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Spotlights on Recent *JACS* Publications

AND FOUR TO GO: IDENTIFICATION OF A TETRACOORDINATE OXYGEN DICATION

Tetravalent oxygen, which has four bonds and a double positive charge, has long been believed to exist in theory but has never been unequivocally observed. Protonation of one of the two lone pairs on H_2O to form H_3O^+ is the well-known basis of aqueous acid chemistry, but protonation of the remaining lone pair to form the H_4O^{2+} dication is challenging to demonstrate. George Olah and co-workers previously proposed the intermediacy of such an oxadionium cation in reactions of H_3O^+ in a superacid—stronger than 100% sulfuric acid.

Now a group led by Evgenii Stoyanov, Mark Mascal, and Christopher Reed has used infrared spectroscopy to demonstrate hydrogen bonding between an oxatriquinane and the strongest known acid, a carborane superacid (DOI: 10.1021/ja209942s). Oxatriquinanes are tricyclic analogues of the H_3O^+ ion. It was shown that the lone pair in oxatriquinanes can engage in strong, near-symmetrical H-bonding with the carborane acid $H(CHB_{11}Cl_{11})$. At this point, this is as close as it gets to the formation of a tetravalent oxygen species with a formal 2+ charge. **Leigh Krietsch Boerner, Ph.D.**

CHOOSE YOUR OWN ANALYTICAL RANGE

Nature can detect DNA across a very broad range of concentrations. This high dynamic range, which is required for various cellular functions, is achieved by combining multiple receptors. The useful dynamic range of single-site receptors, however, is typically less than 2 orders of magnitude.

A research team led by Kevin W. Plaxco has combined sets of DNA receptors with different binding affinities to create biosensors that detect specific DNA sequences over customized concentration ranges (DOI: 10.1021/ja209850j). They generated families of molecular beacons—stem-loop DNAs that fluoresce upon binding other specific DNA sequences—by making modifications that do not perturb the beacons' DNA-binding sites. The researchers mixed various combinations of the molecular beacons to create biosensors with specific dynamic-range profiles. For example, a 59/41 mixture of a high-affinity and a low-affinity receptor resulted in a sensor with a 100-fold greater useful concentration range than a single receptor alone. A mixture of four different receptors showed a more than 10,000-fold improved dynamic range.

The approach extends concentration range without impairing specificity, a trade-off that has plagued past biosensor range-improvement efforts. **Celia Arnaud,** *C&EN*

NANOPARTICLE ASSEMBLIES LIGHT UP LIPIDS IN LIVE CELLS

A new synthetic method developed by Nicholas Kotov, Libing Wang, and co-workers makes it possible to connect spherical nanoparticles to rod-shaped nanoparticles in well-defined two-dimensional arrangements for applications in live cell analysis (DOI: 10.1021/ja2088713).

The research team used complementary DNA strands to attach gold nanospheres and nanorods to each other with precise spacing. The length of the DNA strands limits the spaces between the particles to just a few nanometers, which imparts plasmonic properties—rapid energy transfer via waves of electron density—to the nanoparticle assemblies that can enhance the signal of nearby chemicals during Raman spectroscopic analysis. The team studied the optical and plasmonic properties of different nanosphere−nanorod arrangements and demonstrated the use of plasmonic assemblies as intracellular probes with the ability to boost the Raman signal of lipids in live cancer cells.

The method makes it possible to selectively fabricate nanoparticle assemblies with specific structural patterns, which is not possible with most previously reported nanoparticle assembly methods. In this way, the technique could help shed light on the relationship between the spatial arrangement of nanoparticle assemblies and their resulting optical and plasmonic properties. Ultimately, researchers hope to use nanoparticle assemblies as nanoscale biosensors and intracellular probes for real-time monitoring of biomolecules in live cells. **Christine Herman**

UNRAVELING TUBERCULOSIS AT ITS SEAMS

Tuberculosis is a widespread, devastating infection caused primarily by the bacterium *Mycobacterium tuberculosis*, and resistance to standard antibiotic treatments requires new drugs to be developed to combat these infections. Benzothiazinones (BTZs) have potential as drugs to fight resistant tuberculosis infections. To aid the development of new drug candidates, Kai Johnsson, Katarína Mikušová, and colleagues have taken a detailed look at the tuberculosis microbe's mechanism of resistance and sensitivity to BTZs (DOI: 10.1020/ja211042r).

BTZs attack the enzyme DprE1, which is involved in synthesis of the microbe's sturdy cell wall. Because bacteria require a cell wall for survival and human cells do not have such structures, enzymes involved in cell wall synthesis are attractive targets for development of new drugs to treat microbial infections.

M. tuberculosis's DprE1 is part of the pathway that makes arabinan compounds—sugars that act as glue to holds the bug's cell wall together. When BTZs interact with DprE1, the enzyme is covalently modified and turned off; the cell wall's arabinan compounds are no longer produced. DprE1 enzymes that show resistance to BTZs are not covalently modified and continue making cell wall compounds. This understanding of the mechanisms of BTZ's and DprE1's activities could help guide the design of new BTZ drugs to combat drug-resistant tuberculosis infections. **Kenneth J. Moore**

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