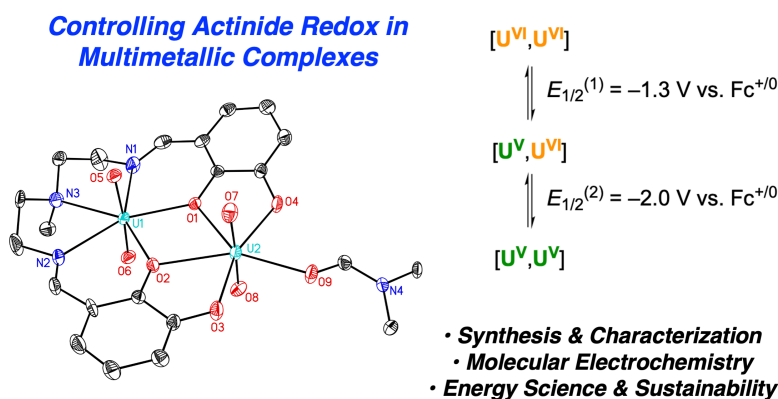


## Understanding Influences on Actinide Redox Chemistry in Multimetallic Complexes

Prof. James D. Blakemore

Metals are critical for many aspects of energy production and utilization. Thus, an important area of contemporary chemistry is focused on understanding and controlling the properties of metal-containing molecules and materials that are related to energy systems. In the Blakemore Group, we study the chemistry of clean energy systems, and are working on a number of projects spanning heavy element chemistry, molecular catalysis, and artificial photosynthesis.

In one project, the Blakemore Group is exploring how bringing actinide elements into close proximity results in changes in their redox properties.<sup>1</sup> The redox chemistry of the actinide elements, particularly the early actinides thorium (<sup>232</sup>Th) and uranium (<sup>238</sup>U) determines how used nuclear fuels and materials can be recycled and separated, meaning that studies in this area could afford insights to improve the sustainability and diminish the environmental impact of producing electricity with nuclear fission. However, designing systems that afford control over actinide redox chemistry remains difficult due to poor understanding of the influences of ligands and multi-metallic species. The goal of this project for REU students is to prepare new multi-metallic uranium coordination complexes based upon robust ligands that feature phenoxide donor groups and map the influences of secondary metal ions on these redox properties of these compounds.<sup>2</sup> The uranyl ion (UO<sub>2</sub><sup>2+</sup>) will be paired with tailored ligands and secondary metal ions, affording a family of tunable complexes. Reactivity studies and study of reduced forms will also be carried out.



*This figure shows the structure of a model bimetallic uranium complex (left) and a scheme showing the reduction pathway accessible to the complex (right). The presence of two uranyl ions results in a positive shift in the first reduction potential of the complex, implicating a role for uranyl as a Lewis acidic redox modulator.<sup>3</sup>*

Students working on this project will gain skills in inorganic and organometallic synthesis, handling of air- and moisture-sensitive compounds, molecular electrochemistry (voltammetry, electrolysis), NMR spectroscopy (<sup>1</sup>H, <sup>19</sup>F, <sup>31</sup>P, multidimensional techniques), and single-crystal X-ray diffraction analysis. The work is enabled by use of Schlenk lines, inert-atmosphere gloveboxes, and a variety of custom-made glassware. Students will also gain an understanding of the important role of chemistry in energy science through interactive discussions and group meetings.

### Lead references for recently published articles from the Blakemore Group:

- [1] Golwankar, R. R.; Kumar, A.; Day, V. W.; Blakemore, J. D. Revealing the Influence of Diverse Secondary Metal Cations on Redox-Active Palladium Complexes. *Chem. Eur. J.* **2022**, *28*, e202200344; doi: 10.1002/chem.202200344.
- [2] Kumar, A.; Lionetti, D.; Day, V. W.; Blakemore, J. D. Redox-Inactive Metal Cations Modulate the Reduction Potential of the Uranyl Ion in Macrocyclic Complexes. *J. Am. Chem. Soc.* **2020**, *142*, 3032-3041 doi: 10.1021/jacs.9b11903.
- [3] Kumar, A.; Blakemore, J. D. On the Use of Aqueous Metal-Aqua pK<sub>a</sub> Values as a Descriptor of Lewis Acidity. *Inorg. Chem.* **2021**, *60*, 1107-1115; doi: 10.1021/acs.inorgchem.0c03239.