

## Spotlights on Recent JACS Publications

### ■ THE PROTECTIVE POWER OF BLUE

Ning Gu, Yu Zhang, and colleagues have found that Prussian blue nanoparticles (PBNPs) may help to protect cells against oxidative damage often associated with inflammation and cell death (DOI: [10.1021/jacs.5b12070](https://doi.org/10.1021/jacs.5b12070))

Prussian blue, an organometallic iron compound used to create deep blue color, has been approved by the U.S. Food and Drug Administration as a thallium antidote since 2010. Now researchers show that the same properties that enable the compound to safely clear thallium from the human body may also make the nanoparticles protective antioxidants. In experiments that generate oxidative stress through chemicals, UV irradiation, high glucose, and more, PBNPs efficiently quench and inhibit oxygen radicals and hydrogen peroxide. Laboratory and animal experiments suggest that PBNPs are effective scavengers of reactive oxygen species (ROS), and that PBNPs can reduce or even prevent the production of ROS in mammalian liver tissue. Mice pretreated with PBNPs show almost no liver changes after oxidative stress, while untreated mice exhibit inflammatory cell migration and other symptoms of acute liver disease.

Unlike many other often toxic iron-containing nanoparticles, PBNPs have the potential to be potent antioxidants for controlling ROS-induced cell damage. This research combines thorough characterization and mechanistic studies, but as the authors note, further work is needed to understand the mechanisms of PBNPs' interactions with mammalian cells.

Jenny Morber, Ph.D.

### ■ UNDERSTANDING HOW SUPERCAPACITORS CHARGE

In this Perspective, Clare Grey, Alexander Forse, and colleagues review recent studies of supercapacitor charging mechanisms (DOI: [10.1021/jacs.6b02115](https://doi.org/10.1021/jacs.6b02115)). Supercapacitors, which are high-power energy storage devices, have fundamentally different charge mechanisms from standard capacitors as charges build up through the fast flux of ions in and out of porous carbon electrodes. As a result, they store much more energy than standard capacitors, and at the same time they can charge and discharge more quickly than batteries. For example, supercapacitors are used in electric vehicles where large power surges are required for acceleration.

Reviewing results from in situ experimental methods and computer simulations, the researchers explain how a range of different charging mechanisms can operate in supercapacitors. Interestingly, charging is generally more complex than the classical ion adsorption mechanism. The prevalence of the different charging mechanisms depends on the types of carbon electrodes and electrolytes. These variations pose a significant challenge for the future design of enhanced supercapacitors. By selecting and matching electrodes and electrolytes, it will be possible to fine-tune the charge mechanisms to optimize supercapacitors for power performance and/or energy density.

Alexander Helleman

### ■ ENERGY TRANSFER IN METAL–ORGANIC FRAMEWORKS: MORE THAN MEETS THE DYE

Metal–organic frameworks (MOFs) have recently found a new application as model systems for photosynthesis. Chromophores in MOFs, which mimic the reaction centers that serve as sinks for solar energy in photosynthesis, are separated by distances of about 1–2 nm, similar to the interchlorophyll distances in plants. Excitons have been assumed in previous research to arrive at these depots through a process of step-by-step random hopping, in which energy transfers between adjacent ligands. However, in a new study, Cheng Wang and co-workers show that the majority of energy appears to eschew the nearest neighbors and jump over longer distances (DOI: [10.1021/jacs.6b01345](https://doi.org/10.1021/jacs.6b01345)).

The researchers synthesize two MOFs composed of identical fluorescent nodes and organic struts but with a longer distance between nodes in one than the other. By inserting a fluorescent dye into the pores of these structures, the researchers can follow the path of excitons. Combining experimental results with modeling, the researchers find that energy-jumping *beyond* nearest neighbor nodes accounts for up to 67% of the energy transfer rates, suggesting a far different pathway than bouncing among adjacent nodes. The authors suggest that this work can help shape the design of efficient energy transport networks as well as potentially adding insight into the mechanisms behind photosynthesis.

Christen Brownlee

### ■ DISSYMMETRIC DIPYRRIN–METAL COMPLEX IS MORE LUMINESCENT THAN BODIPY

BODIPY, less familiarly known as 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, is a fluorescent molecule commonly used as a biological probe or a laser dye. BODIPY contains a boron atom attached to a dipyrin ligand made from two pyrrole rings bridged by methine. However, metal complexes containing two or three dipyrin ligands are only weakly luminescent, and until now little effort has been made to improve their photophysical properties.

Here, Ryota Sakamoto, Hiroshi Nishihara, and their colleagues have constructed eight new dipyrin–zinc complexes, each containing two different dipyrin ligands (DOI: [10.1021/jacs.6b02128](https://doi.org/10.1021/jacs.6b02128)). The dissymmetric (low symmetry) complexes have higher quantum efficiencies than the corresponding fully symmetric complexes. By changing the structure of either dipyrin, the researchers are able to tune the red and near-infrared emission wavelengths of the molecules. The most luminescent molecule in the series has a higher quantum yield than a BODIPY derivative that fluoresces at a similar wavelength.

These types of metal–dipyrin complexes have previously been applied effectively as structural components in supra-molecules, coordination polymers, and metal–organic frameworks. The present work may extend the utility of such materials as luminophores or photosensitizers.

Melissae Fellet, Ph.D.

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## ■ SMALL OLIGOMERS PHASE-SEPARATE INTO ORDERED NANOSTRUCTURES

Well-ordered nanostructures constructed by self-assembly often consist of large molecules such as block copolymers—polymers comprising two or more chemically distinct segments in one chain. Now, a new study by E. W. Meijer and co-workers shows similar self-assembly behavior exhibited by a surprising class of molecules: small end-functionalized oligodimethylsiloxane oligomers (DOI: [10.1021/jacs.6b02172](https://doi.org/10.1021/jacs.6b02172)).

The researchers find these small oligomers self-assemble into nanodomains resulting from phase separation between their aromatic end groups and their dimethylsiloxane midblocks. The nanodomains are spaced less than 5 nm from each other, and this ultra-small spacing may aid in the development of improved microelectronics fabrication techniques.

When end groups with certain aggregation properties are used, the phase morphology of these nanostructures can be varied by modulating the volume fraction of the functionalized oligodimethylsiloxanes. Here, combining molecules with different molecular weights to yield a polydisperse mixture results in a disordered material. Hence, molecular monodispersity is required for ordered nanophase separation of such small oligomers. The researchers envision these insights on oligomer self-assembly may assist in the bottom-up approach to creating nanolithography templates with increasingly smaller dimensions.  
**Christine Herman, Ph.D.**

## ■ SMALL, BUMPY, STABLE: THESE CATALYSTS ARE TOPS

In catalysis, size and shape matter. To maximize efficiency, researchers want very small particles, which minimize non-interacting interior atoms, and highly active surfaces, which promote strong and fast reactions. But synthesis is challenging: tiny, high surface energy particles also tend to be unstable during production.

Na Tian, Shi-Gang Sun, and colleagues report a technique that stabilizes high-index facets on platinum nanoparticles of 10 nm or less (DOI: [10.1021/jacs.5b13473](https://doi.org/10.1021/jacs.5b13473)). The team grows these catalyst particles using high-density platinum seeds supported on graphene in a dilute platinum plating solution. The working electrode potential varies with time in a square waveform known to produce high energy facets, while the high-density seeds ensure the platinum crystal nuclei do not dissolve. Tellingly, the researchers are unable to grow these platinum catalysts under the same conditions without the platinum nanoparticle seeds.

This technique has produced the first-reported sub-10 nm tetrahedral platinum nanoparticles. The synthesized catalysts demonstrate greater activity for ethanol electrooxidation and greater stability than seed particles or commercially available carbon-supported platinum catalysts. This method is also suitable for reshaping commercial Pt/C catalysts to improve activity and stability, and thus provides a relatively straightforward solution to a frustrating conflict between catalyst size, shape, and stability.

**Jenny Morber, Ph.D.**