

Spotlights on Recent JACS Publications

■ ICE-ENCAPSULATED HYDROGEN GAS STABLE INSIDE CARBON NANOTUBES

Far beneath the Earth's surface, fossil fuels are believed to be stored as gas hydrates, which are composed of gas molecules encapsulated within clathrates—cage-like structures made of hydrogen-bonded water molecules. Given their natural ability to grab onto gas molecules, gas hydrates have captured the attention of researchers interested in developing new approaches to carbon sequestration and hydrogen storage, among other applications. Although H₂ was long believed to be too small to stabilize the host lattice of ice clathrates, hydrogen gas has been demonstrated to form gas hydrates when subject to high pressures, a development that sparked a wave of efforts to develop gas hydrates as a new medium for hydrogen storage.

Now, researchers led by Xiao Cheng Zeng and Joseph S. Francisco demonstrate the potential of hydrogen gas hydrates to exist within the confines of single-walled carbon nanotubes (SW-CNTs) (DOI: 10.1021/ja5041539). The team uses molecular dynamics simulations to predict that the H₂ hydrates, stable at near-ambient temperatures, spontaneously form a molecular wire within a 1D nanochannel and exhibit structures dependent on the width of their SW-CNT containers. If confirmed in the laboratory, these structures may lead to the development of safe, environmentally clean, and large-scale hydrogen storage media.

Christine Herman, Ph.D.

■ MOLECULAR BOXES ACT LIKE LITTLE CARBON MONOXIDE HOTELS

Researchers led by Jeffrey Long have created tiny cages that can grab carbon monoxide from a molecular soup, allow it to stay a while, and then let it check back out (DOI: 10.1021/ja505318p).

Though most people probably recognize carbon monoxide gas as a wintertime home hazard, the simple molecule has become increasingly important for industrial chemical synthesis. Several technologies currently compete to create carbon monoxide efficiently. However, many produce large amounts of waste hydrogen, and this hydrogen and carbon monoxide gas mixture requires further processing for purity. The hybrid metal and carbon cages developed by Long and colleagues could be exploited to filter carbon monoxide from other gases, including hydrogen and nitrogen.

Once separated, the “contaminants” can also be put to use. Hydrogen, for example, is an essential component in many fuel cells. The key to these cages is weak binding between the carbon monoxide and its captors that makes the process completely reversible. Other technologies have proven effective at grabbing carbon monoxide, but not as good at releasing the molecules. Here, the carbon monoxide can be easily freed and the cages reused. By carefully choosing the metal atoms within the cage, researchers can tailor the molecular tools to their needs.

Jenny Morber, Ph.D.

■ LIGHT AND FLOW: EASIER ROUTES TO ALKALOIDS

Photoredox catalysis is a process that relies on visible light-induced single-electron transfer, where organic amines often participate as sacrificial electron donors. Although this process has been thoroughly studied as a synthetic method, it remains yet to be widely utilized in natural product synthesis.

Now, Corey Stephenson and Joel Beatty take advantage of the reactivity of amines in photoredox catalysis for natural product modification, in conjunction with continuous flow chemistry (DOI: 10.1021/ja506170g). With an Ir(III)-based catalyst in a flow photochemical reactor, the researchers successfully convert (+)-catharanthine, an abundant natural product, on the multigram scale to a cyanated intermediate that can be readily transformed into three complex alkaloids in three or fewer steps.

This innovative study sets a pioneering example of using photoredox catalysis to modify natural products, which allows for expedient access to structurally related derivatives. Moreover, it opens a creative avenue for developing shortcuts or alternative routes to challenging synthetic targets.

Xin Su, Ph.D.

■ OPEN IT UP RIGHT: KEY STEP TO TETRAHYDROLIPSTATIN

A potent inhibitor of pancreatic lipases, (–)-tetrahydrolipstatin (THL), or orlistat, is an over-the-counter anti-obesity drug. Since it was first synthesized in 1987, THL, an α -alkylated β,δ -dihydroxy acid which exists in the β -lactone form, has been prepared through a broad array of stereoselective approaches.

Prompted by the recent discovery of epoxide carbonylation for forging β -lactones, Geoffrey Coates, George O'Doherty, and co-workers have achieved a novel enantioselective total synthesis of THL from an achiral ynone in 10 steps with 31% overall yield (DOI: 10.1021/ja505639u). The researchers also succeed in constructing seven other THL stereoisomers. The pivotal step is a late-stage regio- and stereoselective carbonylation of a *cis*-epoxide enantiomer to a *trans*- β -lactone, catalyzed by an aluminum porphyrin-based Lewis acid/[Co(CO)₄][–] bimetallic complex.

The utility and excellent stereochemical control of the new, versatile carbonylation reaction is clearly demonstrated in this total synthetic route. “Further application of bimetallic carbonylation catalysts for the synthesis and medicinal chemistry studies of natural products” containing the β -lactone motif is underway, the authors report.

Xin Su, Ph.D.

■ MOLECULAR SANDWICH MAKES NICE SHEETS

Ultrathin sheet-like crystals are valued for electronic displays, solar cells, lasers, computing, and more. While much effort has focused on controlling the fabrication of tiny particles and wire-

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like materials, there exist only a few strategies to assemble sheet-like nanostructures from individual molecules.

Now, Wen-Bin Zhang, Kan Yue, Stephen Cheng, and colleagues bind pairs of electronically dissimilar cluster-like molecules together to directly grow sheet-like crystals in solvents (DOI: 10.1021/ja504497h). As the chained pairs struggle to snuggle close to or retreat from the solvent molecules, they assemble into a kind of molecular sandwich. Under just the right conditions, the nanoclusters in the sandwich's center line up in regular patterns to form crystals. Electrostatic repulsions from the "bread" layer of ionic nanoclusters discourage crystal growth beyond a couple of layers.

This work provides a roadmap for others hoping to adopt these methods, with careful studies on the effects of solvent polarity, number and size of building counterions associated with the ionic nanoclusters, and size matching of the hydrophobic and ionic chained nanoclusters. This work also provides an alternative to other methods of sheet-like crystal fabrication, each with its own particular strengths and obstacles.
Jenny Morber, Ph.D.