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Spotlights on Recent *JACS* Publications

USING CARBON NANOTUBES FOR TUNING CATALYTIC ACTIVITY

In 2007, reseachers at China's Dalian Institute of Chemical Physics reported that the catalytic activity of iron oxidenanoparticles could be tuned by encapsulating them in carbon nanotubes (CNTs) (DOI: 10.1021/ja0713072). Subsequently, researchers led by Xulian Pan and Xinhe Bao at Dalian, as well as other groups, reported a series of experimental studies showing that the catalytic activity for a number of transition metal catalysts can be enhanced or reduced by encapsulating them inside CNTs. Now those researchers and their co-workers study the underlying mechanisms that would explain the effect of CNTs on their catalytic activity (DOI: 10.1021/ja511498s).

They combine density functional theory with the experimental results that have been reported for several CNT-encapsulated transition metal catalysts. They find that the nanospace and π electrons—highly mobile electrons present in the curved graphene sheets that make up nanotubes—affect the dissociative binding energy of several probe molecules. It is decreased on the encapsulated particles with respect to those outside of the nanotube.

For encapsulated iron, the weakened binding results in an increased catalytic activity in CO hydrogenation, while for ruthenium the confinement results in the opposite effect in CO hydrogenation and NH_3 decomposition. Nanotubes and the confinement effects may be used to modulate important catalytic processes.

Alexander Hellemans

PROBING THE RIBONUCLEOTIDE REDUCTASE MECHANISM

Ribonucleotide reductases (RNRs) are key mediators of the metabolism of nucleic acid building blocks in both prokaryotes and eukaryotes. These multimeric enzymes catalyze the transformation of ribonucleotides to deoxyribonucleotides via a "radical hopping mechanism" in which electrons and protons translocate 35 Å from one amino acid residue to the next in a chain across different enzyme subunits. Yet the precise mechanism by which this transfer occurs has remained unclear.

Frank Neese, JoAnne Stubbe, Marina Bennati, and colleagues have generated enzyme variants containing aminotyrosine at several key tyrosine residues to "trap" different radical intermediates (DOI: 10.1021/ja510513z). They use high-frequency electron paramagnetic resonance and electron–nuclear double resonance to probe the hydrogen-bonding and electrical interactions among the different residues. Double mutants and density functional theory calculations are used to validate and explore proposed connections.

The results support a colinear proton-coupled electron transfer (PCET) mechanism in the RNR alpha subunit. How the network works in the beta subunit, and how electrons bridge the gap between subunits, are yet to be worked out. "Nature appears to have utilized multiple PCET strategies to achieve this long-range oxidation over 35 Å," the authors conclude.

Jeffrey M. Perkel

FLUOROGENIC DYE TWEEZERS COAX CELLS TO GLOW RED

Andrey Klymchenko, Dominique Bonnet, and colleagues have designed a set of dyes that fluoresce brightly in the red to infrared region when they bind biomembrane targets (DOI: 10.1021/ja5111267). The dyes could offer background-free imaging for a wide range of in vitro and in vivo applications.

Fluorogenic organic probes fluoresce upon binding biological targets, yielding high-contrast imaging of cellular processes. There is an urgent need to develop probes that fluoresce in the far-red region because mammalian tissues are almost transparent in this zone.

Now the researchers offer a solution through the design of a new set of polarity-sensitive squaraine dimers. They fluoresce only weakly in aqueous media because they are quenched by folding into intramolecular π-stacked aggregates. In contrast, on binding a membrane receptor, where the medium becomes apolar, the dimers unfold to fluoresce in the far-red region. They are the brightest fluorogenic dyes reported to date and the most promising one shows 82-fold fluorescence enhancement after unfolding. The dyes could be used to probe a variety of molecular interactions, including ligand–receptor binding, in cell cultures and in live animals.

Deirdre Lockwood, Ph.D.

MODELING THE RIBOZYME MECHANISM

Philip C. Bevilacqua, Sharon Hammes-Schiffer, and co-workers decipher the mechanism of a self-cleavage reaction catalyzed by the *glmS* ribozyme (DOI: 10.1021/ja510387y). Ribozymes are RNA molecules that catalyze biochemical reactions, such as cleaving bonds to regulate gene expression and linking amino acids together during protein synthesis. Though only first discovered in the early 1980s, ribozymes have emerged as fundamental players in RNA processing and protein production.

The authors use a mixed quantum mechanical/molecular mechanical simulation method for modeling chemical reactions in complex biomolecular systems, as well as experimental methods, to explore the mechanism of *glmS*. Specifically, they probe how the *glmS* ribozyme cleaves a phosphodiester bond, which connects one unit of an RNA molecule to another. They find that the reaction likely proceeds upon deprotonation by an external base, followed by formation and cleavage of phosphate bonds, as well as proton transfer to the leaving group. Notably, a guanine base plays a critical catalytic role by having its pK_a shifted away from rather than toward neutrality, as is conventional.

Elucidation of the mechanism of *glmS* has broad implications for our understanding of how ribozymes have evolved and how they function. Structural analyses of other classes of small nucleolytic ribozymes, such as hammerhead, hairpin, and twister ribozymes, suggest that they likely carry out their catalytic functions by similar mechanisms with a guanine similarly positioned to carry out catalysis.

Eva J. Gordon, Ph.D.

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