

## Spotlights on Recent JACS Publications

### ■ PRECISE MAGNETIC FIELD-DEPENDENT KINETIC MEASUREMENTS ON DONOR–ACCEPTOR SYSTEMS

In the 1960s, researchers found that reaction rates can be influenced by external magnetic fields, and since that time the study of these effects has developed into its own field of study, so-called spin chemistry. These magnetic field effects are small in most types of reactions; however, in certain cases, the effects can be more evident, for example when photoinduced charge separation forms radical pairs whose stability is controlled by their interaction with the magnetic moment of atomic nuclei as well as with external magnetic fields.

Christoph Lambert, Ulrich Steiner, and co-workers have studied magnetic field effects in three rigid, iridium-bridged donor–acceptor triads, finding that stronger magnetic fields can substantially slow down the recombination of charge-separated states (DOI: [10.1021/jacs.5b04868](https://doi.org/10.1021/jacs.5b04868)). Inversely, the lifetime of charge-separated states can be an indication of magnetic field strength and direction.

The work, entailing the quantitative modeling of the magnetic field effect over a broad range of magnetic fields, has applications to the construction of artificial photosystems that are sensitive to the Earth's magnetic field and to the study of magnetoreceptors that constitute the magnetic compass of birds.

Alexander Hellemans, Ph.D.

### ■ SUCCESS AND INSPIRATION FROM FRUSTRATION IN LEWIS PAIRS

Researchers in the 1940s found that Lewis acids and bases with bulky groups could not form classical adducts, but it was not until more than 60 years later that Douglas W. Stephan and his team reported the first example of hydrogen activation by a sterically hindered phosphine/borane compound, marking the debut of “frustrated Lewis pair” (FLP) chemistry (*Science*, DOI: [10.1126/science.1134230](https://doi.org/10.1126/science.1134230)).

In a recent Perspective, Stephan highlights some of the most exciting achievements in FLP chemistry, including hydrogenation and activation of small molecules. More significantly, he also provides an outlook for the future development of this chemistry (DOI: [10.1021/jacs.5b06794](https://doi.org/10.1021/jacs.5b06794)). It is noteworthy that in some important transformations FLP-based catalysts have surpassed their transition metal counterparts in terms of efficiency. In this regard, FLP chemistry not only offers a metal-free toolbox that is complementary to conventional catalysis, but also enables exploration into unknown space of chemical reactivity.

As a major triumph in the renaissance of main group chemistry, FLP chemistry is in its infancy with regard to stereoselective hydrogenation, which is of great interest to synthetic organic chemists. Further understanding of FLP reactivity will unleash its potential in catalysis, polymerization, and materials chemistry and beyond.

Xin Su, Ph.D.

### ■ EASY MORPHOLOGY PREDICTION OF LIQUID–LIQUID PHASE SEPARATED AEROSOLS

Airborne particles in the atmosphere may have a significant impact on global climate, and the effect is often dependent on the structure and reactivity of these aerosols. Aerosols that contain both organic and inorganic components can undergo liquid–liquid phase separation in response to environmental conditions, which changes both their shape and their chemistry. Understanding and even predicting these changes—something that has been hard to do experimentally—could help researchers determine rates and outcomes of reactions catalyzed by such particles. Yuqing Qiu and Valeria Molinero demonstrate a simple and direct way to predict the morphology of liquid–liquid phase separated aerosols (DOI: [10.1021/jacs.5b05579](https://doi.org/10.1021/jacs.5b05579)).

The authors use various computational techniques to determine the equilibrium structure of such aerosols and subsequently compute the contact angle of liquid–liquid droplets, factoring in only the liquid–liquid and liquid–vapor surface tensions of the liquids involved. They find that their predictions are in good agreement with existing theory and experimental data. This new thermodynamic model should have broad application for predicting the morphology of a range of two-phase atmospheric aerosols and ultimately their impacts on the Earth's climate.

Hui Jin, Ph.D.

### ■ CHORISMATASE REACTION MECHANISMS DECIPHERED

Chorismatases are bacterial enzymes that convert chorismate, a key metabolic intermediate, into pyruvate plus any of three secondary metabolite precursors. Three subfamilies have been described, but how exactly they work has remained unclear. Now Jennifer Andexer and colleagues have worked out the reaction and product selectivity mechanisms for all three chorismatase types (DOI: [10.1021/jacs.5b05559](https://doi.org/10.1021/jacs.5b05559)).

Using <sup>18</sup>O-labeled reactants, site-directed mutagenesis, and X-ray crystallography, the team has determined that all three mechanisms begin via substrate protonation by a key glutamic acid residue. What happens next, though, differs: one enzyme subfamily employs hydrolysis, while two others undergo an intramolecular rearrangement. A single active-site amino acid difference between these latter two chorismatases is proposed to give the enzymes the unique flexibility to produce distinct chemical products.

The authors conclude that only three amino acid residues are responsible for the discrimination and significantly different activity of the subfamilies. Using sequence alignments and phylogenetic analyses, they also assign other chorismatases into their appropriate subfamilies. The results could simplify the discovery of new secondary metabolites and biosynthetic gene clusters, they suggest.

Jeffrey M. Perkel

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