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Spotlights on Recent *JACS* Publications

MAKING MAGIC WITH SCALING GOLD QUANTUM BOXES

Nanoclusters made of the same materials can sometimes form a "magic" series, where stepwise increases in the number of atoms produce sequentially larger scale structures. These magic series have been regarded as analogues to atoms: the metal nanocluster mimics the nucleus while free electrons resemble an atom's valence electrons. Thus, the natural question arises of whether such magic nanoclusters exhibit the periodicity of atoms, sharing similar but scaled-up properties. In a new study, Katsuyuki Nobusada, Rongchao Jin, and co-workers show that this is indeed the case for a magic series of gold nanoclusters (DOI: 10.1021/jacs.5b12747).

The researchers have investigated a series of gold nanoclusters, increasing by eight gold atoms to arrive at the next member. Each of the four nanoclusters has the same cubic shape, and the optical absorption spectra of the series members exhibit similar profiles. The short-wavelength peak redshifts slightly higher as the size of the nanoclusters increases, along with the onset of absorbance, or optical gap. Such quantum confinement, the authors say, can be explained by a classical "particle-in-a-box" model. They envision that future work might uncover more magic series and periodicities.

Christen Brownlee

SIZE AND STRUCTURE MATTERS: PROBING POLYOXOMETALATE CLUSTERS BY IM-MS

Ion mobility spectrometry, combined with mass spectrometry into a technique known as IM-MS, is a powerful analytical method that provides information on molecular size and conformation, particularly when used with quantitative modeling and comparison to theoretical values. This technique has recently become commercially available in the form of traveling wave IM-MS and has been exploited primarily in the structural study of large biomolecules. However, reliable calibrants for large anions, such as polyoxometalate (POM) species, have been unavailable.

Leroy Cronin and co-workers address this limitation in a new study by reporting collision cross section (CCS) IM data for four different POM clusters of different sizes and shapes (DOI: 10.1021/jacs.6b00070). They are able to validate other standard techniques to model the CCSs of three POMs—a trimer, tetramer, and hexamer—assembled from the building block $\{Se_2W_{29}\}$.

With these data, the researchers then took the method another step forward by identifying a newly synthesized, previously unreported POM compound, providing a putative chemical formula and surmising that its structure is analogous to the tetramer studied in the previous system. The authors suggest that, in the future, more calibrants can be developed to increase the power and usefulness of the IM technique.

Christen Brownlee

CHIRAL CYCLOPENTADIENYL LIGANDS: UPRISING IN ASYMMETRIC CATALYSIS

In transition metal-based asymmetric catalysis, chiral ligands are crucial for stereochemical control as well as catalytic efficiency. While the majority of chiral ligands are derived from scaffolds such as BINOL and BINAP, the family of chiral cyclopentadienyl (Cp^x) ligands has recently emerged as a complementary and promising ligand type in asymmetric catalysis.

In their recent Perspective, Nicolai Cramer and colleagues give a historic overview of the development of Cp^x ligands and the corresponding metal complexes, encompassing extensive screening to rational design and more (DOI: 10.1021/jacs.5b12964). The authors also provide various examples of asymmetric syntheses based on Cp^x metal complexes, including C−H activation and cycloisomerization reactions, among others.

Progress in this area undoubtedly heralds its future direction, where simplicity and tunability in ligand design must be balanced. Hence, suitable sub-scaffolds that enable convenient structure modification and broad complexation compatibility need to be identified. These efforts, along with better mechanistic understandings, will further advance chiral Cp^x ligands' utility in asymmetric catalysis.

Xin Su, Ph.D.

SHEDDING LIGHT ON MEMBRANE PROTEIN−SUBSTRATE INTERACTIONS

Integral membrane proteins are thought to comprise about 30% of all proteomes, yet there is still so much to learn about this important class of biomolecules and their biological interactions. Better understanding is hampered by technical challenges associated with analytical biophysical approaches, including the ability to express and extract sufficient quantities of purified proteins. Although recent progress has been made toward deriving their structures by adding electron cryomicroscopy, MicroED, and solid-state NMR to X-ray crystallography approaches, Barbara Imperiali and co-workers report a complementary way to study these proteins using luminescence resonance energy transfer (LRET) (DOI: 10.1021/jacs.5b13426).

Much like the better known FRET, LRET uses luminescent lanthanides instead of conventional fluorophores as donor molecules in energy-transfer measurements. The researchers test this approach with PgIBs—monomeric oligosaccharyl transferases—from two different *Campylobacter* species, using LRET to measure distances between these proteins and peptide or glycan substrates. Their findings provide experimental support for binding distances surmised from *C. lari*'s previously reported PgIB crystal structure, validating LRET's use in a defined system. The authors suggest that this technique could offer valuable information about numerous other integral membrane proteins of interest to the chemical and biological communities.

Christen Brownlee

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SINGLE-MOLECULE VIEW INTO ORGANOMETALLIC CATALYST INITIATION

Catalysts with excellent activity, selectivity, and easy recyclability are of fundamental importance for the production of next-generation medicines, fuels, and materials. Better catalysts can be designed using information gleaned from mechanistic and kinetic studies. Single-molecule spectroscopy is unique in that this technique allows the direct observation of unsynchronized or rare processes; it has recently emerged as a powerful tool to explore molecular catalysts.

Now Randall Goldsmith and colleagues report a single-molecule investigation on the initiation dynamics of a surface-supported organometallic catalyst (DOI: 10.1021/jacs.6b00357). Base-initiated kinetics reveal highly heterogeneous behavior for this particular palladium catalyst, and the heterogeneity increases with increasing base concentration. The authors model a two-step mechanism and identify specific stages where heterogeneity in catalyst behavior may exist.

By linking specific microscopic steps in the catalyst mechanism to the fluorescent signal, the researchers can use fluorescence microscopy to gather kinetic information resolved at the level of single catalyst molecules. As new ways are developed to encode information on chemical dynamics into fluorescence, single-molecule techniques "hold the potential to be a powerful new addition to the toolkit for mechanistic investigation of organometallic species," the authors conclude.

Hui Jin, Ph.D.

ENANTIOMERIC EXCESS HELPS IDENTIFY ORIGIN OF ENANTIOSELECTIVITY

Enantiomeric excess (ee) is the measure for quantitative evaluation of enantioselective catalysis. Used in reaction development and optimization, an ee value reflects the difference in the rate of formation of two enantiomers. The difference in reaction rates stems from two diverging modes of catalyst–substrate interaction that may in turn be understood by examining data sets of ee values from systematically designed experiments.

Here, Matthew Sigman, Dean Toste, and co-workers compile a large ee data set by modifying substituents on both the catalyst and an achiral boronic acid ligand (DOI: 10.1021/jacs.6b00356). Based on the key transition state interaction identified via mechanistic studies, the researchers develop a catalytic system in which enantiomeric products can be obtained with high selectivity simply by fine-tuning the structure of the achiral additive.

This study provides a powerful tool for comprehensive understanding of selectivity in catalysis. Since the structure–selectivity dependence is ubiquitous in asymmetric catalysis, the reported strategy has a broad impact on reaction design and mechanism elucidation.

Xin Su, Ph.D.

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