

## Spotlights on Recent JACS Publications

### ■ ORGANIC NANOTUBES: EXTENDED COVALENT INTERACTIONS PROVIDE INCREASED STABILITY

Organic nanotubes are made of small molecules or macromolecules that self-assemble via weak, non-covalent interactions. Organic nanotubes have been used in numerous applications, such as ion sensing and photovoltaics, but one of their greatest limitations is the inherent instability of the tubular structures that arises from the lack of strong, covalent interactions between the molecules.

Recently, Kenichiro Itami, Hideto Ito, and co-workers have reported a light-induced, cross-linked helical polymer that yields robust, covalent organic nanotubes from readily accessible starting materials (DOI: [10.1021/jacs.6b05582](https://doi.org/10.1021/jacs.6b05582)). The starting polymers—known as poly(*m*-phenylene diethynylene)s—contain chiral amide side chains, and when these side chains participate in hydrogen bonding, the polymers self-assemble into a helical formation. Once the polymers are in position, they can be cross-linked to yield covalent organic nanotubes. The group envisions that their simple “helix-to-tube” approach could lead to the development of a broad range of new organic nanotube-based materials for a variety of applications for which nanotube stability is essential.

Christine Herman, Ph.D.

### ■ NEW SINGLE-SITE CATALYST FOR OLEFIN POLYMERIZATION

The production of common commercial polymers typically relies on industrial slurries of granular solid catalysts, which yield solid polymers in a final form of free-flowing powders or beads. Without a degree of morphological control, conventional reactor conditions lead to the accumulation of insoluble polymer products on the walls and tubing of the reactor, a problem known as reactor fouling. For applications that require polymers with more clearly defined morphological and molecular features, single-site heterogeneous catalysts are needed. Now, researchers led by Mircea Dincă describe one such catalyst for olefin polymerization that is capable of producing polyethylene molecules with a narrow range of molecular weights (DOI: [10.1021/jacs.6b05200](https://doi.org/10.1021/jacs.6b05200)).

The method relies on cation exchange in a metal–organic framework (MOF), which exchanges zinc ions with reactive transition metal ions including titanium and chromium. This exchange enables the high surface area MOF solid to approach the reactivity of single-site catalysis, making it possible to tune the molecular weight of the polymer products. A method like this one, which can control polymer morphology, may play an important role in industrial settings that rely on continuous-flow processes.

Christine Herman, Ph.D.

### ■ SMART SYNTHETIC MANEUVER TO A COMPLEX MEROTERPENOID

(+)-Psiguadial B, a recently isolated plant natural product with potent cytotoxicity toward human liver cancer cells, features a meroterpenoid framework fused with a diformyl phloroglucinol

unit. The structural complexity of (+)-psiguadial B, and in particular the chiral carbon-rich bicyclic terpene moiety, makes this molecule an interesting yet challenging target for synthetic chemists.

Toward this goal, Sarah Reisman and co-workers have developed an innovative and highly stereoselective strategy that can efficiently deliver (+)-psiguadial B in 15 steps from a simple diazoketone starting material (DOI: [10.1021/jacs.6b07229](https://doi.org/10.1021/jacs.6b07229)). The key to this approach is the streamlined construction of the cyclobutane-fused terpene skeleton, involving a tandem Wolff rearrangement/asymmetric ketene addition followed by a palladium-catalyzed C(sp<sup>3</sup>)–H alkenylation.

The reported total synthesis provides a facile and general method for the enantioselective construction of *trans*-fused cyclobutane rings that can be found in a number of natural products. The synthetic route is also expandable in terms of stereochemical diversity, as it enables access to both psiguadial B enantiomers using a single chiral catalyst, making it easier to obtain large compound libraries for structure–property studies.

Xin Su, Ph.D.

### ■ TWIN VIEWS OF A NEW GERMANIUM CLUSTER

For decades, researchers have known that group 13 and 14 metalloids can form ligand-stabilized clusters that display interesting bonding and exotic architectures. Although many more examples of these materials exist for group 13 elements, several germanium clusters stabilized by silicon-based ligands have been formed by reaction in an acetonitrile suspension. In a recent study, Luis Perla and Slavi Sevov, using the same type of reaction, produce the first germanium-based metalloid clusters stabilized instead with stannyl ligands, which they then react further with palladium (DOI: [10.1021/jacs.6b06545](https://doi.org/10.1021/jacs.6b06545)).

Like their predecessors, these novel clusters have highly unusual bonding and architectures. Single-crystal X-ray diffraction shows that they are composed of two germanium icosahedra, decorated with stannyl ligands, sharing a common Pd<sub>3</sub> face. Alternatively, the same structure can be described as an open germanium deltahedron with a Pd<sub>3</sub> triangle trapped inside. Geometric and electronic analysis confirms that both views are equally accurate. The authors suggest that other compounds as curious and intriguing as this one could be synthesized from constituents with different characteristics, such as bulkiness or lability.

Christen Brownlee

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