JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Spotlights
pubs.acs.org/JACS

Spotlights on Recent *JACS* Publications

DEFINING BOUNDARIES FOR THE INTERACTIONS OF ANIONS AND π-ACIDS

The nature of interactions between anions and electron-accepting naphthalenediimide (NDI) can be manipulated by adjusting the electronic properties of the anions and NDIs. The conditions under which the interactions take place, such as solvent and light, also matter. Applying a broad range of experimental techniques, Sourav Saha and co-workers demonstrate that, depending on their electronic properties, the interaction between an anion and NDI can range from weak anion$-\pi$ interactions to anion-induced charge-transfer or electron-transfer phenomena, each of which gives rise to a distinct optical and magnetic response (DOI: 10.1021/ja303173n). These interactions, especially anion-induced electron transfer to NDIs, which generates colorful paramagnetic radical anions of NDIs, can be useful for optoelectronic and magnetic materials.

While Saha had previously demonstrated colorimetric sensing of a fluoride anion through electron transfer from the fluoride to NDI (DOI: 10.1021/ja107382x), the complete elucidation of different modes of anion$-$NDI interactions described in the latest work provides insights to guide future research in anion sensors, molecular electronics, magnetism, and many other areas. Understanding the properties of anion$-\pi$ interactions can also inform synthetic efforts involving anions and NDI compounds. For example, electron-transfer interactions between an anion and NDI can be exploited, or avoided, to obtain desired functional materials. **Yun Xie, Ph.D.**

FLIP-FLOPPING OF STEROIDS IN LIPID MEMBRANES

In 1971, Roger Kornberg and Harden McConnell gave the transfer of phospholipids from one leaflet of a lipid membrane to another the catchy name "flip-flop" (DOI: 10.1021/bi00783a003). Although spontaneous flip-flopping was later discounted for phospholipids, the process is thought to be critical for the asymmetrical distribution of steroids and fatty acids in a membrane. Despite its suggested importance, researchers have struggled to study the phenomenon. The difficulties have produced a confusing range of possible values, from microseconds to hours, for the time it takes for a steroid molecule to flip from one leaflet to the next.

Now Alberta Ferrarini and colleagues describe a theoretical approach to help explain the kinetics of steroid flip-flopping in lipid membranes (DOI: 10.1021/ja304007t). In their model, the investigators take into account the various aspects of steroid chemistry as well as the coupling between rotational and translational degrees of freedom in the molecules.

By studying steroids such as cholesterol and testosterone, Ferrarini and colleagues find that the molecular shape and polarity influence the way in which a molecule flip-flops and how fast it completes the movement. From their analyses of a model membrane with low steroid concentrations, the investigators predict flip-flop values in the microsecond to millisecond range. **Rajendrani Mukhopadhyay, Ph.D.**

ENGINEERING ANTIBODIES WITH JUST THE RIGHT AMOUNT OF SUGAR

The disease-fighting properties of immunoglobulin G (IgG) antibodies have been exploited in the design of engineered therapeutic agents that can outwit invading pathogens, thwart development of autoimmune diseases, and fight off cancer. An important component of IgG antibodies, called the Fc domain, is responsible for interacting with special immune cells and alerting them to attack their targets, such as cancer cells or pathogenic organisms. The Fc domain is decorated with carbohydrate molecules, which enhance its interactions with the immune cells. However, in commercially available IgG's such as monoclonal antibodies and intravenous immunoglobulin (IVIG), the carbohydrates are often heterogeneous in nature, which can diminish the ability of the antibodies to trigger an effective immune response.

To address this issue, Lai-Xi Wang and co-workers have devised a clever strategy for controlling the carbohydrate structures in the Fc domain (DOI: 10.1021/ja3051266). They strip the IgG's of their carbohydrate assortments and replace them with a single defined carbohydrate structure, with the help of two enzymes that they created specifically for the task. Using this approach, homogeneous versions of rituximab, a therapeutic IgG used in the treatment of lymphoma and arthritis, are created. This innovative approach could facilitate development of improved antibody-based therapeutics for a wide range of diseases. **Eva J. Gordon, Ph.D.**

NEW CATALYST PROMOTES ENANTIOSELECTIVE POLYCYCLIZATION OF POLYENES

Chemists are one step closer to mimicking nature's ability to catalyze multiple cyclization reactions in a single step with control of three-dimensional structure, thanks to a new catalyst developed by Karavadhi Surendra and E. J. Corey (DOI: 10.1021/ja305851h).

Researchers are interested in developing new synthetic methods for the preparation of polycyclic natural products, such as terpenoids, many of which are biologically active. Toward this end, the research team developed a catalytic complex that is able to both activate terminal C$-$C double bonds in polyene substrates and control the relative and absolute configuration of the product.

The team created a 1:1 complex of *o*,*o*′-dichloro-BINOL and $SbCl_5$, which they used to demonstrate the enantioselective cyclization of nine polyene precursors into tricyclic or tetracyclic products, with high yields. The $SbCl_5$ complex is a very strong chiral acid that outperforms previously reported polycyclization-promoting complexes in both reaction rate and enantioselectivity, making this study a significant contribution to the field of enantioselective synthesis. **Christine Herman, Ph.D.**

Published: August 6, 2012

dx.doi.org/10.1021/ja307593d | *J. Am. Chem. Soc.* 2012, 134, 13533−13534

FIRST-TIME EXPLORATION OF 2,6-DIAZASEMIBULLVALENE STRUCTURE AND REACTIVITY

A new study by Zhenfeng Xi and co-workers sheds light on a previously unexplored class of highly strained ring systems (DOI: 10.1021/ja305581f).

Chemists are interested in the family of molecules known as 2,6-diazasemibullvalenes (NSBVs) because of their homoaromatic delocalized structure and strained ring systems that give them the ability to undergo intramolecular skeletal rearrangements and generate a wide range of ring-expansion products. However, due to their inherent structural instability, NSBVs are challenging to isolate, and their structure and reaction chemistry have been largely unexplored for the past 30 years since the first discovery of a NSBV compound by Klaus Müllen and colleagues (DOI: 10.1002/anie.198206372).

Results from previous theoretical studies suggested that NSBVs should undergo Cope rearrangements more rapidly than the all-carbon SBV analogues. In an effort to experimentally investigate these and other properties, Xi's research team has synthesized and isolated eight NSBV compounds, performed the first single-crystal structural analysis of a NSBV compound, investigated the chemical reactivity of NSBVs, and performed theoretical calculations to explain the observed experimental behaviors. These findings open the door to further explorations on the chemical and physical properties of this interesting class of molecules. **Christine Herman, Ph.D.**

DNA–GOLD NANOPARTICLE COMBO GETS STRAIGHT A'S

By adding tails of several adenines (polyA), a natural component of nucleic acids, to short DNA sequences, Huajie Liu, Chunhai Fan, and co-workers have developed a new way to attach DNA to gold nanoparticles (AuNPs) (DOI: 10.1021/ja304118z).

Researchers are increasingly using DNA to assemble nanosized components into complex constructions. Since complementary strands of DNA bind to each other, they can self-assemble into intricately organized structures, bringing with them attached nanoparticles. Many previous investigations have taken advantage of this capacity by modifying DNA with thiols, which stick to AuNPs through a strong interaction between Au and S. However, getting these thiol-modified DNA strands to attach to AuNPs in desired numbers and conformations has remained a challenge.

The current work relies on another interaction that is just as strong—the interaction between Au and adenine. Attaching tails made of polyA to DNA strands, the researchers create AuNP–DNA conjugates with nucleic acids bound in precise upright conformations and in controllable numbers based on the length of the tail. Tests show that these conjugates can easily hybridize with other DNA strands, forming complexes that may be useful as DNA sensors. The authors note that this system holds multiple advantages over thiol-based AuNP–DNA conjugates for building nanostructures and nanodevices. **Christen Brownlee**