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Spotlights on Recent *JACS* Publications

DEFINING LEWIS BASICITY SCALES TOWARD CARBOCATIONS

One of the most fundamental tasks in physical organic chemistry is to understand the reactivity of organic species, which forms the basis for reaction design and product prediction. A key parameter to gauge organic reactivity is Lewis acidity/basicity, a quantitative measure for the electron-accepting/donating capability of a molecule or ion in terms of bond formation.

Of particular interest are the Lewis basicities of various organic bases toward carbon-centered Lewis acids due to their widespread use in synthesis. Now, Herbert Mayr and co-workers determine the Lewis basicity of common bases, including phosphines, pyridines, and *tert*-amines, by measuring their equilibrium constants with benzhydryl cation references (DOI: 10.1021/ja511639b). Based on large and wide-spanning sets of data, the researchers are able to draw scales of Lewis basicities toward carbocations in dichloromethane and acetonitrile.

The thermodynamic scales defined by this study complement the kinetics ones previously reported by the same group, and may be used to calibrate semiempirical quantum chemical modeling. More importantly, these findings represent a significant step toward understanding intrinsic barriers of organic reactions, and thus eventually chemical reactivity.

Xin Su, Ph.D.

I KNOW WHY THE CAGED NANOCRYSTAL SINGS

Omar Yaghi, Peidong Yang, and co-workers have struck on a new way to examine the chemistry of inorganic nanocrystals: by trapping them in metal−organic cages onto which they can attach other functional groups (DOI: 10.1021/ja512951e).

Inorganic nanocrystals occupy an important chemistry niche, being bigger than small molecules but far smaller than structures at the microscale. To determine the potentially useful properties of these structures, researchers have typically relied on adding functional groups to their surfaces. However, getting these functional groups to arrange selectively has been a challenge.

To overcome this hurdle, the current study wraps silver nanocrystals with metal−organic frameworks (MOFs)—open frameworks made of cages that include both organic components and metal, in this case aluminum. The researchers create these cages by coating the nanocrystals with a precursor aluminum oxide film, which is converted into thin MOF enclosures that have pristine interfaces with the nanocrystal surfaces. On these enclosures, the researchers are able to arrange cobalt ions as functional groups. Using a technique known as surface-enhanced Raman scattering, they track the metalation process and show where the cobalt ions are attached. The authors suggest that this general method could be used to explore arranging other functional groups on nanocrystals.

Christen Brownlee

FINDING HOW THE MEDICINE CRUMBLES

Gold coins will bend in your teeth; diamond will break them. The hardness of metals and ceramics has been studied for centuries, but the same investigations are rarely applied to organic solids. This difference is in part due to a lack of necessary tools, but now, nanoindentation enables researchers to probe the mechanical behavior of small organic crystals.

Manish Mishra, Upadrasta Ramamurty, and Gautam Desiraju use nanoindentation to investigate five forms of a common organic antiulcer drug, and find that its hardness is dependent on slip plane movements in the molecular crystals (DOI: 10.1021/ja512817f). To increase hardness, the researchers find, the crystal should be designed for increasing lattice resistance to sliding between molecular layers. Engineering hardness in molecular solids is important, for example, in the processing and storage of pharmaceuticals and explosives. If a material is too soft, it becomes too pasty to mill, but if it is too hard, it becomes difficult to press into tablet form.

The molecular-level understanding provided by this study should help researchers to design and optimize mechanical properties in a diverse array of molecular crystals, in addition to the antiulcer drug highlighted here.

Jenny Morber, Ph.D.

CREATING STABLE MICELLES THAT OPEN ON COMMAND

Micelles are tiny spheres made of lipid molecules that are suspended in aqueous solution. With their hydrophobic interior and hydrophilic exterior, micelles represent a promising delivery format for hydrophobic molecules, such as drugs and dyes. Micelles potentially can carry molecules through the bloodstream to targeted regions in the body. However, a major obstacle has been that some blood proteins disrupt the micelles and cause them to spill their contents before they reach their destination.

Now Matthew Levy and colleagues report a way to stabilize micelles in the bloodstream and release their contents only when prompted (DOI: 10.1021/ja512012m). The investigators have modified lipids on their hydrophilic ends with short stretches of RNA. These RNA stretches form a special structure called a parallel G-quadruplex that holds together lipid monomers through intermolecular interactions.

With this approach, Levy and colleagues create micelles that survive in serum for more than 24 h. To open the micelles, the investigators add short antisense oligonucleotides that take down the G-quadruplexes and release the micelles' contents. The investigators say the approach of using G-quadruplexes as a stabilizing factor could be used in more elaborate systems and nanoscale devices.

Rajendrani Mukhopadhyay, Ph.D.

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