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Spotlights on Recent *JACS* Publications

MUCONATE ASSEMBLY FROM DOUBLY SELECTIVE ACRYLATE CROSS-COUPLING

(*Z*,*E*)-Dienyl muconate motifs are found in a variety of biologically active natural products, including the cytotoxic agent (+)-superstolide A and the antibiotic (−)-macrolactin A, and have thus become highly pursued intermediates in organic synthesis. While the coupling of two acrylates would appear to be the most straightforward and efficient way to prepare functionalized muconates, problems such as competing homocoupling and weak directing ability have forced chemists to take detours.

Yun-He Xu, Teck-Peng Loh, and co-workers report a breakthrough on a direct route to such structures, in which they are able to access the (*Z*,*E*)-muconate fragment from oxidative cross-coupling between two acrylates with both stereo- and chemoselectivity (DOI: 10.1021/ja512237d). In the presence of a ruthenium-based catalyst, a wide range of α-monosubstituted and α,β-disubstituted acrylates can be *Z*-selectively coupled to unsubstituted acrylates, directed by the cyclometalation of ester groups.

This transformation can be conducted on a preparative scale, and the products are readily converted to useful organic building blocks, demonstrating the reaction's utility as a synthetic tool. As a novel strategy that complements established approaches to the (*E*,*E*)-1,3-diene structure, it may inspire continuing efforts to exploit such a selective catalytic mode.

Xin Su, Ph.D.

TURNING A NEGATIVE INTO A POSITIVE

Two-dimensional nanosheets, such as graphene oxide (GO), have intriguing properties that could be useful in many applications. These applications might be dramatically expanded by layering different 2D materials. However, most known 2D nanosheets are negatively charged and thus resist layering. Now, Takayoshi Sasaki and co-workers have developed a method that can switch the surface charge of 2D nanosheets, increasing the possibilities of materials that can be stacked (DOI: 10.1021/jacs.5b00317).

By dripping solutions of negatively charged 2D nanosheets into water containing long, positively charged molecules, the researchers successfully modify the surface charge of materials including GO, $Ti_{0.87}O_2^{0.52-}$, and $Ca_2Nb_3O_{10}^-$. Rather than clumping together, with positively charged sides of some sheets sticking to negatively charged sides of others, the nanosheets remain suspended in solution, likely due to the long positive molecules running off the edges of nanosheets and folding over. Next, slow addition of the now-positively charged nanosheets to pristine negatively charged ones of different materials creates superlattices made of stacked nanosheets with opposite charges. The researchers suggest that this method could be used to modify a variety of nanosheets with different charges, allowing for composite materials to be made from a much broader array of building blocks.

Christen Brownlee

HYDROGEL-BASED SENSOR FOR NAKED-EYE DETECTION OF BIOMARKERS

Supramolecular hydrogels that exhibit macroscopic responses to stimuli, such as the presence of biomarkers, hold promise for numerous biological applications. Now, Itaru Hamachi and colleagues report a new technique with a built-in signal amplification system that enables biomarker detection with the naked eye (DOI: 10.1021/ja5131534).

The researchers create supramolecular hydrogels composed of molecules self-assembled into a fiber network that degrades in the presence of hydrogen peroxide. This degradation causes what is known as a "gel−sol" phase transition that is visible to the naked eye. By building in a signal amplification system based on a self-destructing dendritic molecule and embedding specific enzymes, the team exploits the H_2O_2-responsiveness of the hydrogel. As a result, they create a sensor that is sensitive to the biomarkers hydrogen peroxide, glucose, and uric acid.

The researchers create an array chip and introduce human plasma spiked with uric acid, a biomarker for hyperuricemia disease. The sensor can detect the molecule at levels "close to the practical values required to conveniently monitor disease conditions," the researchers write. The ability to detect biomarkers within a complex matrix such as human blood plasma is an important characteristic that demonstrates the method's potential for applications in clinical diagnostics without expensive instruments.

Christine Herman, Ph.D.

OXIDATIVE ADDITION GOES REDUCTIVE WITH METAL-FREE ORGANOCATALYSTS

Oxidative addition is an elementary step in many organometallic catalytic cycles, in which, for example, nonpolar σ-bonds can be activated for addition to double or triple bonds through reductive elimination. This process is usually achieved by coordination to transition metal centers in catalysts, accompanied by an increase in metal valence states.

Recently, Toshimichi Ohmura, Yohei Morimasa, and Michinori Suginome have discovered the organocatalytic counterpart of metal-catalyzed oxidative addition (DOI: 10.1021/jacs.5b00546). The researchers show that boron−boron σ-bond activation is a formally reductive process where two boryl groups are added to 4,4′-bipyridyl nitrogens.

Although organocatalysts have been shown to activate nonpolar σ-bonds, it is the first time that intermediates of the reductive addition have been isolated and identified. This study, in addition to being crucial for establishing the mechanism of σ-bond activation by nonmetallic organocatalysts, will inspire the development of other types of bond formation under similar conditions, demonstrating that organocatalysis is a powerful synthetic tool that can be used in parallel with traditional transition metal catalysis.

Xin Su, Ph.D.

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