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A CHIMIA Column

Short Abstracts of Interesting Recent Publications of Swiss Origin

Multielectron Redox Chemistry of Uranium by Accessing the +II Oxidation State and Enabling Reduction to a U(I) Synthon

Megan Keener, R.A. Keerthi Shivaraam, Thayalan Rajeshkumar, Maxime Tricoire, Rosario Scopelliti, Ivica Zivkovic, Anne-Sophie Chauvin, Laurent Maron* and Marinella Mazzanti*
J. Am. Chem. Soc. **2023**, *145*, 16271–16283
https://doi.org/10.1021/jacs.3c05626
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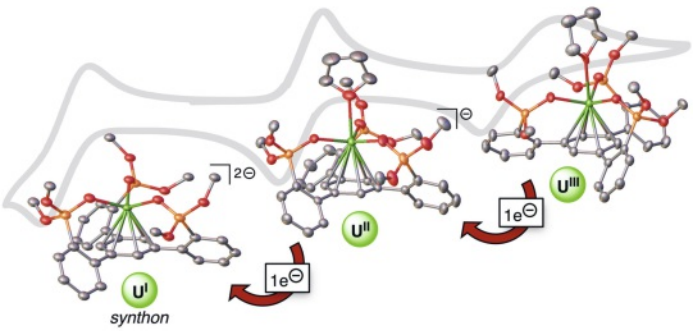
The challenge in synthesizing molecular uranium complexes in oxidation states lower than +3 is addressed in this study. A U(III) complex is reduced by one- or two-electrons using an arene-tethered tris(siloxide) tripodal ligand, yielding mono-reduced complexes [K(THF)-U((OSi(O^{t}Bu)$_2$Ar)$_3$-arene(THF)] (**2**) and [K(2.2.2-cryptand)-U((OSi(O^{t}Bu)$_2$Ar)$_3$-arene(THF)] (**2-crypt**), and di-reduced U(I) synthons [K$_2$(THF)$_3$-U((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)]$_\infty$ (**3**) and [(K(2.2.2-cryptand))]$_2$-[U((OSi(O^{t}Bu)$_2$Ar)$_3$-arene)] (**3-crypt**). Spectroscopic, magnetic, and computational analyses reveals that **2-crypt** represents a stabilized U(II) through δ-bonding between the arene anchor and uranium frontier orbitals, while **3** and **3-crypt** feature U(III) ions supported by a di-reduced arene anchor. Cyclic voltammetry studies identify quasi-reversible redox events corresponding to different U oxidation states. Complexes **2** and **3** demonstrate two- and three-electron transfer capabilities, exemplified by their reactions with azobenzene and cycloheptatriene, respectively. This work demonstrates the utility of the arene-tethered ligand for accessing low-valent uranium chemistry and multielectron transfer pathways.

Authors' comments:
"We identified a robust and easily tunable ligand conferring stability and redox flexibility to uranium complexes. A broad range of oxidation states and reactivity will be accessible by ligand tuning.

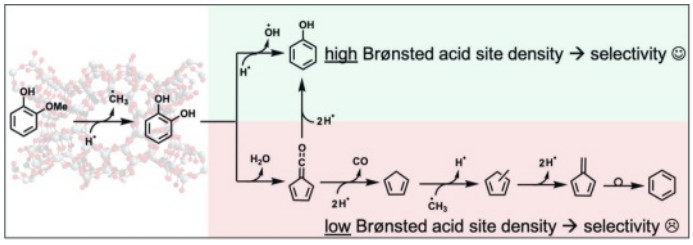


Tuning the zeolite acidity enables selectivity control by suppressing ketene formation in lignin catalytic pyrolysis

Zeyou Pan, Allen Puente-Urbina, Syeda Rabia Batool, Andras Bodi, Xiangkun Wu, Zihao Zhang, Jeroen A. van Bokhoven* and Patrick Hemberger*
Nat. Commun. **2023**, *14*, 4512
https://doi.org/10.1038/s41467-023-40179-z
Paul Scherrer Institute, ETH Zurich

Revealing catalytic mechanisms on a molecular scale contributes significantly to the design of catalysts and the fine-tuning of selectivity to optimize various processes. In this particular investigation, it was uncovered that the density of Brønsted acid sites on the zeolite catalyst plays a crucial role in governing the catalytic pyrolysis process of the lignin model compound guaiacol. The reaction diverges into two paths: one leading to the formation of a reactive ketene intermediate, fulvenone, through the dehydration of catechol; and the other producing phenol. Interestingly, at higher densities of Brønsted acid sites, the creation of fulvenone is hindered due to the specific surface coordination of its precursor, catechol. This study, employing *operando* photoelectron photoion coincidence spectroscopy with VUV synchrotron radiation to analyze reactive intermediates and products, presents compelling evidence that the suppression of ketene formation is responsible for a noteworthy fivefold increase in phenol selectivity. Additional investigations involving fulvenone reaction pathway calculations and ^{29}Si NMR-MAS spectroscopy results validate the findings. Notably, the adaptable *operando* methodology proposed here holds the potential to be applied across a diverse range of heterogeneous catalytic reactions.

Authors' comments:
"Our versatile *operando* approach simultaneously detects and quantifies highly reactive and elusive species as well as stable reaction products, shedding light onto the complex interplay between active sites and intermediates towards selective products."



Prepared by Cesare Berton, Patrick A. Cieslik, Fan Liu, Stanislav Prytuliak, Simon Klinger, Jonas Genz, Dominik Roth, Samy Kichou, Eda Nisli, and Jason P. Holland*
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Saddles as rotational locks within shape-assisted self-assembled nanosheets

Joseph F. Woods, Lucía Gallego, Amira Maisch, Dominik Renggli, Corrado Cuocci, Olivier Blacque, Gunther Steinfeld, Andres Kaech, Bernhard Spingler, Andreas Vargas Jentzsch, and Michel Rickhaus
Nat. Commun. **2023**, 14, 4725
https://doi.org/10.1038/s41467-023-40475-8
University of Zurich

In today's scientific landscape, the pursuit of various applications hinges significantly upon the properties of two-dimensional (2D) materials. To approach this objective, self-assembly commonly relies on directional intramolecular interactions. Harnessing weaker, less directive forces presents greater challenges and often yields less well-defined outcomes. By explicitly integrating topography as a guiding influence, Woods and coworkers unveil a robust method of shape-assisted self-assembly, demonstrated across an array of derivatives. By inducing constraints on rotational motion through the orchestration of molecular curvature, a distribution of angles, elongated columns and subsequent 2D structures can be arranged. Evident in both crystalline and soft materials, the resulting long-range order accentuates shape as a pivotal design principle, ushering precise molecular self-assembly and the genesis of novel materials.

Authors' comments:
"Varying the alkyl chain length one carbon at a time has a drastic effect upon the extent of self-assembly when assisted by negative curvature. The elucidated structures show rotational motion to be locked out by the saddle shape of the molecule."

High-affinity peptides developed against calprotectin and their application as synthetic ligands in diagnostic assays

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Nat. Commun. **2023**, *14*, 2774.
https://doi.org/10.1038/s41467-023-38075-7
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Inflammatory conditions like ulcerative colitis and Crohn's disease are diagnosed or tracked using the calprotectin biomarker. However, current antibody-based tests for calprotectin are variable due to differing antibodies and assays. Moreover, the binding sites of these antibodies lack structural characterization, raising uncertainty about their ability to detect calprotectin dimer, tetramer, or both. This study introduces calprotectin ligands derived from peptides, offering advantages like uniform chemical composition, thermal stability, precise immobilization, and cost-effective synthesis. Through screening a 100-billion peptide phage display library against calprotectin, a high-affinity peptide (K_d = 26 ± 3 nM) binding extensively (951 Å^2) to calprotectin was identified using X-ray analysis. Significantly, this peptide exclusively binds the calprotectin tetramer, enabling accurate quantification in patient samples through ELISA and lateral flow assays. Thus, it serves as a valuable affinity reagent for advanced inflammatory disease diagnostic assays.

Authors' comments:
"This was a very nice and productive collaboration between EPFL and the Swiss diagnostics company BÜHLMANN. The results show how valuable synthetic peptides can be as affinity reagents in diagnostic assays."