JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Spotlights on Recent *JACS* Publications

FATTY ACID HYDROXYLATION OF CYTOCHROME P450 ENZYMES

Using quantum mechanical and molecular dynamics simulations, Sason Shaik and colleagues elucidate how the hydrogen-peroxide-dependent cytochrome $P450_{SP\alpha}$ class of enzymes helps hydroxylate long-chain fatty acids (DOI: 10.1021/jacs.6b01716).

The cytochrome P450 class of enzymes is highly versatile, catalyzing biochemical reactions including hydroxylation and sulfoxidation. Among this class, the $P450_{SP\alpha}$ family catalyzes the hydroxylation of long-chain fatty acids in a hydrogen-peroxide-dependent manner and with high regioselectivity and stereoselectivity. The team sets out to understand this biochemically important and industrially useful catalysis using molecular dynamics and quantum mechanical/molecular mechanical techniques.

They show that a previously accepted mechanism for how hydrogen peroxide helps generate the reactive intermediate responsible for the enzymes' catalysis is erroneous. The intermediate and principal oxidant, Compound I, is formed through homolytic rather than heterolytic cleavage of hydrogen peroxide. Furthermore, the enzymes' regioselectivity is due to diastereomeric interactions at the active site. Finally, the researchers find that differences in function among $P450_{SP\alpha}$ and two closely related P450 hydroxylases are attributable to a difference in only a few active site residues.

Deirdre Lockwood, Ph.D.

GOLD NANOROD TEMPLATES YIELD PLATINUM NANOSTRUCTURES

Hollow metallic nanoparticles exhibit many unique features that differentiate them from their solid counterparts, such as high surface-to-volume ratio, low density, and tunable optical properties. Metallic nanotubes have also been shown to have unique catalytic properties. Yet the synthesis of such structures with controllable inner diameter and wall thickness has remained a challenge. Now, researchers led by Zhihong Nie and Jinlong Gong describe a new method for the synthesis of platinum nanotubes and nanorings with dimensions smaller than 50 nm, ultrathin side walls, and excellent performance as oxygen reduction catalysts (DOI: 10.1021/jacs.6b01328).

To create the nanostructures, the team employs a unique simultaneous metal alloying/etching process that eliminates noble metals in organic solvent. They find the catalytic activity for oxygen reduction is roughly 2−3 times higher than that of commercial catalysts. The authors say the method may be extended for the synthesis of other unique hollow nanostructures with different compositions for applications ranging from catalysis to energy storage and biomedicine.

Christine Herman, Ph.D.

BETA TESTING PROTEIN STRUCTURE AND STABILITY

Investigating the influence of non-natural modifications on the structure and function of proteins provides a foundation for efforts to design synthetic polypeptides with unique and useful properties. β-Amino acids, slight variants of the natural α-amino acids, are potentially valuable replacements in this regard but until now have been studied in the context of local rather than global structure. Samuel Gellman, Katrina Forest, and co-workers extend this approach to examine the impact of β-amino acid substitution on protein tertiary structure and stability (DOI: 10.1021/jacs.6b01454).

The authors replace four strategically selected α-amino acid residues in a small α-helical domain of the protein villin (the villin headpiece subdomain, or VHP) with β residues. A native-like structure is retained in each case, but the impact on conformational stability depends on both the substitution position and the type of β residue, i.e., β3 vs cyclic β. All β^3-amino acid-containing variants are less stable than is native VHP, and two of the four cyclic β-amino acid variants are more stable than the analogous β^3 variant.

These findings highlight the utility of β-amino acid substitution for mimicking native protein tertiary structure and illustrate diverse potential consequences for conformational stability. Therefore, this study contributes to a knowledge base that should facilitate the design of proteins with novel characteristics. Such biomolecules have a variety of potential biomedical and biomaterial applications.

Eva J. Gordon, Ph.D.

NEW FLUORESCENT NANOSTRUCTURES THROUGH SURFACE MODIFICATION

YuHuang Wang, George Schatz, and their colleagues have developed a method to synthesize new fluorescent nanostructures from semiconducting single-walled carbon nanotubes by adding hydrocarbon groups to the nanotube surface (DOI: 10.1021/jacs.6b03618). By modifying the surface of carbon nanotubes with alkyl or aryl groups, the team creates 30 different fluorescent nanostructures that may have applications in bioimaging, chemical sensing, or room temperature single photon generation.

Carbon nanotube structures, corresponding to many chiralities, can emit at specific wavelengths in the new infrared region. The reported surface modification allows a large number of new fluorescent structures to be created from each chirality. Interestingly, modifying tubes this way also alters the light-emitting behavior of the nanostructures and makes it possible to selectively detect certain chemicals. As a result, this new approach provides simple and significantly more versatile methods to tune the fluorescent properties of the nanotubes.

To change the wavelength of near-infrared fluorescence, the researchers vary the length and side chain structure of the added alkyl chain or attach the alkyl or aryl group to the tube through only one or up to two connections. The approach provides a way to engineer carbon nanomaterials after their synthesis and also to design new fluorescent nanostructures, the researchers write.

Melissae Fellet, Ph.D.

Published: June 1, 2016

DOI: 10.1021/jacs.6b05266
J. Am. Chem. Soc. 2016, 138, 6689−6689