Scientists discover new structures for unique hybrid materials by altering their chemical bonds

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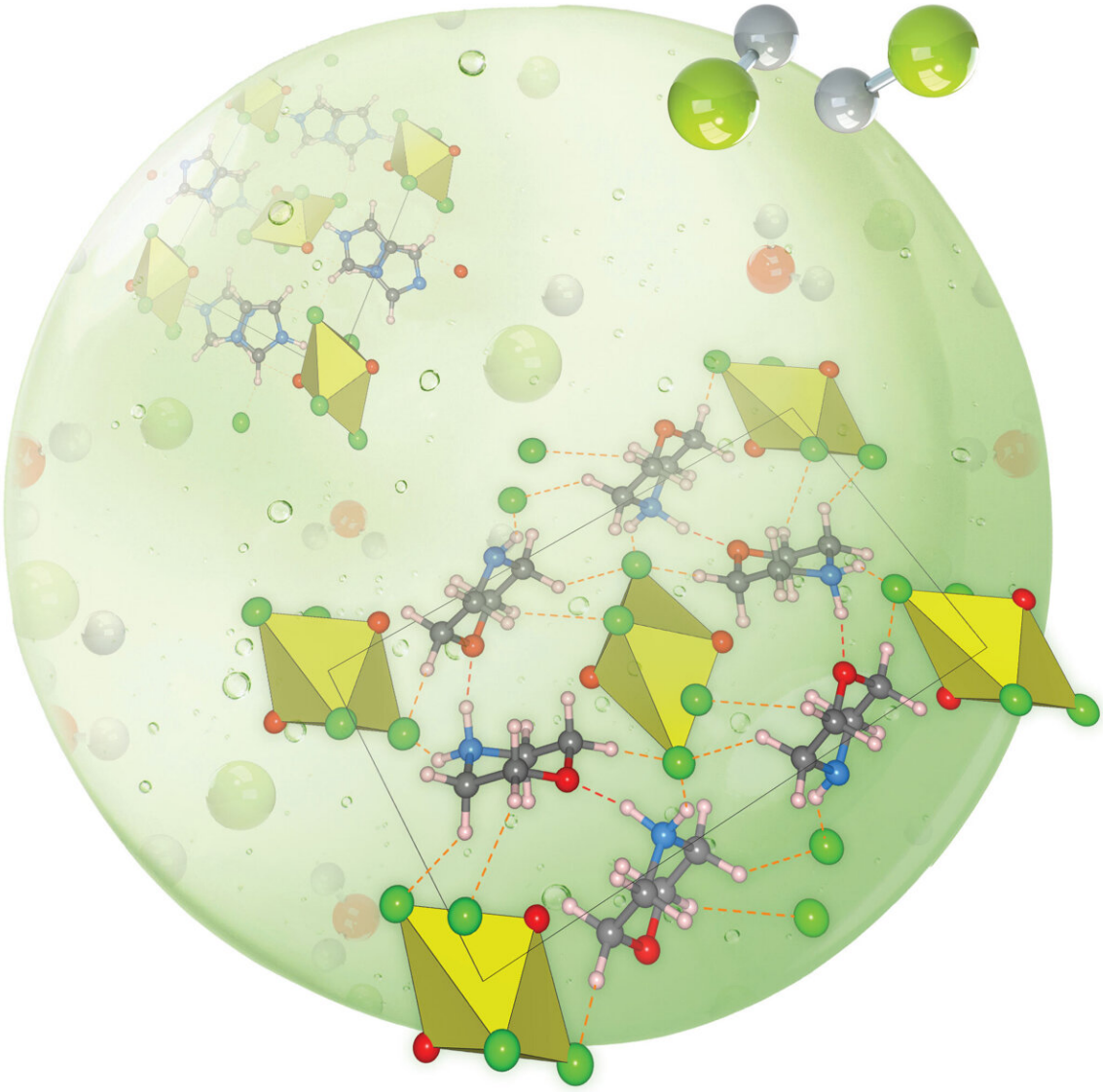

An artist's representation of some of the new structures Rajapakha and the team have designed. Credit: *Angewandte Chemie International Edition* (2023). DOI: 10.1002/anie.202305073

Putting a suite of new materials synthesis and characterization methods to the test, a team of scientists from the University of Iowa and the U.S. Department of Energy's (DOE) Brookhaven National Laboratory has developed 14 organic-inorganic hybrid materials, seven of which are entirely new. These uranium-based materials, as well as the detailed report of their bonding mechanisms, will help advance clean energy solutions, including safe nuclear energy. The work, currently published online, was recognized as both a Very Important Paper and a Hot Topic: Crystal Engineering in *Angewandte Chemie International Edition*. It will appear in July's print issue.

While it's important to understand what a structure is made from, it is just as important to understand what holds it together. Scientists and students from the University of Iowa, with the help of Sara E. Mason, a group leader in theory and computation at the Center for Functional Nanomaterials, a U.S. Department of Energy (DOE) Office of Science User Facility at DOE's Brookhaven National Laboratory, and adjunct associate professor at the University of Iowa, embarked on a quest to understand and manipulate the bonds that support the structure of uranyl tetrahalide, a uranium compound.

"This study was beyond collaborative," said study co-author Sara E. Mason. "On the synthesis side, we discovered entirely new crystal structures, which is really cool on its own. On top of that, we saw some interesting thermochemistry, the chemical energy stored in the bonds of

those structures. Then there was the modeling of these structures. We could have kind of ended our study there, but Harindu Rajapaksha, the student driving this research, really wanted to push it further and use the thermochemistry and the modeling to understand these systems at a level that hasn't been possible before."

The layers of work the team contributed resulted in a comprehensive quest to understand and manipulate the bonds that support the structure of uranyl tetrahalide, an important uranium compound. The theoretical and experimental research provided insight into the way hydrogen molecules form bonds that can stabilize these complex molecular structures, paving the way for scientists to alter them for many applications.

Uranyl tetrahalide: The remix

When designing hybrid materials to study, why look at uranium? For this team, the answer is both practical and personal.

"In order to effectively manage nuclear waste, we need a better understanding of issues like material separations and recycling," said Tori Forbes, a professor and director of the Materials Analysis, Testing, and Fabrication Facility at the University of Iowa. "We need to know how uranium behaves in solids and in water, so we are probing the most basic chemistry of uranium to acquire knowledge that can be used for advanced technologies and strategies to improve the back end of the nuclear fuel cycle."

Looking towards a future with clean energy deployed at scale, uranium is a material that has piqued a lot of scientific interest. Uranium makes up a vast majority of the byproducts from nuclear energy, which is a zero-carbon-emission energy source. Understanding the chemistry of uranium and related systems is integral for implementing nuclear energy safely

and effectively. That isn't the only intriguing aspect of this element though. Some researchers enjoy the challenge of working on such complex structures.

"I'm a chemist by training," said Mason, "so I'm fascinated by what's really deep in the periodic table, like uranium. The deeper you go, the more electrons you have, and the more electrons you have, the weirder, more exotic, and more exciting the electronic structure and bonding is. There's this 'final frontier' of the periodic table aspect to it. These are never-before-characterized structures. These are brand new! From a pure, chemical curiosity, this is all really cool."

This work also built on the foundation of uranyl hybrid materials research that the team published in *Inorganic Chemistry* in 2022. Both studies used density-functional theory, a computational modeling method that uses quantum mechanics to predict materials' electronic structure—the way electrons move in certain materials—alongside complementary methods to characterize these structures. In larger molecules, the atomic structure of a chemical system gets more complex, and more electrons are available to interact. Those interactions can make certain calculations difficult, which is why scientists rely on a few different methods to investigate the structure and properties of these systems. By building on the foundations of their previous work, the team now had enough structures to compare the theoretical work to the experiment, which limited them in the past.

Making connections

LEGO bricks will snap together and form a strong bond until they are pried apart. Their precisely molded plastic studs and recesses were designed to always work in the same way with all kinds of structures, opening a world of possibilities with each configuration. Molecules have a number of systems to bond atoms together. Some are melded to each

other like glue, some click together like LEGO bricks.

Non-covalent hydrogen bonds can be thought of like an electrostatic force. There is a bond donor, like the studs on the top of a LEGO brick, that interacts with a bond acceptor, or the back of the brick where the studs fit snugly. These bonds can occur both intra- and intermolecularly, as well as between separate molecules or within the same molecule structure, which allows for all kinds of interesting molecular geometries to arise. The strength of these bonds and the energy held within the bonds change based on the structures they're in. Understanding the properties of these variations can allow scientists to get creative and discover how to take apart and rebuild useful materials in unexpected ways.

Forbes found that these bonds were more interesting than they appeared on the surface. She explained that "non-covalent interactions (NCIs) like this are often the bonds that get overlooked because they are considered weak. However, when you combine them into a larger network, then it is the sum of these interactions that can have huge impacts on the chemistry. This is more a systems-level approach to understand the chemistry holistically. These types of network systems are incredibly important to the stability of materials and the overall behavior of uranium in water."

"NCIs are significant in several applications, including drug development and to nuclear waste reprocessing," explained Rajapaksha. "Our goal was to create a methodology for quantitatively characterizing the NCI network in a well-studied uranyl tetrahalide model system and describe how NCIs affect two crucial uranyl solid phase properties: vibrational and formation enthalpies—a direct indicator of a species' stability. These properties are significant because vibrational spectroscopy, a method of identifying molecules by the way they absorb light, is a frequently utilized technique for specialized methods that can identify uranyl

species."

Enthalpy is the measurement of the internal energy and pressure energy of a thermodynamic system, which determines the strength of the bonds. When broken, the energy stored in these bonds is released as heat, which can be measured through a process called calorimetry. In this process, a tool called a calorimeter measures the change in temperature that occurs when that heat is transferred out. If that word looks familiar, it's because calorimetry determines how many calories are in food. Instead of burning materials, however, the team used acid to create a chemical reaction that broke the bonds and gave off heat. Getting the computational modeling to agree with the experimental data, however, took a bit of work.

"Rajapaksha got that to work out really nicely," said Mason. "He had this high-quality agreement between the model thermochemistry and the measured thermochemistry. This is important because it means that we can rely on his measurements. Even if it's a system that hasn't been synthesized yet, he can model it correctly. He can trust those predictions. If we have a reliable way of calculating the thermochemistry, then we can spot trends and gain a new, more complete physical understanding of the bond, chemically speaking, which can allow us to tune and control these interactions."

The shape of things to come

While the team has learned some interesting things about uranyl tetrahalide systems, they say the most important finding is the cooperative methodology they have developed to characterize these materials. There are other complex chemical structures that the same principles can be applied to, and their applications could have world changing impacts.

"We are really thrilled about our findings," said Rajapaksha, "and we intend to expand this work in the future to include less-explored systems, such as neptunyl. Neptunium 237, a pollutant, is a long-lived isotope that contributes to the radioactivity of spent nuclear fuels. Basic knowledge in this field would be extremely valuable to basic sciences and nuclear waste management. We have, so far, obtained pretty intriguing results by applying our methodology to the neptunyl system, which we aim to publish soon."

More information: Harindu Rajapaksha et al, Guiding Principles for the Rational Design of Hybrid Materials: Use of DFT Methodology for Evaluating Non-Covalent Interactions in a Uranyl Tetrahalide Model System, *Angewandte Chemie International Edition* (2023). DOI: 10.1002/anie.202305073

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