Nuclear Science and Security Consortium
Virtual Scholar Showcase 2020

New Precursors for Actinide Nanomaterials

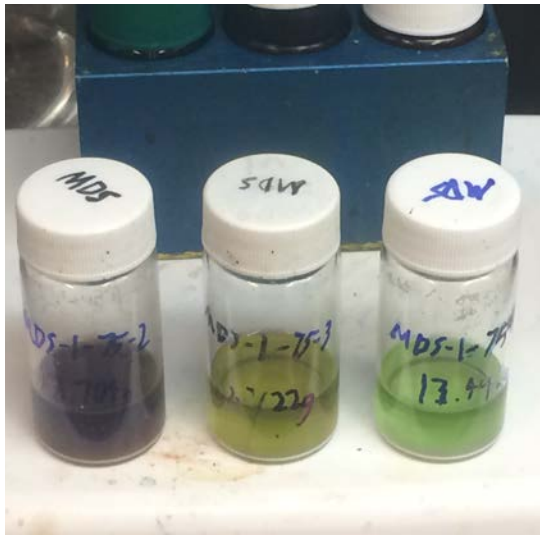
06/03/2020

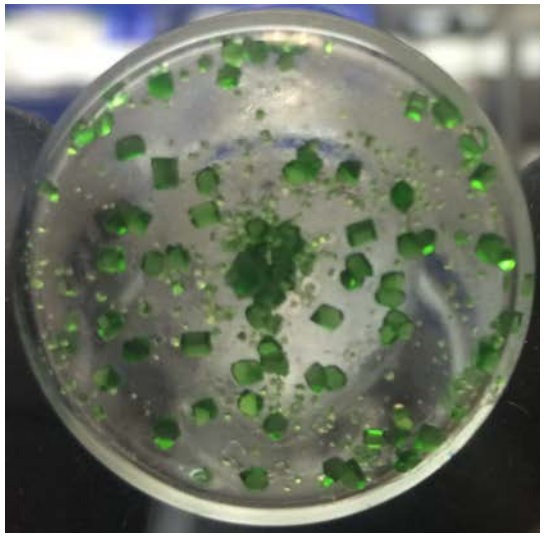
Mark Straub
UC Berkeley

NSSC
NUCLEAR SCIENCE and SECURITY CONSORTIUM

June 2 - 3, 2020

Introduction





Mark Straub

Advisors: **John Arnold, Stefan Minasian**

Focus Area: **Radiochemistry and Forensics**

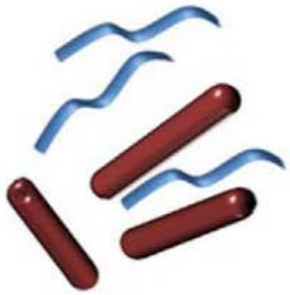
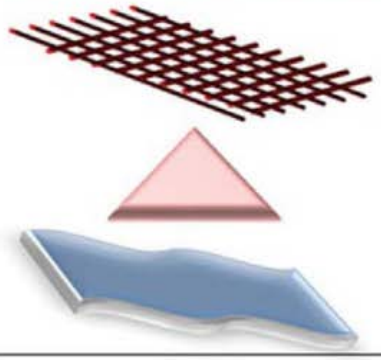
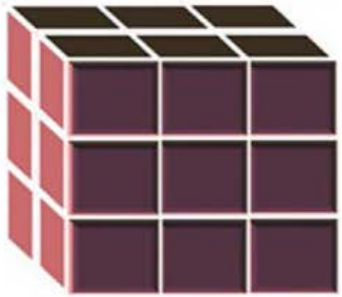
Relevance to the NNSA Mission

- **Microscopic particles are released during processing, transport, and burnup of nuclear materials[1]**
  - Can be analyzed for age, chemical form, and enrichment[2]
- **Certified reference materials (CRMs) of actinide nanomaterials: needed as controls for forensic assignments[3,4]**
- **Developing synthetic routes to nanostructured CRMs:**
  - Composition and morphology can be controlled with a detailed understanding of chemical bonding

1. Mayer, K.; Wallenius, M.; Fanghänel, T. *J. Alloys Compd.* **2007**, *444–445*, 50.
2. Moody, K. J.; Hutcheon, I. D.; Grant, P. M. *Nuclear Forensic Analysis,* Second Ed.; CRC Press, **2014**.
3. Mathew, K. J.; Stanley, F. E.; Thomas, M. R. et. al. *Anal. Methods* **2016**, *8* (40), 7289.
4. Inn, K. G. W.; Johnson, C. M.; Oldham, W. J. et. al. *J. Radioanal. Nucl. Chem.* **2013**, *296* (1), 5.

Project Overview

- **Goal: develop methods to access new uranium nanomaterials**

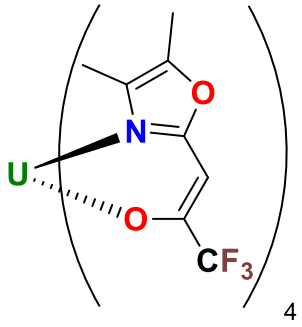
Isotropic nanomaterials	Anisotropic nanomaterials		
			
0D	1D	2D	3D
Nanoparticles	Nanorods, wires	Thin films, plates	Frameworks

- **Many accessible compositions of U_xO_y**
  - Controlling structure is challenging
  - Phase-pure nanomaterials are rare

Spino, J.; Santa Cruz, H.; Jovani-Abril, R.; Birtcher, R.; Ferrero, C. *J. Nucl. Mater.,* **2012***, 422,* 27.
Sajanlal, P. R.; Sreeprasad, T. S.; Samal, A. K.; Pradeep, T. *Nano Rev.*, **2011**, *2*, 5883.

Uranium oxide nanomaterials: precedent

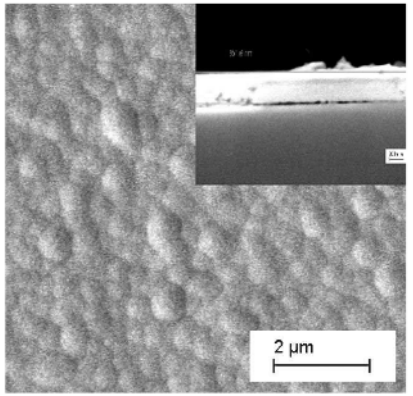
- **Chemical vapor deposition (CVD) from uranium precursors:**



CVD

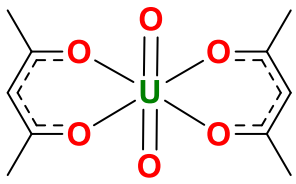
500 °C

2 h



Mixed UO_3/U_3O_8 films

- **Solution synthesis of UO_2 nanoparticles (NPs):**



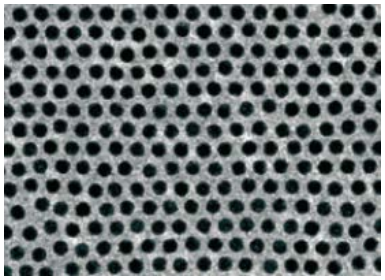
Oleylamine

Oleic acid

1- octadecene

295 °C

5 min.

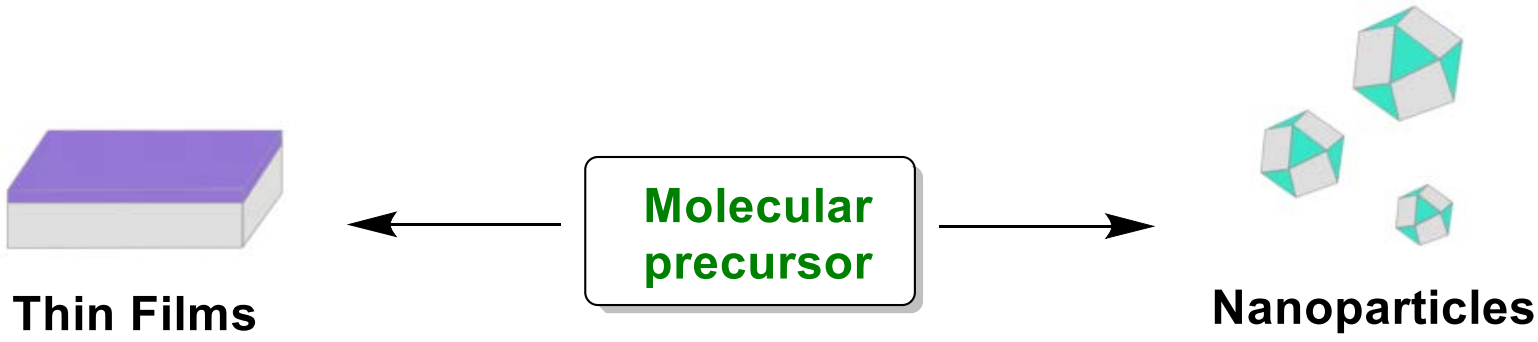


3-6 nm UO_2 NPs

1. Shiokawa, Y.; Amano, R.; et. al. *J. Radioanal. Nucl. Chem.,* **1991**, *152*, 373.
2. Wu, H.; Yang, Y.; Cao, C. *J. Am. Chem. Soc.* **2006,** *128,* 16522.

Routes to oxide nanomaterials

- ***Synthesizing new uranium nanomaterials:***
  - **Tunable precursors**
  - **Well-defined decomposition**
  - **Nucleation and growth control**

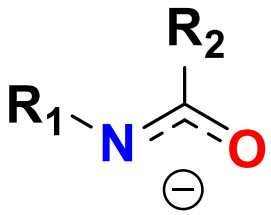


6

Requirements for molecular precursors

- **Decompose to form uranium oxide**
  - Single pathway ideal

- **Volatile (gas-phase methods) or soluble (solution methods)**

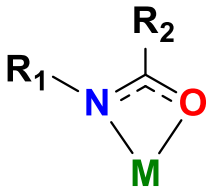


Amidates

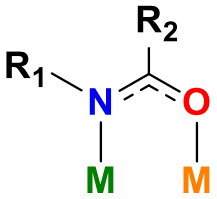
Lim, B., Rahtu, A., Park, J., Gordon, R. *Inorg. Chem*. **2003**, *42*, 7951.
Lee, A.; Schafer, L. *Eur. J. Inorg. Chem*., **2007**, *16*, 2245.

Amidate ligand overview

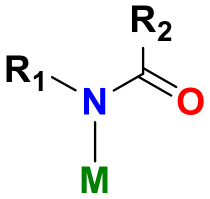
Chelating



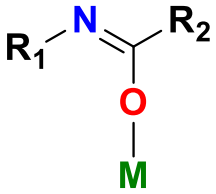
Bridging



N-bound



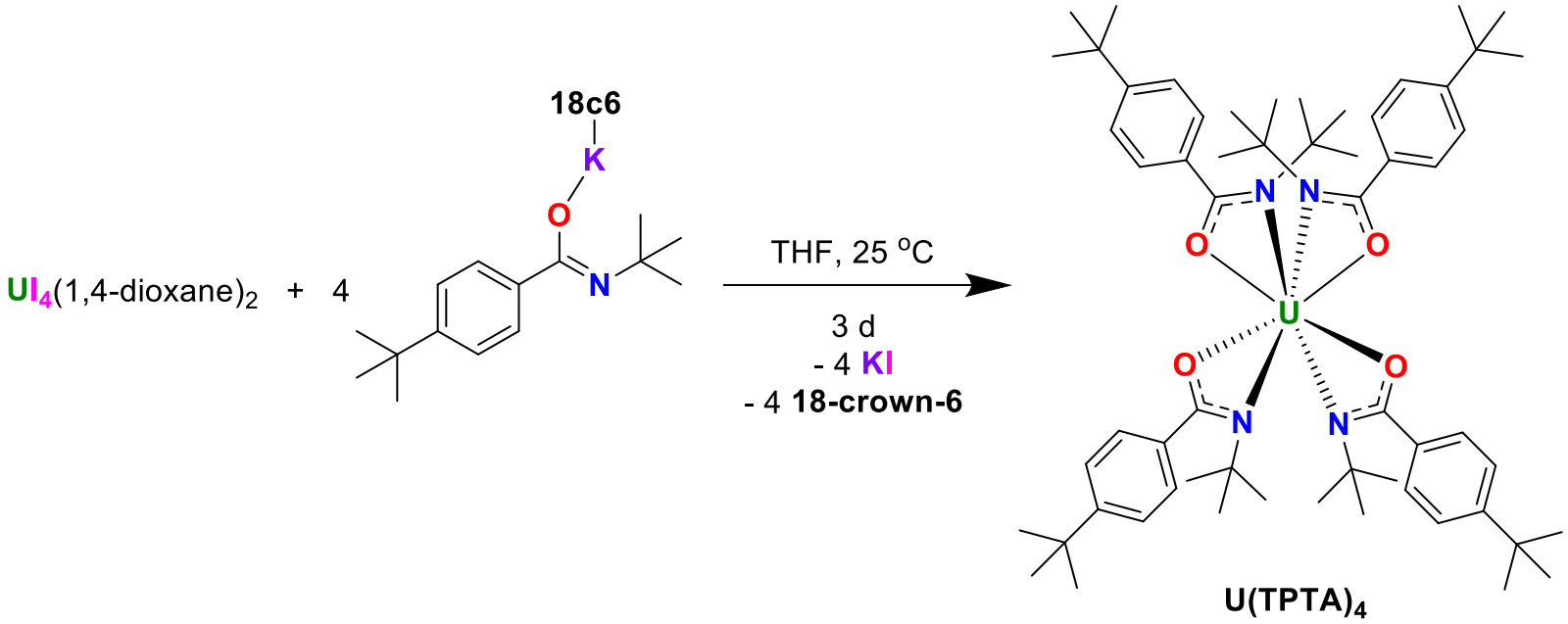
O-bound



- **Metal oxide precursors**
- **Highly tunable**
- **Thermal properties can be controlled by changing R_1 and R_2**

Synthesis of uranium amidate precursors

- **Goal: new molecular precursors for UO_2 nanomaterials**

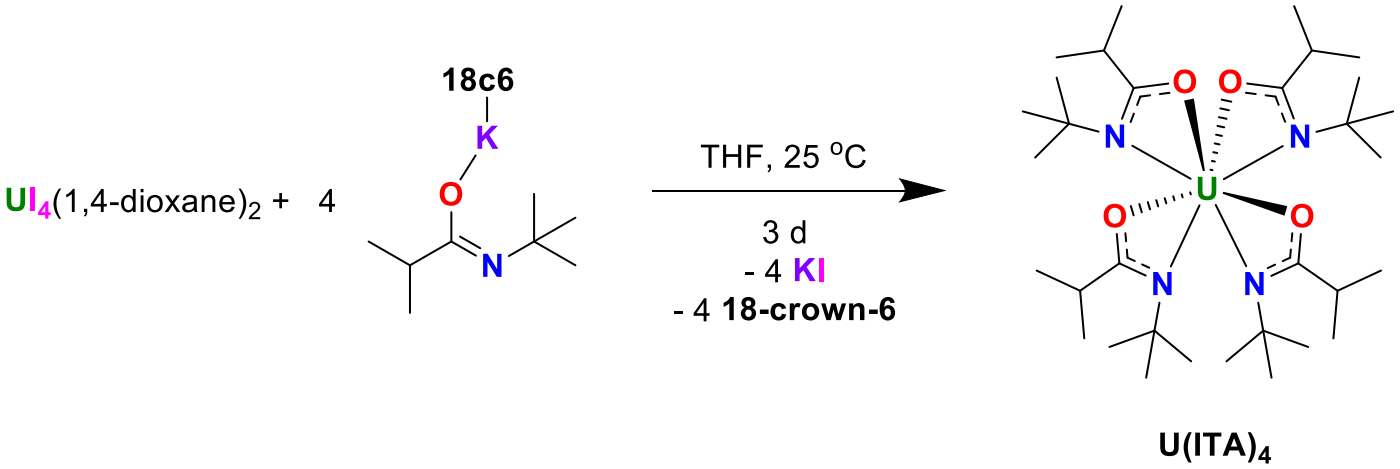


light green crystals

- **Characterized using nuclear magnetic resonance (NMR) spectroscopy and x-ray crystallography**

Volatile uranium amidates

- **Bis(alkyl)-substituted amidates may offer higher volatility**
  - Advantageous for CVD precursors

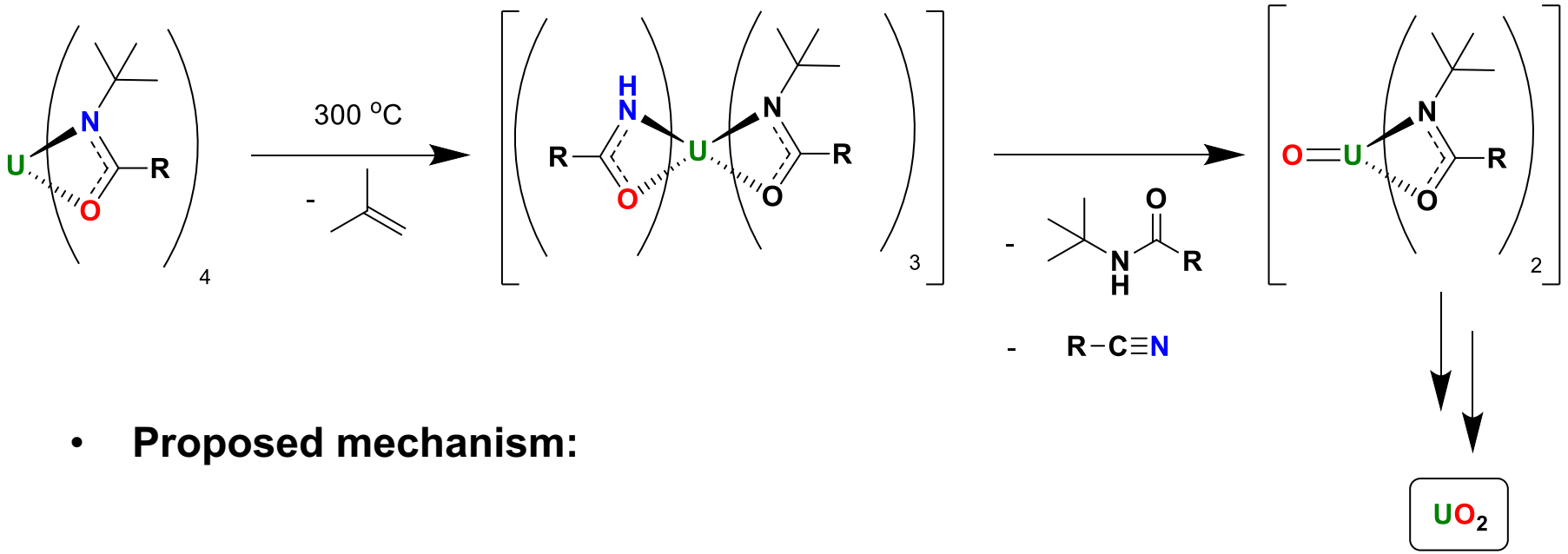


$U(ITA)_4$

emerald green crystals

- **Significantly more volatile**

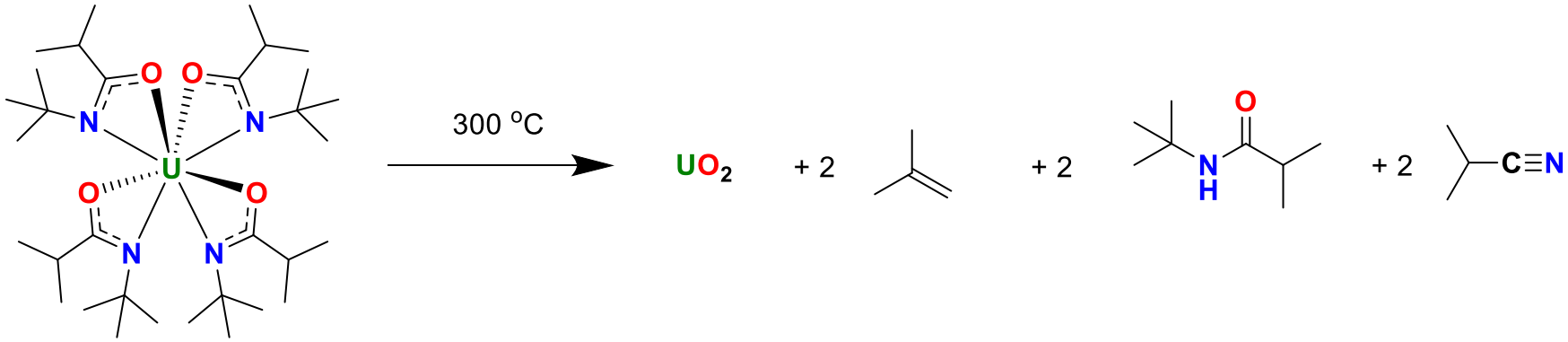
$U(amidate)_4$ decomposition



- **Proposed mechanism:**
  - 1. Alkene elimination
  - 2. Protonolysis
  - 3. Nitrile elimination

11

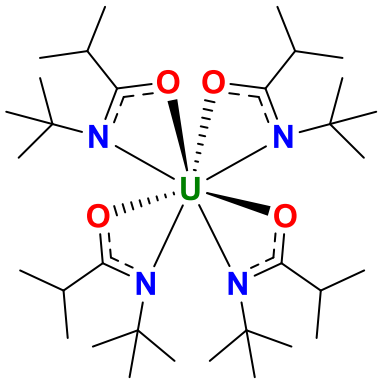
$U(amidate)_4$ decomposition



- **Proposed mechanism:**
  - 1. Alkene elimination
  - 2. Protonolysis
  - 3. Nitrile elimination

12

$U(ITA)_4$ decomposition



300 °C

16 h

* = Amide

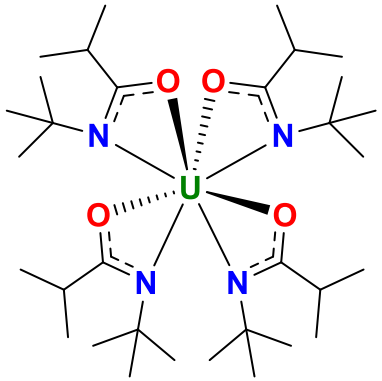
* = Nitrile

* = Isobutylene

13

Collaboration for uranium oxide CVD

- **Established a collaboration with Dr. Sanjay Mathur at the University of Cologne for chemical vapor deposition (CVD) of UO_2 films**



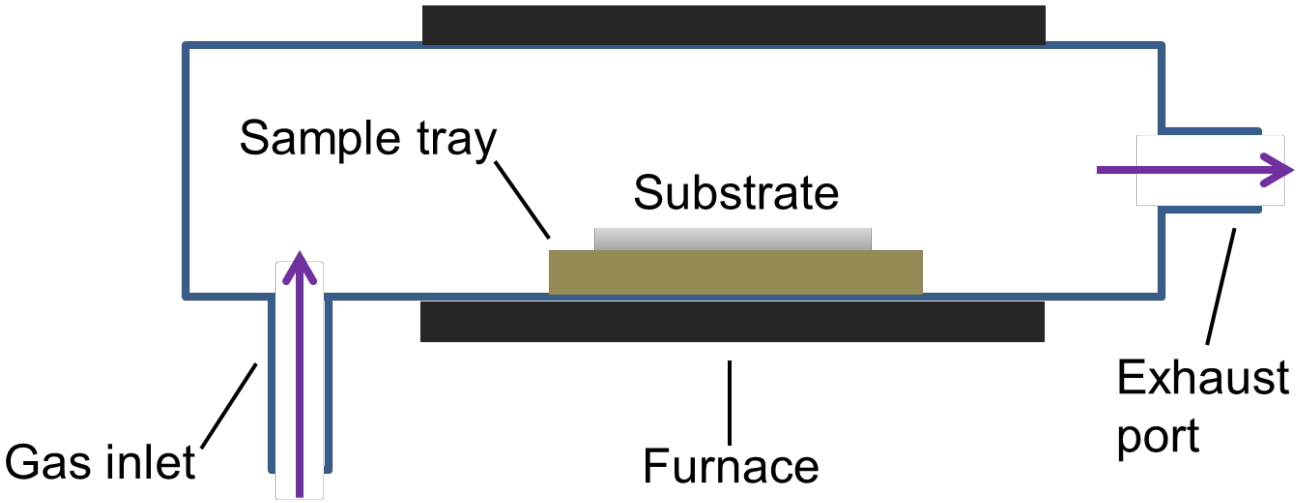
- **Shipped precursors to Cologne, worked together to design deposition experiments**

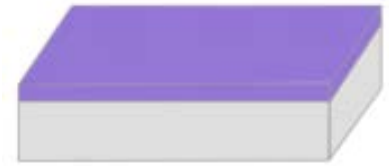
Straub, M. D.; Leduc, J.; Mathur, S. and coworkers. *Angew. Chem. Int. Ed.,* **2019**, *58*, 5749.

14

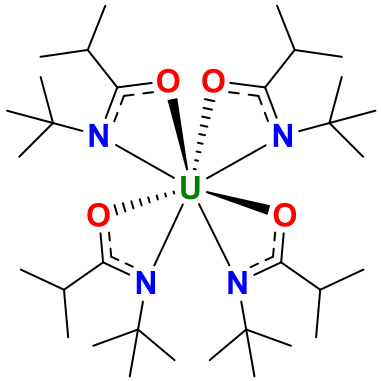
CVD of UO_2 from amidate precursor

MOCVD Apparatus





UO_2 film



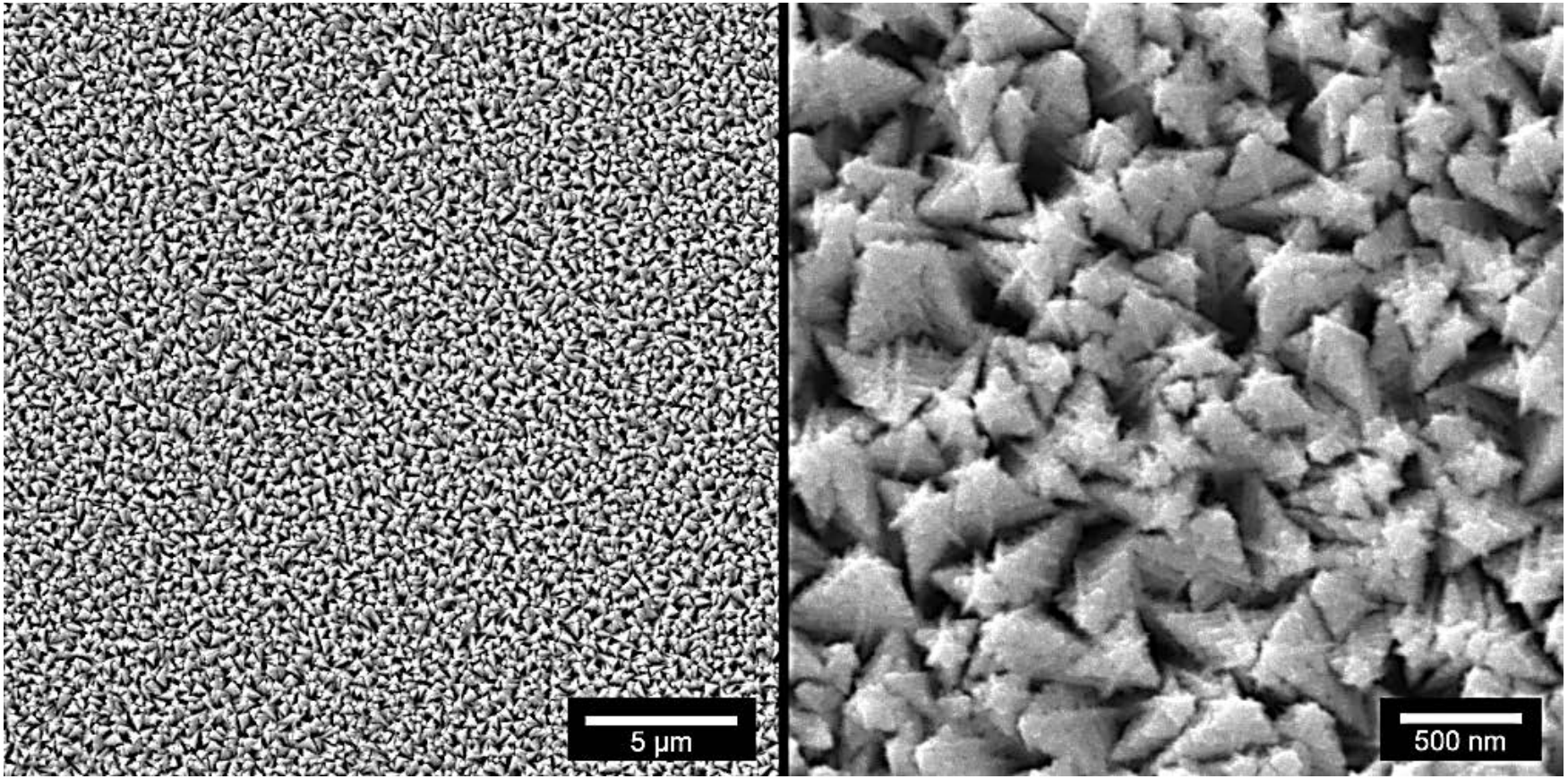
$U(ITA)_4$

- *Precursor temp: 160 °C*
- *Si substrate temp: 500 °C*
- *Pressure: 7.5 x 10^{-7} torr*

With Dr. Sanjay Mathur and coworkers

15

SEM: top view

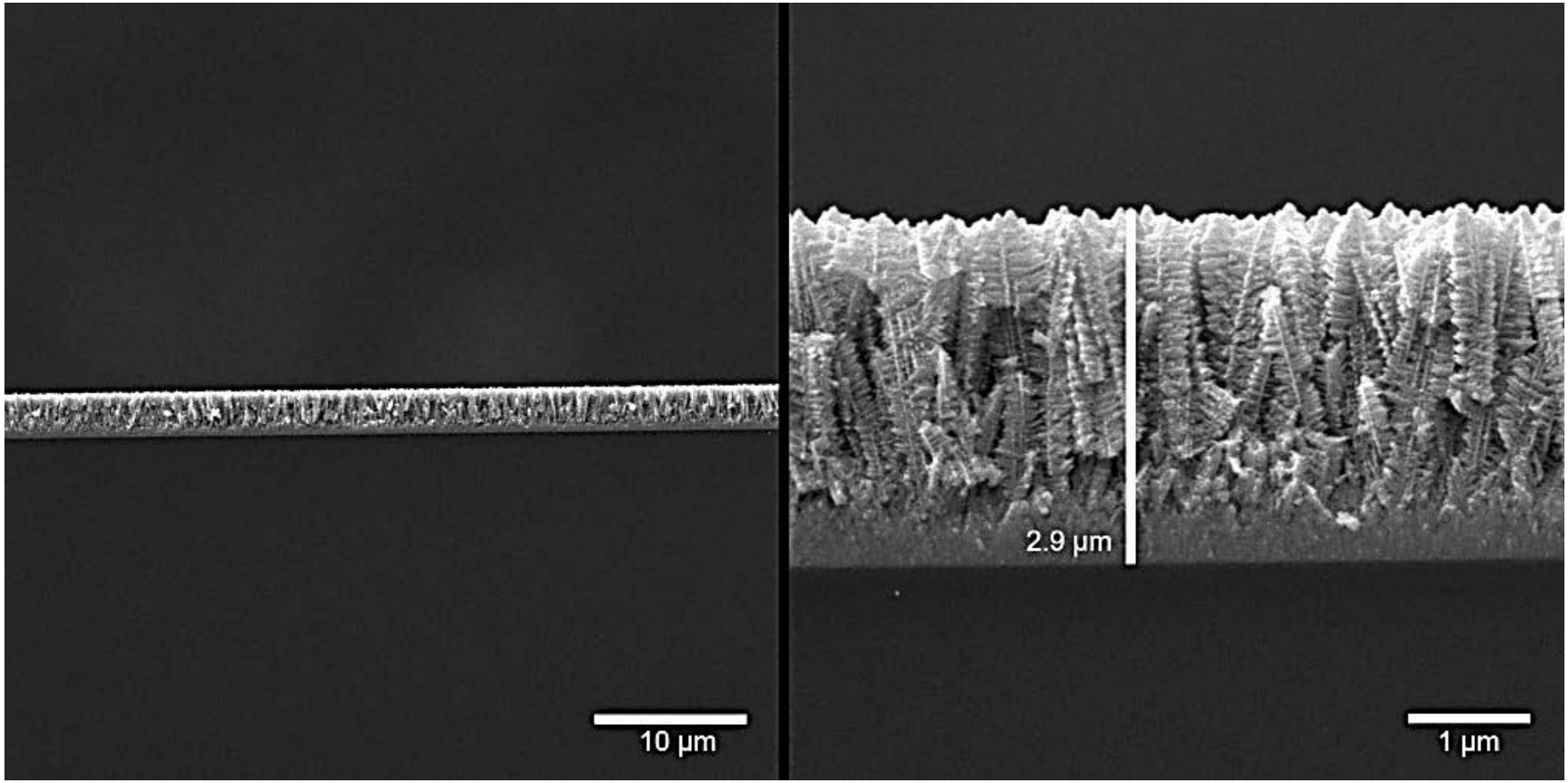


- **Custom precursor design → new UO_2 nanostructures!**

With Dr. Sanjay Mathur and coworkers

16

SEM: side view

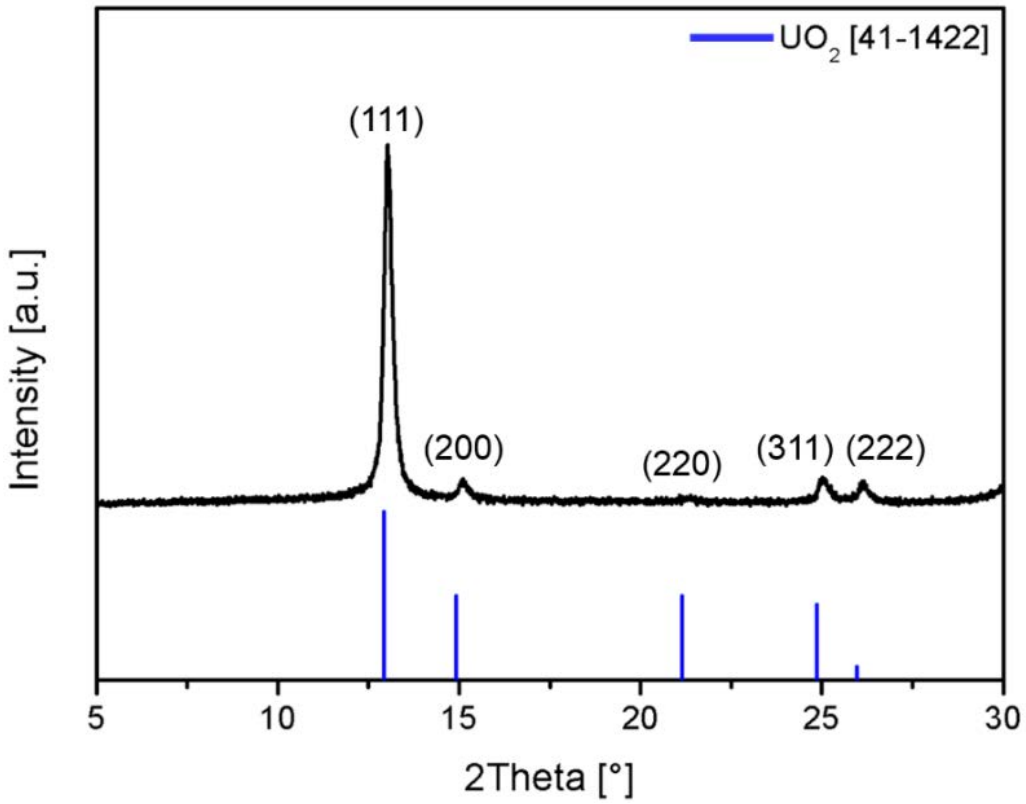


- **Custom precursor design → new UO_2 nanostructures!**

With Dr. Sanjay Mathur and coworkers

17

Powder x-ray diffraction (PXRD)

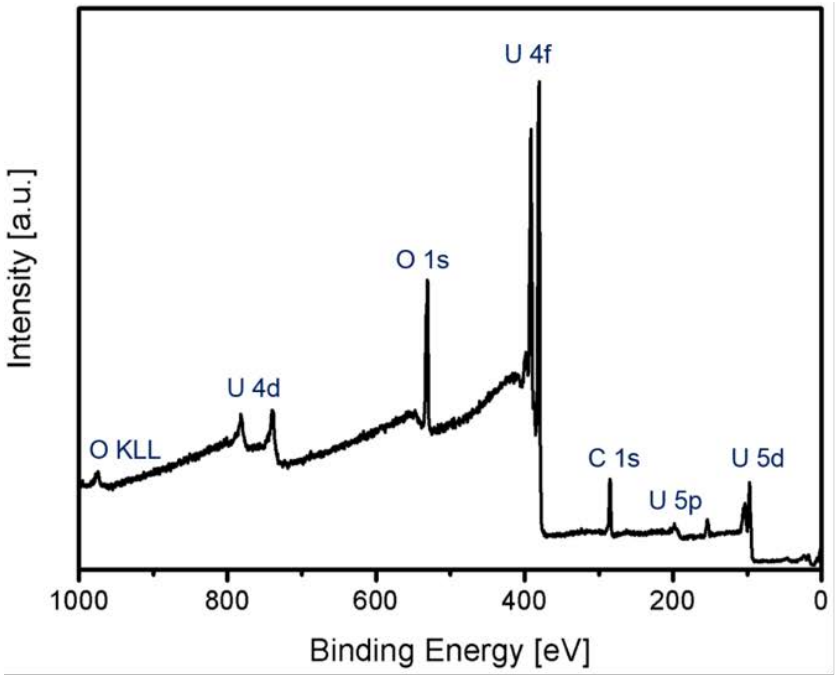


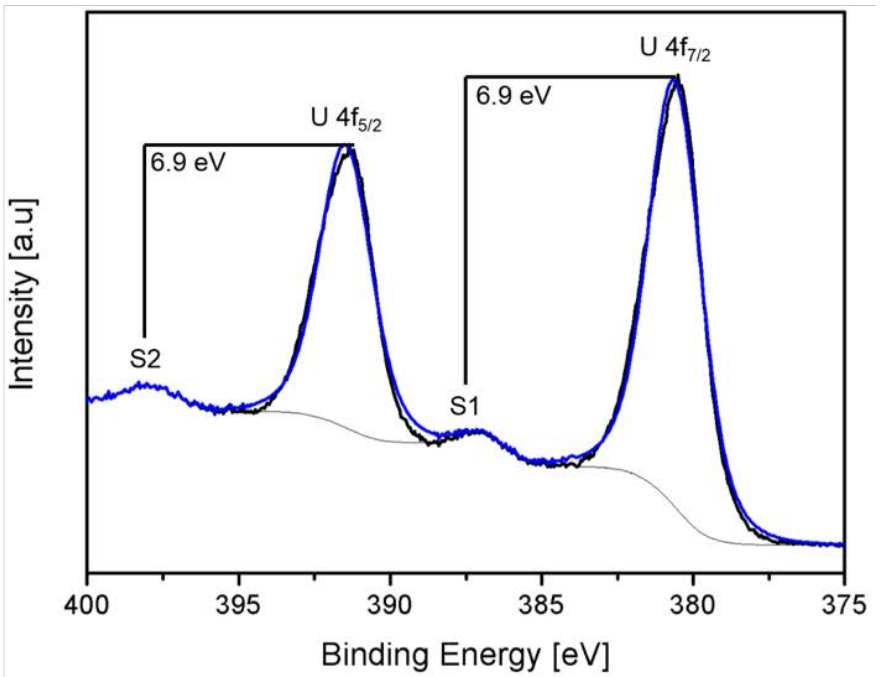
- **Preferred growth along {111} planes**

With Dr. Sanjay Mathur and coworkers

18

X-ray photoelectron spectroscopy (XPS)





- **What other high surface area UO_2 nanomaterials can we access using a molecular precursor approach?**

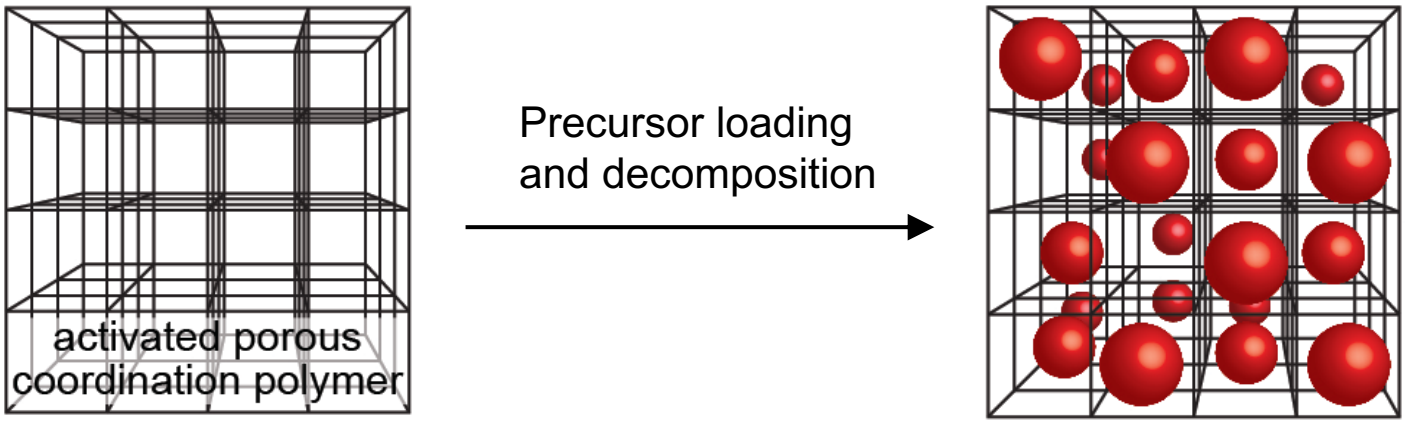
With Dr. Sanjay Mathur and coworkers

19

Templated actinide dioxide particles

- **Ultra-small (< 3 nm) actinide dioxide (AnO_2) particles can be released during burnup and reprocessing of nuclear fuels[1]**

- **Models for these AnO_2 NPs are difficult to isolate**
  - Aggregation is common at small sizes



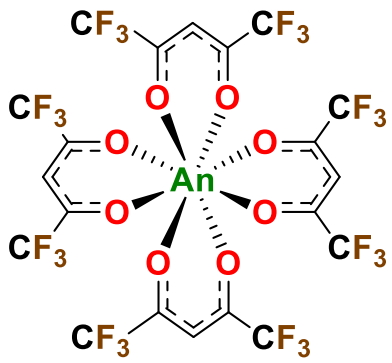
- ***Solution: use a template to control particle size!***

1. Moody, K. J.; Hutcheon, I. D.; Grant, P. M. *Nuclear Forensic Analysis,* Second Ed.; CRC Press, **2014**.

20

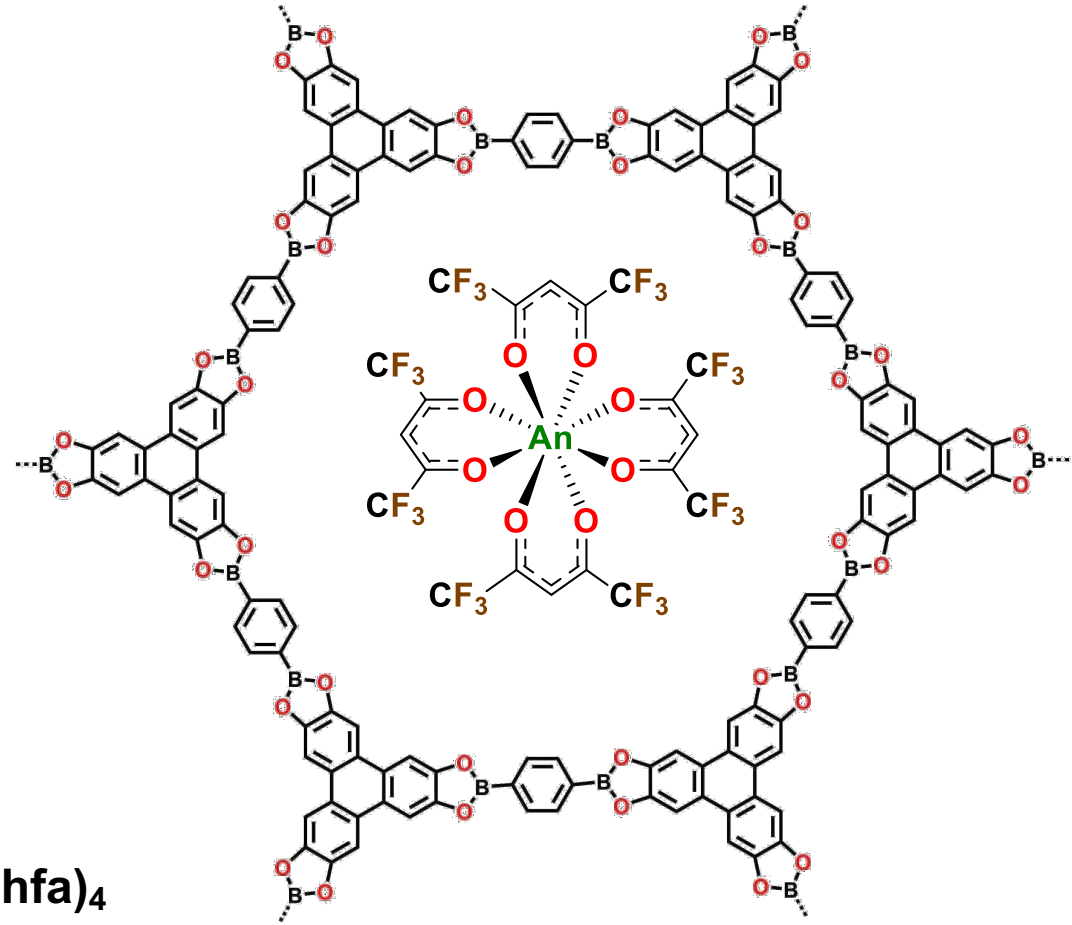
Formation of an inclusion compound

- **Molecular precursors can be loaded into a porous framework, then decomposed *in situ* to AnO_2 NPs**



An = U, Th

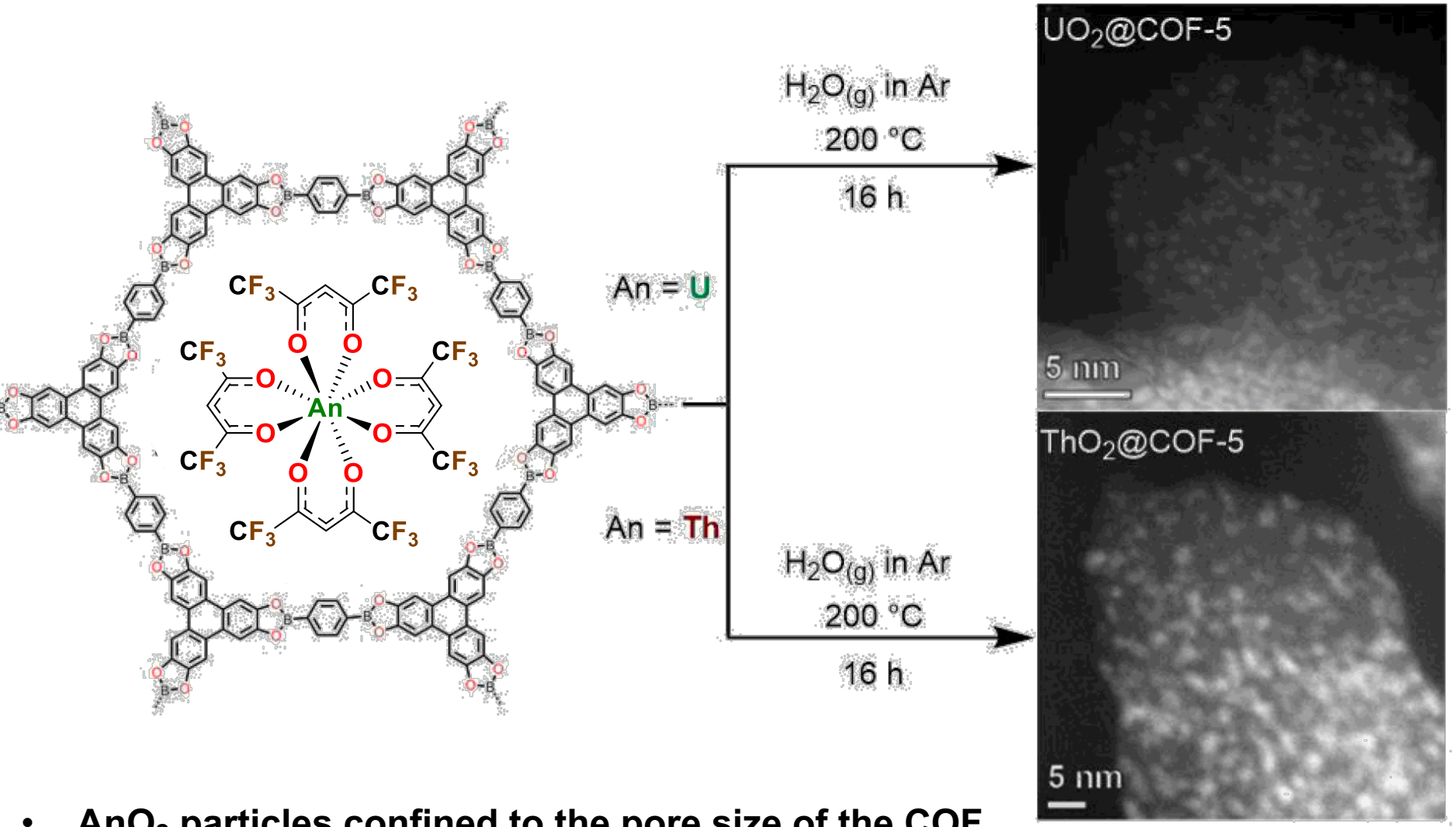
10^{-4} torr
(static vacuum)
2 d



- **COF-5 absorbs up to 50 wt% $An(hfa)_4$**

21

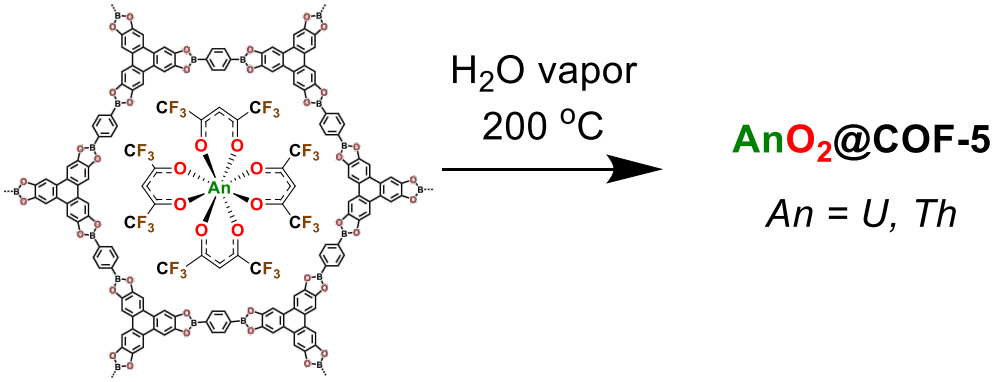
AnO_2@COF-5 nanoparticle synthesis



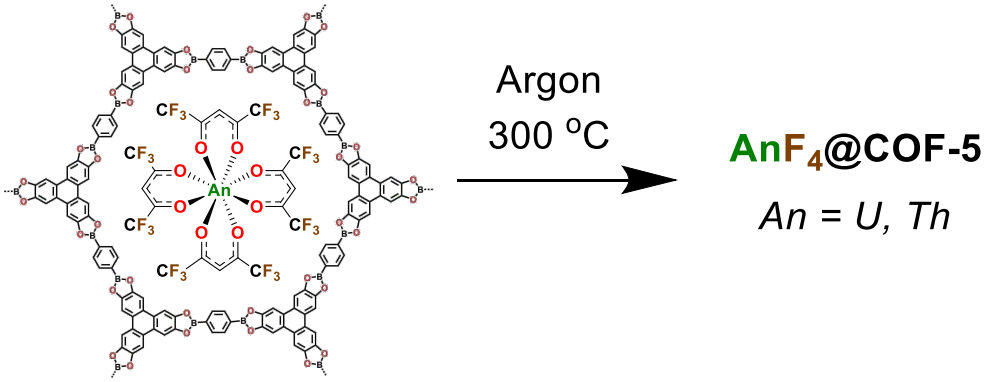
- AnO_2 particles confined to the pore size of the COF

Mechanistic control of products

- **Hydrolysis of An(hfa)$_4$@COF-5 with water vapor gives AnO_2:**

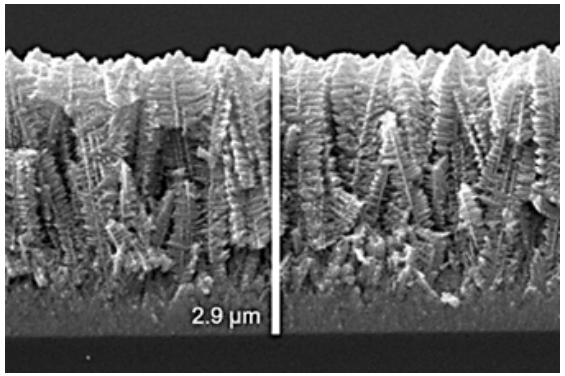


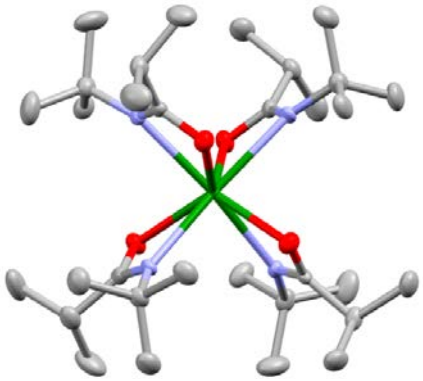
- **Pyrolysis instead gives AnF_4 via fluoride abstraction:**

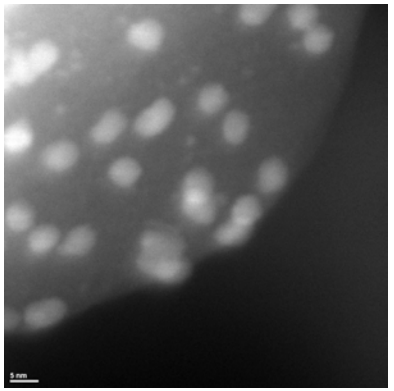


23

Conclusions







- **Custom molecular precursors → new actinide materials!**
  - **UO_2 thin films (2-D)**
  - **UO_2 nanotrees (3-D)**
  - **Templated UO_2 and ThO_2 nanoparticles (0-D)**

- **These methods could be used to produce nanostructured UO_2 CRMs with any desired $^{238}U/^{235}U$ ratio**

NSSC experience

NSSC-LANL Keepin Nonproliferation Summer Program (2017)

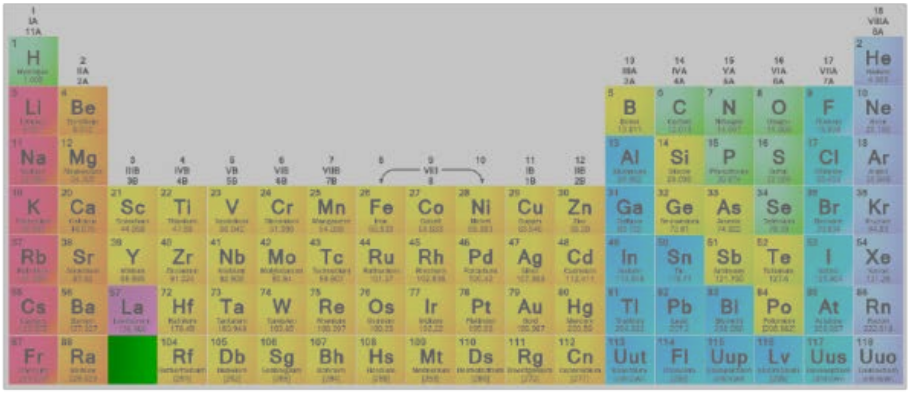
- **Mentors:** Jackie Kiplinger and Julianna Fessenden
- **Project:** review article on modern pre- and post-detonation nuclear forensics

Radiochemistry and Nuclear Forensics Course (TA)

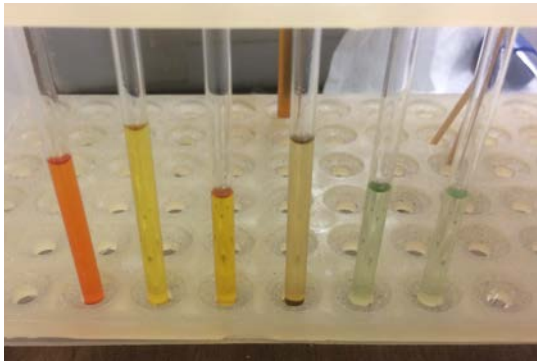
- Hands-on lab course introducing students to radiochemical methods

Beyond the PhD

- **Seeking job opportunities at national labs!**
  - Graduating this year



- **Interests:**
  - Inorganic chemistry and materials science
  - Nuclear energy and waste
  - Renewable energy technologies



Acknowledgements

UC Berkeley:

Prof. John Arnold

Michael Boreen
Jade Fostvedt
Joe Brackbill
Erik Ouellette
Christopher Ye
Anukta Jain

LBNL:

Dr. Stefan Minasian

Dr. Liane Moreau
Dr. Yusen Qiao
Dominic Russo
Jacob Branson
Ziad Shafi

Acknowledgements

This material is based upon work supported by the Department of Energy National Nuclear Security Administration under Award Number DE-NA0003180.