

Spotlights on Recent JACS Publications

ONE MOLECULAR SYSTEM TO IMAGE THEM ALL

Researchers have long relied on various molecular imaging techniques to visualize biological objects or biochemical events at physiological, cellular, and molecular levels within living cells, tissues, or whole organisms. Each imaging modality has its own advantages and limitations. Thus, by combining multiple modalities, it is possible to gather additional information or clarify information reaped from a single modality. In a new study, Stéphane Petoud, Éva Tóth, Philippe Durand, and their colleagues significantly simplify the quest to image the same target with multiple complementary modalities through the development of a single molecular probe incorporating different lanthanide ions that make it useful for visible and near-infrared luminescence, PARACEST-MRI, and T_1 -weighted MRI (DOI: 10.1021/jacs.5b12084).

The researchers design their system specifically to image enzymatic activity. After incorporating an enzyme-specific substrate with these prototypes and using the lanthanide appropriate for the desired imaging technique, the researchers expect to detect enzyme-dependent changes in the signal. The authors note that this is the first time that a single molecular system has been used as a responsive imaging agent in three different modalities. Because the use of different lanthanide ligands induces only a minor change in the probe's structure, they add, these complexes are expected to have uniform biodistribution and cytotoxicity.

Christen Brownlee

THE POTENTIAL OF CONDUCTING POLYMERS

Conducting polymers (CPs) have played an important role in the development of electrocatalysts and photocatalysts for applications in energy, sensing, and environmental protection. This fact may not be surprising, given that CPs have high catalytic activities and conductivities, in addition to their unique electrochemical and optical properties. These polymers are also typically low-cost and amenable to large-scale operations and fabrication into flexible films and nanostructures.

In a new Perspective, Qinqin Zhou and Gaoquan Shi describe recent advances in CP-based catalysis, outline the underlying mechanisms, and discuss the challenges in developing CP-based catalysts (DOI: 10.1021/jacs.5b12474). CP-based catalysts have been found to perform well in dye-sensitized solar cells and fuel cells, yet the catalytic mechanisms underlying their performance are still unclear. The recent advancements on CP-based photocatalysts are encouraging, but related research is still at an initial stage. The authors thus highlight the need for more systematic studies on CP catalysis, as well as efforts toward the development of effective techniques for preparing CP nanostructures, controlling CP compositions and structural defects, and assembling flexible CP-based devices. **Christine Herman**, Ph.D.

SELF-EXFOLIATING NANOSHEETS WITH ANTIBACTERIAL ACTIVITY

Covalent organic nanosheets (CONs) are two-dimensional materials that are commonly synthesized from crystalline porous polymers. Typically, a multilayered organic sheet made of molecular building blocks is subjected to exfoliation techniques to "delaminate" the material and release individual nanosheets. But creating thin CON layers has proven nontrivial, owing to strong $\pi - \pi$ stacking between the layers and the hydrolytic instability of most crystalline porous polymers.

Now, researchers led by Rahul Banerjee report a new method for creating self-exfoliating nanosheets that exhibit antibacterial activity against both Gram-positive and Gram-negative bacteria (DOI: 10.1021/jacs.5b13533). The team has rationally designed a chemically stable CON composed of ionic guanidinium halide building blocks, and they find the material is capable of selfexfoliation to yield layers with nanoscale thinkness. The scientists attribute the observed behavior to the repulsion that occurs between the positively charged guanidinium units. The team finds the nanosheets have permanent porosity, are chemically stable, and exhibit antimicrobial properties, which they say could lead to their development as antimicrobial coatings for medical devices and water purification systems.

Christine Herman, Ph.D.

QUANTIFYING THE PERFORMANCE OF MACROCYCLIC LIGAND CATALYSTS

Tetra-amido-N macrocyclic ligand complexes, trademarked TAML activators, are iron-containing coordination complex catalysts that perform oxidations using H_2O_2 , similar to peroxidase enzymes. These two different types of catalysts both follow the same three-step mechanism: First, peroxide binds to the catalyst and activates it. Next, the substrate reacts with the active catalyst. Finally, the active catalyst is inactivated.

TAML activators can be used for water purification at pH 7. However, the rate constants, particularly for the inactivation reaction, are difficult to determine experimentally at that pH. Matthew DeNardo, Matthew Mills, Alexander Ryabov, and Terrence Collins combine kinetic measurements with a mathematical model to determine the three rate constants for 15 different TAML catalysts at neutral pH (DOI: 10.1021/jacs.5b13087). Although rate constants for the molecules differ by 3–6 orders of magnitude, quantitative relationships linking the rate of substrate conversion with the rates of activation and inactivation show a similar pattern for all catalysts investigated: catalysts more reactive to the substrate also inactivate faster.

Quantitatively understanding how structure and activity impact catalyst lifetime could help researchers develop new uses for TAML activators and advance their design so that their activity, already surpassing that of peroxidase enzymes in many features, can be brought closer to that where peroxidase enzymes are superior, namely the catalyst activation rate. **Melissae Fellet**, Ph.D.

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