

Spotlights on Recent JACS Publications

■ TOUGH-TO-SYNTHESIZE POLYMERS EXHIBIT TUNABLE PROPERTIES

Over the past 30 years, thiophene-based materials have played a critical role in the development of organic electronics. Challenges in modulating the energy band gaps of these π -conjugated compounds have resulted in slow progress toward more advanced applications, such as optoelectronic devices and photovoltaic cells. Now, researchers led by Juan Casado and Xiaozhang Zhu describe an unprecedented series of thiophene-based polymers with unique photophysical properties that may make them good candidates for such applications down the road (DOI: [10.1021/jacs.5b05940](https://doi.org/10.1021/jacs.5b05940)).

The team reports a series of monodisperse oligomer derivatives known as regioregular oligo(thieno[3,4-*b*]-thiophene)s, which are tough to synthesize due to stability and regioregularity issues. The compounds have well-defined planar structures, with each monomer repeat unit derived from two key precursors. The oligomers exhibit a broad absorption range, from the UV–vis to the near-infrared regions, and are found to have extremely long effective conjugation lengths of roughly 30 thiophene repeat units. The researchers find that the energy band gaps are tunable, with the largest oligomers exhibiting the smallest energy band gaps—an important characteristic for potential applications in high-performance organic electronic devices.

Christine Herman, Ph.D.

■ LEARNING THE TRICKS AND TRADE OF A VERSATILE ENZYME

Enzymes in nature are profoundly well-tuned to turn their particular substrates into specific products. By understanding in detail how enzymes work, scientists hope to engineer novel enzymes that catalyze customized reactions and churn out hard-to-synthesize products. The enzyme cytochrome P450, which has a heme-based catalytic center, typically acts using oxygen as a substrate. However, the enzyme will instead use reactive nitrogen or carbon species and catalyze non-natural reactions such as olefin cyclopropanation or C–H amination if a heme-coordinating cysteine is mutated into a histidine.

To figure out how cytochrome P450 swaps activities, and thus how it may be possible to engineer enzymes that catalyze particular non-natural reactions, a team of researchers led by Frances Arnold has crystallized and solved the first structure of a histidine-ligated cytochrome P450 (DOI: [10.1021/jacs.5b07107](https://doi.org/10.1021/jacs.5b07107)). The mutant histidine, despite its relative bulkiness, still manages to coordinate the heme cofactor, which causes portions of the mutant enzyme's protein fold to differ significantly from the cysteine-ligated cytochrome P450.

To take it a step further, the researchers generate 18 more mutants at the ligating cysteine, one for each of the remaining common amino acids. None of the mutants lose their heme cofactors, demonstrating the adaptability of cytochrome P450. The lessons learned may serve as a springboard to enzyme customization.

Erika Gebel Berg, Ph.D.

■ OUT OF MANY, ONE MOF

Metal–organic frameworks (MOFs)—synthetic crystalline materials in which metal ions or clusters link together with organic molecules to form a scaffold—are usually composed of one type of ion and one type of linker. At most, researchers have been able to create MOFs with two kinds of inorganic units or up to three kinds of organic linkers; adding more building blocks has remained a challenge due to difficulties in designing structures in which each component can participate, along with an increased likelihood of product mixtures.

Pushing the envelope for these materials, Binbin Tu and co-workers have synthesized a new MOF containing three geometrically and compositionally different inorganic building blocks that arrange into four kinds of polyhedral cages (DOI: [10.1021/jacs.5b07687](https://doi.org/10.1021/jacs.5b07687)). By mixing zinc and copper ions with 4-pyrazolecarboxylic acid, the researchers create triangular copper-based clusters, octahedral zinc-based clusters, and square pyramidal zinc-based clusters that self-assemble into unit cells.

The microporous and mesoporous cages in each unit cell contain designed defect sites in which additional linker molecules can be added to change functionality. These sites are also readily accessible to guest molecules of appropriate size, allowing the researchers to use the constructs as scaffolds to form nanoparticles quickly. The authors suggest that this unusual structure demonstrates that more complex MOF engineering is possible.

Christen Brownlee

■ UNEXPECTED BEHAVIOR OF POLYMERS AT THE OIL–WATER INTERFACE

Scientists understand quite a bit about the behavior of polymers in dilute solution where diffusion is controlled in predictable ways by the polymer's molecular weight, its conformation, and the viscosity of the solution. But when the system includes an interface—such as the boundary between oil and water—the picture is not as clear.

Now, researchers led by Daniel Schwartz report surprising new findings about polymer behavior at the oil–water interface (DOI: [10.1021/jacs.5b07108](https://doi.org/10.1021/jacs.5b07108)). The team studies the diffusion of poly(ethylene glycol) (PEG) molecules at the interface of water and polydimethylsiloxane oil. Using a high-throughput molecular tracking method, the researchers make two observations that are consistent with previous studies: at the interface with low-viscosity oil, the polymers exhibit simple Brownian diffusion, while at interfaces with high-viscosity oil, they move more quickly than expected and display “intermittent hopping”.

But the team was surprised to find that regardless of the viscosity of the oil, the interfacial polymers adopt a conformation that is swollen compared to what is expected in oil or water alone. The findings may help researchers in the effort to design and manipulate polymer materials at hydrophobic interfaces, for applications ranging from plastic fabrication to the study of protein folding.

Christine Herman, Ph.D.

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