

## Spotlights on Recent JACS Publications

### MADE-FROM-SCRATCH PROTEIN SELF-ASSEMBLES INTO NANO-ARCHITECTURES

Tailor-made proteins, which are designed from scratch rather than copied from nature, play an important role in the fields of chemistry and synthetic biology. So-called *de novo* proteins help researchers understand the relationship between protein structure and function and are an essential step toward applied biotechnology. They may one day lead to one of the ultimate goals of chemistry: the chemical reconstitution of living systems.

Ryoichi Arai and co-workers report the creation of a new *de novo* protein with interesting self-assembly properties (DOI: [10.1021/jacs.5b03593](https://doi.org/10.1021/jacs.5b03593)). The protein is made by attaching a previously reported three-dimensional structure of a *de novo* dimer protein, known as WA20, to a trimer segment of the naturally occurring fibrin protein. The dimer–trimer fusion self-assembles into several distinctive types of homooligomers in multiples of six, including a hexamer with an apparent barrel-like structure and a dodecamer with a tetrahedron-like structure. The observed supramolecular architectures suggest “the *de novo* WA20-foldon is an effective building block for the creation of artificial nano-architectures,” the authors conclude. **Christine Herman**, Ph.D.

### MECHANISTIC SKETCHES FROM KINETIC PROFILING

Reaction progress kinetic analysis (RPKA) is an emerging technique for mechanistic studies of organic catalysis based on kinetic profiling. Unlike classical kinetic analysis that requires a large number of repetitive measurements, RPKA, which enables instantaneous and continuous monitoring over catalytic processes, uses modern experimental and computational tools to minimize such redundancy.

In this tutorial-style Perspective, Donna G. Blackmond walks readers through seven themes, or characteristics of reactions, that come up in a variety of catalytic networks. She shows that RPKA can be used to extract both qualitative and quantitative mechanistic information and provides step-by-step instructions for this type of analysis (DOI: [10.1021/jacs.5b05841](https://doi.org/10.1021/jacs.5b05841)). RPKA can help determine the nature of kinetically relevant species, the catalyst resting state, and the rate-limiting step, even in the presence of complex factors such as off-cycle equilibria, product feedback loops, and competitive reactions.

With the unparalleled convenience and broad scope of RPKA, the author envisions that it will likely receive wider adoption and eventually shift kinetic analysis from being the “last resort”, as has been long viewed by the synthetic organic chemistry community, to the “first choice” for elucidating mechanisms of new reactions.

**Xin Su**, Ph.D.

### PRESTO-CHANGO PENCIL LEAD SPEEDS POWER FROM FUEL

Catalysts speed reactions, and electrocatalysts speed the type of reactions that break bonds to release electrical energy, or

inversely, that turn electrical energy into chemical fuels. Electrocatalysts generally come in two forms, each with their own strengths and weaknesses. Tiny molecular electrocatalysts work well and predictably, but may become poisoned and can be difficult to contain. Heterogeneous electrocatalysts that use surface sites are more durable and easily integrated, but local variation can make control more difficult.

Tomohiro Fukushima, Yogesh Surendranath, and their collaborators join the best features of these two types of electrocatalysts by functionalizing the edges of graphite sheets through a reaction that forms nitrogen-containing pyrazine groups (DOI: [10.1021/jacs.5b06737](https://doi.org/10.1021/jacs.5b06737)). These groups can be electron-donating or electron-accepting, which permits tunability for forward or reverse reactions. In experiments, the as-prepared catalyst demonstrates high activity for oxygen reduction, even greater than that of its molecular analogs.

Graphite is gaining a reputation as a heterogeneous electrocatalytic powerhouse. It is efficient, low cost, environmentally friendly, and durable. With this strategy, the researchers now add molecular catalyst-like control. As clean energy fuel needs grow ever larger so does the necessity for efficient, earth-abundant catalysts. Graphite, already an attractive alternative to scarce metals, can now potentially provide even more control.

**Jenny Morber**, Ph.D.

### RADICAL-CONTAINING LIGAND FACILITATES URANYL ION REDUCTION

Radioactive uranium contaminates and travels in ground and surface water mostly as the uranyl cation,  $[\text{UO}_2]^{2+}$ . Uranium becomes insoluble, and thus essentially immobilized, once the metal is reduced from U(VI), as in the uranyl ion, to U(IV). Therefore, reactions that reduce the double bonds between uranium and oxygen can help remediate environmental contamination or process nuclear fuel.

Here, Suzanne Bart and her colleagues use a redox noninnocent ligand to facilitate double reduction of the uranyl ion (DOI: [10.1021/jacs.5b06217](https://doi.org/10.1021/jacs.5b06217)). The researchers attach a pyridine-(diimine) ligand to the uranyl cation. The stable compound is the first fully characterized U(VI) complex with a ligand radical. The radical on the ligand enables the subsequent double reduction of the metal in this complex. Adding 2 equiv of silylating agent provides a U(IV) complex with siloxide ligands, which the researchers then replace with halides.

Stoichiometric functionalization of uranium–oxygen bonds is exceedingly rare, the authors write, as most reductive silylations of U(VI) require excess silylating agent. Many of these known reactions are also only single reductions of the metal. Therefore, this new reaction solves long-standing problems in uranium derivatization, and it shows how redox noninnocent ligands can be used to advance actinide chemistry.

**Melissae Fellet**, Ph.D.

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