

Spotlights on Recent JACS Publications

■ DNA GETS THE GOLDEN TOUCH

Combining gold nanoparticles (AuNPs) with DNA has a history now spanning two decades, with potential applications in biodiagnostics, medicines, and biosensors. In a recent study, Haojun Liang and Tingjie Song show a new way of using AuNPs and DNA together, taking advantage of a technique called toehold-mediated DNA strand displacement (DOI: 10.1021/ja304746k). This technique involves displacing a single-stranded DNA on a double-stranded complex with another single-stranded stretch with the help of short sequences of bases known as a toehold.

Here, the researchers develop a method to control assembly of AuNPs using a similar toehold technique. They start with two types of DNA-modified AuNPs, each functionalized with one of two oligonucleotides. In a series of reactions, short, single DNA strands are successively base-paired and displaced from these AuNPs. Finally, the short, single-stranded DNA is displaced by the opposing DNA–AuNP complex. The end result is a double-strand of DNA carrying two AuNPs.

Through this technique, the researchers effectively aggregate AuNPs linked by strands of DNA. Additionally, by using the programmable aspect of DNA base pairing, they create AND and OR logic gates with DNA–AuNP complexes that display their results by changing the opacity of the solution. The authors suggest that this simple system might be used as a building block for more complicated multi-component logic gates and molecular machines. **Christen Brownlee**

■ MAKING SOMETHING USEFUL FROM EMITTED GREENHOUSE GASES

Carbon dioxide (CO₂), a gas thought to bear responsibility for global warming when it is emitted to the atmosphere, may have a new role to play: as feedstock for fuel. Pratim Biswas and co-workers have developed a nanostructured film that efficiently converts CO₂ to methane (CH₄), which can be used as an energy source (DOI: 10.1021/ja304075b).

Climate change has been widely tied to so-called greenhouse gases in the atmosphere, particularly CO₂. To combat this environmental threat, researchers have looked toward a variety of interventions, such as CO₂ sequestration from emissions. Taking this concept a step further, others are seeking ways to convert this captured CO₂ into fuels or other useful chemicals. Though researchers have demonstrated some success in developing photocatalysts that convert CO₂ into CO or CH₄ using light, these materials have operated with low efficiency.

Investigators in this new study have constructed a material that greatly improves the efficiency of this conversion process. Their film, made of titanium dioxide decorated with ultrafine nanoparticles of platinum and activated by simulated solar irradiation, demonstrates the highest efficiencies for conversion of CO₂ to CH₄ thus far reported by researchers. The authors suggest that this economically manufactured and operated film could be an important tool that can help combat climate change while generating a useful energy source. **Christen Brownlee**

■ NEW EXPLANATION FOR PRESERVATION OF POLYMERS BY AMINE ANTIOXIDANTS

Antioxidants are crucial to life and have commercial uses such as preventing disruptive substances from forming in gasoline and protecting plastics from degradation. Michelle Coote and co-workers have uncovered new information about the protective action of hindered amine light stabilizers (HALSs), a type of amine-based radical-trapping antioxidant (DOI: 10.1021/ja3006379). Phenols and amines are the two main classes of radical-trapping antioxidants (RTAs), and while the mechanism by which phenol RTAs act is well known, the reaction pathways of amine RTAs are far less clear.

The researchers propose a new mechanistic cycle that is kinetically and thermodynamically justified based on high-level theoretical calculations and explains all experimental observations. The new catalytic cycle relies on abstraction of a β -hydrogen atom from an alkoxyamine, NOCHR'R", though a number of different mechanisms are likely to be involved, depending on the chemical nature of both the HALS and the material being protected.

HALSs are effective at low concentrations and protect organic materials against oxidative degradation at both high and low temperatures, as well as under UV irradiation. HALSs are particularly suitable for outdoor use in inhibiting degradation of organic materials due to sun exposure. Elucidating the catalytic mechanisms of HALSs can facilitate the design of more effective HALSs and other types of amine RTAs, including medicinal antioxidants. **Yun Xie, Ph.D.**

■ FUNCTIONALIZED OLIGOMERS CREATE FOLDAMERS IN SOLUTION

A recent study by Takuzo Aida, Takanori Fukushima, and colleagues reveals a unique class of polymer-like molecules that fold into helical structures in a solvent-dependent manner (DOI: 10.1021/ja303117z). The researchers studied *o*-phenylene oligomers of 4–24 repeating units, which are interesting because similar types of conjugated polymers have applications in the photonics and microelectronics industries.

Other *o*-phenylene oligomers were previously found to assemble into a helical structure in crystalline form, but further studies revealed that in solution the oligomers are dynamic and do not exhibit regular helical geometry, particularly when the ends of the chains are unfunctionalized.

The researchers synthesized a series of *o*-phenylene oligomers with different functional groups at their terminal positions and studied the effect of chain length, terminal groups, and solvent on their ability to fold and exhibit optical activity. The team characterized the so-called foldamers and found that a perfectly structured helix occurs only in acetonitrile and only with end-group functionalized chains. Moreover, the helical folding is accompanied by a change in electronic interactions of the phenylene units—the perfect-

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helix foldamer has very different electrochemical properties from the unfolded chain. This finding may open the door to new applications of these electroactive helical structures.
Christine Herman, Ph.D.

■ WATER SPLITTING CATALYSTS: THE SECRET IS IN THE STRUCTURE

Funneling solar energy into alternative fuel sources has long been a goal for the chemical community. By using high-energy X-ray scattering and pair distribution function analysis, David Tiede, along with post-docs Pingwu Du and Oleksandr Kokhan and co-investigators Karena Chapman and Peter Chupas, discover specific atom–atom distances in all parts of a new, efficient cobalt oxygen evolution catalyst (Co-OEC), providing structural information that has eluded scientists using other techniques (DOI: 10.1021/ja303826a).

Many catalysts have been created that mimic the water splitting reaction that occurs in plants' photosystem II reaction, producing hydrogen gas with varying degrees of success. The recently discovered Co-OEC does not degrade easily, does not require harsh reaction conditions, and is made of readily available materials. However, while some configurational information about this catalyst is known, the exact spacial relationships between the atoms are unclear, and therefore scientists do not know precisely how the structure-based parts of the catalyst work.

Tiede and co-workers find that the catalyst consists of truncated lattice sheet domains with distorted coordination geometry, suggesting that the activity may be due to defects in the Co-OEC structure. Further determination of these defects will provide insight into how the catalyst works and may lead to more efficient water-splitting materials, and therefore cheaper alternative energy, in the future.
Leigh Krietsch Boerner, Ph.D.