

Spotlights on Recent JACS Publications

■ OBSERVING “WARM” HYDROGEN TUNNELING

Hydrogen tunneling at room temperature has finally been observed spectroscopically by researchers led by Mathias Schäfer, Jos Oomens, Albrecht Berkessel, and Anthony Meijer (DOI: [10.1021/jacs.6b10348](https://doi.org/10.1021/jacs.6b10348)). H-tunneling is a less common phenomenon than its well-known counterpart, electron tunneling. Tunneling generally involves a particle that penetrates or “tunnels” through a barrier to an adjacent site if the two sites are close enough, typically separated only by angstroms. This phenomenon can affect the kinetic rates and selectivities of chemical reactions that are defined by classical barriers. H-tunneling specifically plays a role in the chemical reactivity of a wide variety of reactions from astrochemistry and biochemistry to catalysis.

Previously, spectroscopic evidence of H-tunneling existed only at cryogenic temperatures, where the cold temperatures considerably slow the motion and thermal reactivity to more easily enable snapshots of the various chemical species. Using infrared ion spectroscopy (backed up by DFT calculations) at room temperature and above, the team finally observes the tunneling of H-atoms in an isomerization reaction in the gas phase. Understanding the role of H-tunneling at realistic, ambient conditions has broad impact for biochemical processes such as enzymatic transformations and catalysis.

Dalia Yablon, Ph.D.

■ SUGAR-COATED NANOSTRUCTURES WITH PROMISING ANTI-VIRAL PROPERTIES

The lethal pathogen Ebola virus was initially described more than 40 years ago. The recent Ebola outbreak in West Africa brought the virus into the media spotlight because of the unprecedented number of cases and fatalities reported throughout the region. Despite progress in treatments based on antibodies and viral RNA polymerase inhibitors—and basic interventions that can improve chances of survival—there remains a need for treatments with demonstrated clinical efficacy against Ebola and similar viral-based lethal pathogens.

In a new Perspective, Nazario Martín and colleagues describe progress toward the development of antiviral agents composed of fullerene-based nanostructures bearing large units of carbohydrates (DOI: [10.1021/jacs.7b01683](https://doi.org/10.1021/jacs.7b01683)). The 3D globular scaffolds can be designed as multivalent glycosylated nanostructures, presenting 120 mannose units on a single scaffold in a manner that resembles virus geometry. In Ebola pseudotyped infection models, the scaffolds exhibit antiviral activity with 50% inhibition of infection (IC_{50}) in the subnanomolar range, making them the most efficient molecules demonstrated *in vitro* against Ebola virus infection. Future studies are needed to determine the potential of the most promising fullerene-based leads for antiviral therapies for practical applications. Nonetheless, the approach shows how advances in materials sciences can be applied to tackling a central challenge in life sciences.

Christine Herman, Ph.D.

■ NEW SYNTHESIS SO HOT, IT’S MOLTEN

Alloying late transition metals with those on the left of the periodic table has led to some combinations with extraordinary catalytic activity. Being able to scale these early–late intermetallic materials down to nanosizes could further improve this activity by taking advantage of nanoparticles’ high surface areas. However, synthesizing these nanomaterials by conventional means has proven virtually impossible. A. Paul Alivisatos and co-workers report a novel synthesis method that readily accomplishes this feat (DOI: [10.1021/jacs.7b01366](https://doi.org/10.1021/jacs.7b01366)).

Focusing initially on Pt_3Y , a compound already shown to be more catalytically active than pure platinum in the oxygen reduction reaction when used in bulk polycrystalline form, the team relies on molten alkali metal triethylborohydrides as both solvents and strong reducing agents. Combining halide precursors of both metals with an alkali triethylborohydride and then heating the mixture past the melting point of the latter has resulted in the formation of a black precipitate, which after an annealing step is confirmed to be nanoparticulate Pt_3Y . The researchers take advantage of this method to also synthesize other early–late intermetallic compounds, including Pt_3Sc , Pt_3Lu , Pt_2Na , and Au_2Y . Further research, they add, will focus on improving this method to make it more applicable to industry.

Christen Brownlee

■ TAILORED LIGANDS ENABLE CHALLENGING C–H HALOGENATIONS

Alkyl halides are valued in organic chemistry for their synthetic versatility and their abundance in biologically active compounds. Current methods for generating $C(sp^3)$ –halogen bonds are often limited in substrate scope, require complex synthetic sequences, or suffer from regioselectivity issues. Substrates that contain α -hydrogen or α -halogen are particularly challenging to functionalize at the β -position, due, in part, to their propensity to undergo undesirable side reactions. As such, transformations that selectively convert primary β - $C(sp^3)$ –H bonds into $C(sp^3)$ –halogen bonds are highly desirable to organic chemists.

Jin-Quan Yu and co-workers report $C(sp^3)$ –H bromination and iodination of α -H-containing carboxylic acid- and amino acid-derived amides (DOI: [10.1021/jacs.7b02196](https://doi.org/10.1021/jacs.7b02196)). The palladium-catalyzed reactions are uniquely enabled by pyridine-type quinoline ligands designed by the Yu group. These methods exhibit good functional group tolerance and high selectivity for β - $C(sp^3)$ –H functionalization. The resulting halogenated products undergo further diversification reactions to generate alkyl carbon–carbon or carbon–heteroatom bonds, demonstrating the versatility of this transformation. The reported work provides rapid access to synthetically diverse compounds and extends the utility of free carboxylic acids in organic synthesis.

Nicole Camasso, Ph.D.

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