NU-1300 as a function of pH was measured (Figure S8). The results indicate an isoelectric point (pI) of 2.7. Above pH 2.7, NU-1300 is negatively charged and should have favorable electrostatic interactions with proteins featuring overall positive surface charges at these pH values. To test the ability of NU-1300 to differentiate between anionic and cationic macromolecules, we selected two similar sized proteins, the predominantly cationic enzyme cytochrome c[27] (Cyt-c, 3.6 × 2.4 × 2.2 nm) as well as the predominantly anionic protein α-lactabumin[28] (α-La, 4.8 × 1.8 × 1.8 nm). It is notable that the short dimensions of these two macromolecules are equal to or smaller than the diameter (2.4 nm) of the main aperture of NU-1300, and thus both should be capable of accessing the pores of the framework. The isoelectric point values for these two proteins (10.3 for Cyt-c and 4.5 for α-La) enable them to carry different surface charges (positive for Cyt-c and negative for α-La) in aqueous solution with pH between 5 and 10. First, pH 6 solutions were used to assess the single component absorption of both Cyt-c and α-La in NU-1300. As expected, NU-1300 absorbed Cyt-c (Figure 4a) and not α-La (Figure 4b) at this pH. It should be noted that changes to the pH can result in the protein undergoing a change in surface charge from positive to negative. In the case of α-La, adjusting the pH from 6 to 4 will alter the surface charge of α-La from negative to positive. In addition, alteration of the ionic strength of the solution by the addition of electrolytes or salts will inhibit attraction between the anionic MOF and the protein. To mimic a protein-separation process based on ion-exchange chromatography, an equimolar (0.02 M) Cyt-c/α-La mixture (3 mL), at pH 6, was added to NU-1300 (5 mg), and the concentrations of Cyt-c and α-La were monitored by UV/Vis absorption spectroscopy[29] (Figure S9). Initially, the absorbance of Cyt-c in solution decreased significantly while the concentration of α-La remained constant (Figure 4c). When the pH was lowered to 4, changing the net charge of α-La to positive, a substantial drop in the solution concentration of α-La was observed, indicating that both Cyt-c and α-La can be absorbed by NU-1300. When the pH was raised to 6, the concentration α-La in solution increased, indicating its release from NU-1300. Finally, by adding an excess of the strong electrolyte $NaNO_3$, the anion permselectivity was eliminated and the release of Cyt-c from NU-1300 was triggered (Figure 4c). This behavior is expected[30] when the molar concentration of added salt exceeds the effective molar concentration of the framework-fixed charged sites within the MOF. Finally, the isolated solid NU-1300 can be recycled and reused for protein separation at least three times (Figure S10).

In summary, we have designed and synthesized a new anionic uranium-based metal–organic framework with the *tbo* topology. The MOF, which has large, mesoporous cavities (2.7 nm to 3.9 nm) interconnected by apertures (2.4 nm), is obtained by combining the triangular D_{3h} symmetry of an anionic $[UO_2(RCOO)_3]^-$ metal node with a square-like tetracarboxylate organic linker. The framework was activated to give a high BET surface area of 2100 $m^2\,g^{-1}$. Importantly, the MOF was found to be water-stable and capable of absorbing positively charged molecules selectively over

a) Cyt-c adsorption in NU-1300 at pH 6



b) α-La adsorption in NU-1300 at pH 6



c) Cyt-c and α-La competitive adsorption in NU-1300

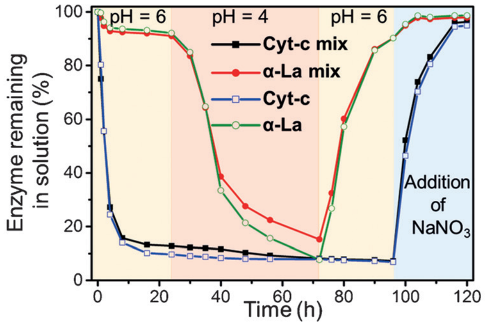


Figure 4. UV/Vis spectra of single-component a) Cyt-c and b) α-La in a pH 6 solution in the presence of NU-1300 monitored with time. c) Percentage of Cyt-c and α-La in both single-component and equimolar Cyt-c/α-La mixture monitored with time. The pH of the solution was adjusted to 4 (pink background) and 6 (yellow background), at 24 and 72 h, respectively. At 96 h, an excess of $NaNO_3$ was added (blue background).

negative ones. These properties, together with NU-1300's mesoporosity, were exploited to separate a representative pair of biological macromolecules, namely cytochrome c and α-lactabumin on the basis of their overall charge. We believe that this proof-of-concept points to the potential applications of charged mesoporous MOFs as a new class of stationary-phase materials for ion-exchange chromatography as well as their potential as high-capacity support materials for heterogenized enzyme catalysis.

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