

Porphyrin-Based Plutonium Metal-Organic Frameworks: A Versatile Platform for Investigating Elusive Plutonium Cluster Chemistry

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Plutonium coordination chemistry has evolved rapidly over the last decade, transitioning from fundamental studies of 1D and 2D coordination polymers to the realization of complex 3D metal-organic frameworks (MOFs). Following the landmark synthesis of Pu-UiO-66 [1], interest intensified in leveraging these porous scaffolds to stabilize elusive coordination environments and high-coordination nodes that are typically inaccessible via traditional high-temperature solid-state methods. Because MOFs offer a modular platform for nanoscale control, they are uniquely suited for investigating the distinct relativistic effects and *f*-orbital participation in bonding that characterize the tetravalent actinides.

Porphyrins serve many important roles in biological systems, such as enabling photosynthesis and oxygen transport. They are highly conjugated, aromatic molecules that possess many resonance structures. Porphyrins and porphyrin derivatives are usually intensely colored, with a strong absorption band (B band) around 420 nm and weaker bands (Q bands) around 520-650 nm. Due to their remarkably poor solubility even in nonpolar solvents, porphyrins can be functionalized with benzoic acid groups to create tetrakis(4-carboxyphenyl)porphyrin (TCPP) linkers.

Herein, we report the solvothermal synthesis of a plutonium-based MOF that incorporates the TCPP linker. The synthesis involved a 9:1 molar ratio of plutonium(IV) nitrate to TCPP in dimethylformamide (DMF), with water and trifluoroacetic acid (TFA) added as modulators. The solution was then heated at 120 °C for four days, slowly cooled to room temperature over two days, and stored in a freezer. Characterization of the resulting microcrystalline material via powder X-ray diffraction (pXRD) confirmed it to be isostructural with the zirconium-based PCN-222 framework [2]. Ancillary analysis using physisorption measurements and absorption and vibrational spectroscopy supported this assignment.

While initial crystal dimensions were restricted to the microscale (10-50 μm), we observed a significant morphological and structural transformation over 14 months. This aging process, likely driven by radiolysis, resulted in the growth of significantly larger crystals reaching 250 μm. Analysis of these larger crystals using single-crystal X-ray diffraction, pXRD, and Raman revealed a phase transition from the original porous framework into a high-symmetry plutonium compound that is tentatively assigned as a plutonium oxyhydroxide.

This work, supported by a comprehensive synthetic roadmap developed across the lanthanide series, establishes a new transuranic architecture for MOFs and provides further insight into the impact of self-radiolysis on the stability and transformation of actinide-based porous materials.

1. Hastings, A. M.; Ray, D.; Jeong, W.; Gagliardi, L.; Farha, O. K.; Hixon, A. E. *J. Am. Chem. Soc.* **2020**, *142* (20), 9363-9371.
2. Feng, D.; Gu, Z.-Y.; Li, J.-R.; Jiang, H.-L.; Wie, Z.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2012**, *51* (41), 10307-10310.