

Spotlights on Recent JACS Publications

■ ONE CATALYST CARRIES SUBSTRATE THROUGH TWO SEQUENTIAL TRANSFORMATIONS

Jan Metternich and Ryan Gilmour have used one photocatalyst to perform sequential transformations of a single substrate (DOI: [10.1021/jacs.5b12081](https://doi.org/10.1021/jacs.5b12081)). This approach contrasts with typical catalytic concepts, where several catalysts are used to transform the same substrate into the same product, or where different catalysts are applied to convert the same substrate into different products.

Metternich and Gilmour use (–)-riboflavin to convert *E*-cinnamic acid derivatives to coumarin scaffolds, which are common in pharmaceutical targets. This process requires two steps, each activated by ultraviolet light. In the first transformation, energy transfer from the catalyst to the substrate isomerizes a double bond. In the second step, a single electron transfer to the catalyst induces substrate cyclization.

Other methods of preparing coumarin scaffolds require functionalized precursors that take extra steps to prepare, so this method streamlines the synthetic route to these scaffolds. **Melissae Fellet, Ph.D.**

■ BRIDGING THE GAP FOR MOLECULAR ELECTRONICS

Molecules adsorbed onto metallic and semiconductor surfaces can significantly change these materials' properties. Enhanced understanding of this phenomenon is particularly important for molecular electronics, where individual molecules mimic conventional electronic components. Because surfaces often contain several different types of adsorption sites for the same molecule, each of which may confer different properties, being able to site-select is vital for reproducible molecular electronics. However, technical limitations have prevented researchers from achieving reliable site selectivity.

In a new study, Satoshi Kaneko, Hisao Nakamura, Kazuhito Tsukagoshi, Manabu Kiguchi, and co-workers develop a new technique that makes site selection possible for the first time by combining surface-enhanced Raman scattering (SERS) with current–voltage (*I*–*V*) measurements (DOI: [10.1021/jacs.5b11559](https://doi.org/10.1021/jacs.5b11559)). *I*–*V* measurements of 1,4-benzenedithiol suspected between two gold electrodes suggest the existence of three different types of adsorption sites. However, only one of the possible adsorption configurations demonstrates an enhanced SERS signal. The correlated electro-optical data provided by this new hybrid technique could eventually make it possible to reliably integrate molecular components into a working device despite multiple molecular adsorption sites.

This new hybrid technique, the authors say, also reveals a relationship between optical and electrical properties in single-molecule junctions in which the strength of the SERS signal rises with the strength of the molecule–metal interaction.

Christen Brownlee

■ BEYOND METHANE CONVERSION: THE FUTURE OF C–H FUNCTIONALIZATION

The initial goal of C–H functionalization chemistry was to efficiently upgrade light, gaseous alkanes to liquid products, but extensive, intensive research and development has led to its broad application in organic synthesis. As the field rapidly expands and progresses, John Hartwig reflects on current challenges and future opportunities in this Perspective (DOI: [10.1021/jacs.5b08707](https://doi.org/10.1021/jacs.5b08707)).

Hartwig catalogs major challenges facing C–H functionalization, including site selectivity, monofunctionalization, and over-reaction. He also highlights the unique benefits of this chemistry, in enabling more straightforward access to target molecules. These points are presented within a framework chronicling the early development and current applications of C–H functionalization.

Although it may now seem far-fetched to claim C–H functionalization as green or sustainable chemistry, Hartwig points out that it is desirable and used frequently in time-sensitive applications such as drug development because it can often significantly cut down reaction steps. He also envisions its increasing use in agrochemicals, materials science, and possibly industrial processes if justified by the overall reaction efficiency, a pursuit that may represent the future of the field.

Xin Su, Ph.D.

■ NEW STUDY SHEDS LIGHT ON A FAMILY OF BRANCHED MOLECULES

Dendralenes are a family of conjugated oligo-alkenes, the lesser-known cousins of polyenes and annulenes. The name dendralene is derived from dendro—the Greek word for tree—and alkene, and their structure can be described as branched, acyclic, and composed entirely of sp_2 -hybridized carbon atoms. Prior to 2000, only two dendralene molecules had been reported in the literature, likely owing to the erroneous belief that the compounds are too unstable to be handled in the laboratory with standard equipment and methods. Now, researchers led by Michael Sherburn present the first comprehensive study on the first 10 members of the dendralene family (DOI: [10.1021/jacs.5b11889](https://doi.org/10.1021/jacs.5b11889)).

Dendralenes exhibit the unique ability to rapidly generate structural complexity starting from low-molecular-weight precursors. The new study sheds light on several other intriguing properties, such as drastic differences in the physical and chemical behaviors of molecules comprising an odd or even number of C=C bonds, a difference that is most pronounced between compounds containing three and four alkenes and gradually fades with increasing number of C=C units, becoming negligible in compounds with more than 10 C=C units. The new revelations on this understudied family of conjugated molecules may lead to the preparation of new compounds with novel electronic properties.

Christine Herman, Ph.D.

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