MAKING EDIBLE NANOSTRUCTURES

ACS MEETING NEWS: Food-grade starting materials yield new metal-organic framework compounds

COMMON FOODSTUFFS aren’t typical synthesis starting materials. But they’re exactly what a team of researchers used to make novel compounds that are porous, crystalline, and edible. By starting with food-grade γ-cyclodextrin (CD), salt substitute (potassium chloride), and grain alcohols, an allylic alcohol, ethers, esters, and an oxetane functional groups, including a vinyl ether, a dienone, phosphoric acid, and potassium ions and separately with other alkali ions to form a new family of CD-MOF compounds. The framework—which could have pharmaceutical and food science applications—was reported on Aug. 25, at the American Chemical Society national meeting in Boston (Angew. Chem. Int. Ed., DOI: 10.1002/anie.201002343).

MOF compounds, which consist of metal ions or clusters connected by organic linkers, have broad commercial appeal for use in gas storage and purification, catalysis, and chemical sensing. But as the study’s first author, Ronald A. Smaldone, a postdoc working with Northwestern chemistry professor J. Fraser Stoddart, explained, the vast majority of MOFs described to date are composed of organic units derived from nonrenewable petrochemical feedstocks and transition metals. Making the compounds from nontoxic, biorenewable starting materials would be environmentally advantageous and could offer cost savings. But that task has remained challenging due to the inherent asymmetry of many natural building units and the difficulty in using them to synthesize crystalline porous products.

To sidestep that problem, the Northwestern team, UCLA’s Omar M. Yaghi, and coworkers linked γ-CD—a symmetrical oligosaccharide composed of asymmetrical units and produced commercially from starch—with potassium ions and separately with other alkali ions to form a new family of CD-MOF compounds.

“Edible MOFs are a stunning example of the power of self-assembly from simple and readily available components,” said Leonard R. MacGillivray, a University of Iowa chemistry professor. This work will likely challenge other researchers to seek the design and construction of frameworks from renewable and benign starting materials, he said. MacGillivray added that the study suggests that merging function and issues of sustainability is a real possibility in this rapidly developing area.

SILVER BULLET FOR FLUORINATIONS

ACS MEETING NEWS: Late-stage cross-coupling may open route to radiotracers

BANKING ON the chemistry of silver, scientists have developed a new cross-coupling reaction that allows them to tack fluoride atoms onto aromatic substituents, even in densely functionalized molecules. The reaction, which was presented last week at the American Chemical Society national meeting in Boston, could be a boon to the synthesis of radiotracers for positron emission tomography (PET), for which new methods to install ¹⁹⁷F during the final stages of synthesis are needed.

The reaction, developed by Tobias Ritter, Pingping Tang, and Takeru Furuya of Harvard University, uses silver oxide to catalyze the fluorination of aryl tin compounds with the electrophilic fluorinating reagent N-chloromethyl-N-fluorotriethylammonium hexafluorophosphate (J. Am. Chem. Soc., DOI: 10.1021/ja105834t). The reaction “is the first example of silver catalysis for carbon-heteroatom bond formation by cross-coupling chemistry,” Ritter noted.

“One area my group is terribly interested in is developing new ways to develop tracers for PET imaging,” Ritter said. Such syntheses dictate that short-lived radioactive isotopes are incorporated during the final steps of making the molecule. “PET with ¹⁹⁷F is currently limited by the absence of general chemistry that can introduce fluoroine into molecules at a late stage,” he explained. He believes the new reaction could help solve that problem.

Ritter’s group demonstrated the versatility of its new cross-coupling by using it to fluorinate polypeptides, polyketides, and alkaloids. They showed that many functional groups, including a vinyl ether, a dienone, alcohols, an allylic alcohol, ethers, esters, and an oxetane survive the reaction unscathed. “To date, no other fluorination reaction has been shown to have a substrate scope as broad as that shown here,” Ritter pointed out.

“Late fluorination processes for highly functionalized molecules are in high demand, and the silver-catalyzed carbon-fluorine bond formation developed by Ritter is a great advance,” commented Véronique Gouverneur, a chemistry professor at Oxford University, in England, who recently developed ¹⁹¹F-labeled Selectfluor (Angew. Chem. Int. Ed., DOI: 10.1002/anie.201002310), a fluorinating reagent that’s very similar to the one Ritter’s group uses. “This work is certain to find immediate application in pharmaceutical research and beyond,” she said.