

Spotlights on Recent JACS Publications

■ CLICK IT IS THE TICKET FOR CONTROLLED MOLECULAR METAL OXIDE SYNTHESIS

Polyoxometalates (POMs)—discrete molecular clusters of metal oxides—can combine with organic components to form hybrid molecules, such as molecular cages and containers. Alone they display interesting electrical, catalytic, chemical, and structural properties.

Leroy (Lee) Cronin and his team describe a new strategy for the synthesis of short chains of POMs, with precisely controlled chain lengths (DOI: 10.1021/jacs.5b02466). The researchers attach to the clusters lock-and-key-like reactive sites, which combine in predictable patterns. This “click” coupling of POM units allows the creation of well-defined POM chains while minimizing side-product formation. Essential to the technique is the careful mixture of single- and double-reactive site units, with asymmetric functional groups. The method described here affords far greater control over the number of metal oxide POM cores than previous strategies.

The researchers suggest that the modularity and mild conditions of their approach should permit the use of a range of other POM cores and, in the future, could produce highly specific oligomers more than twice the size of those highlighted here. With such control, researchers can more easily create mixed POM molecules to study how each unit affects the chain’s properties, or build complex materials and device components.
Jenny Morber, Ph.D.

■ GLOWING LONG WITH SUB-10 NANOMETER RECHARGEABLE LUMINOUS PEARLS

Recent studies have shown tremendous potential for near-infrared persistent luminous nanoparticles in a variety of chemical and biological applications. However, the methods used to synthesize these promising materials typically require annealing at extremely high temperatures and complicated methods to convert large bulk crystals into nanosized particles. In a new study, Gang Han and co-workers have developed a new synthetic method that results in near-infrared persistent luminous nanoparticles with diameters as small as 8 nm without these difficult techniques (DOI: 10.1021/jacs.5b00872).

The researchers use hydrothermal synthesis, in which chemical reactions occur in a sealed heating solution above ambient temperature and pressure, to create $\text{ZnGa}_2\text{O}_4\text{Cr}_{0.004}$ photoluminescent nanoparticles (PLNPs). Subsequent analyses show that these PLNPs form stable colloid solutions, which is important for biomedical applications, in both water and cell culture medium. They can also be easily functionalized with macromolecules including polymers and proteins. Importantly, briefly exciting them with biotissue-penetrable red light results in long-lasting luminescence. Further *in vivo* tests in mouse models simulating deep tissue imaging show that light can repeatedly recharge PLNPs and prompt detectable luminescence there as well. The authors suggest that this new synthetic method holds significant promise for developing PLNPs for numerous techniques that are currently inaccessible.

Christen Brownlee

■ REACTION AND RESOLUTION IN ONE POT

Jinbo Hu and colleagues report an intriguing and unusual example of a non-enzymatic, spontaneous resolving reaction that simultaneously addresses the challenges in the synthesis and separation of *Z*- and *E*-monofluoroalkenes (DOI: 10.1021/jacs.5b02112). The method takes advantage of a liquid–liquid extraction that partitions the isomeric products into different phases in the reaction vessel.

Stereoisomers—organic molecules with different configurations can have different properties. In particular, activity within a biological assay or system is often vastly different among stereoisomers, thus, for biomedical applications, the ability to separate these isomers is of great consequence. Chromatography and crystallization are commonly used to isolate the desired product, but both of these labor-intensive methods have shortcomings.

Here, the authors employ a simple liquid–liquid extraction process in which the reaction intermediate for *E*-monofluoroalkene product moves into the aqueous phase, effecting the spontaneous kinetic resolution of the reaction mixture. Monofluoroalkenes are recognized as mimetic of the peptide bond and are widely used as a structural or mechanistic probe in biological studies. This innovative strategy may find wide applications in life sciences and related fields, facilitate drug screening processes, and stimulate further exploration of spontaneous self-resolving systems.

Sonja Krane, Ph.D.

■ MASS SPECTROMETRY MONITORS HOW MEMBRANE PROTEINS AND LIPIDS MEET

As the “bouncers” of the cell, membrane proteins help determine what gets in and out. They can also trigger cellular activity in response to a stimulus. To understand the structure and function of these important biochemical players, researchers have applied a wide range of techniques, including X-ray crystallography, fluorescence resonance energy transfer, and cryo-electron microscopy. Some of these studies have revealed that the activity of membrane proteins often depends on their interaction with lipids. Now, mass spectrometry approaches are emerging as a useful way to probe these complex interactions.

In this Perspective, Chérine Bechara and Carol V. Robinson chronicle how mass spectrometry is being applied to clarify these membrane receptor dynamics, from early efforts to future directions (DOI: 10.1021/jacs.5b00420). They begin with the critical discovery that intact membrane proteins and their complexes can be protected and stabilized using detergent for eventual analysis in the gas phase by mass spectrometry. Then they explore how this approach has been developed to reveal several different modes of lipid binding. Such techniques may be applied in future research to identify substrates and elucidate the function of so-called “orphan” membrane receptors.

Deirdre Lockwood, Ph.D.

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