

Spotlights on Recent JACS Publications

IMAGING AGENT FOR KIDNEY DISEASE

Chronic kidney disease (CKD), which causes build-up of dangerous levels of fluid, electrolytes, and wastes in the body, currently affects 14% of adults in the U.S.; the number is expected to rise because diabetes, which attacks the kidneys, is becoming more prevalent. Patients with CKD would benefit from contrastenhanced computed tomography (CT) or magnetic resonance imaging (MRI) to detect and monitor their kidney disease along with other commonly associated pathologies, e.g., cardiovascular, that frequently occur in CKD patients. Unfortunately, these patients cannot tolerate the contrast agents routinely used in CT and MRI which carry risks of harm.

Now Eric Gale, Peter Caravan, and colleagues have developed a manganese(II) complex that can serve as an alternative to conventional contrast agents (DOI: 10.1021/jacs.5b10748). The manganese replaces the element gadolinium which, along with iodine, is found in traditional contrast agents.

The researchers demonstrate that the manganese-based compound is stable, inert, and highly effective as a contrast agent for MRI in rodent specimens. Moreover, mice are able to completely eliminate the agent from the body within 24 hours. To show its medical applicability, the investigators have modified the compound with a specific peptide and show that this conjugate selectively identifies blood clots in rat arteries. Because of this combination of desirable properties, the authors conclude that the manganese compound has potential as a contrast agent for patients with kidney disease.

Rajendrani Mukhopadhyay, Ph.D.

POTENTIAL OF PERYLENEDIIMIDES FOR ORGANIC SOLID-STATE LASERS

Organic solid-state lasers (OSSLs) have desirable qualities, including low cost, compatibility with low-temperature processing, and ability to be tuned over a broad spectrum. Optically pumped OSSLs have been demonstrated with a variety of optical resonators, but progress with their electrically driven counterparts has been hampered by two main stumbling blocks. (1) There is a shortage of organic semiconductor materials that exhibit both large stimulated emission and high charge carrier mobility, since the two characteristics are often at odds. (2) Electrically driven OSSLs suffer serious drops in efficiency from a phenomenon known as bimolecular exciton—exciton annihilation (bmEA), whereby excitons accumulate and overlap with each other.

Now, researchers led by Hongbing Fu and Yishi Wu demonstrate an OSSL based on perylenediimide derivatives, which have been widely used in organic thin-film transistors and solar cells but never before incorporated into OSSLs (DOI: 10.1021/jacs.5b10353). The molecules self-assemble from solution into a loosely packed twisted brickstone arrangement that simultaneously exhibits high photoluminescence quantum yield and potentially carrier mobility. The team also finds that the molecules have optimized energy levels that suppress the unfavorable bmEA process, which makes them attractive candidates for applications in electrically driven OSSLs. Christine Herman, Ph.D.

TRIPLE ALLENE ADDITION IN ONE SHOT

Multicomponent reactions can furnish highly functionalized single products by joining three or more building blocks all at once, generating diverse molecular complexity with high atom efficiency and low time cost. While such reactions hold promise for express delivery of complicated synthetic targets, many—particularly asymmetric variants—are difficult to control and harness.

Kuiling Ding, Zheng Wang, and co-workers now report a highly regio- and enantioselective catalytic preparation under mild conditions for chiral allylic arylamines from four simple components: terminal allenes, methanol, carbon monoxide, and arylamines (DOI: 10.1021/jacs.Sb07764). The transformation involves an alkoxycarbonylation—amination cascade catalyzed by a spiroketal-based diphosphine palladium catalyst that bears a close structural resemblance to one used previously by the authors to directly aminate allyl acetates in an asymmetric manner.

This discovery elegantly combines the multimodal reactivity of allenes and the versatility of the catalyst, revealing a shortcut to functionalized optically active amines. Immediately benefiting from this new method is the concise synthesis of a useful cycloheptene-fused chiral β -lactam, but it may, the authors expect, "find wider applications in the efficient synthesis of multifunctional compounds starting from simple olefinic molecules." **Xin Su**, Ph.D.

■ ACHIEVING THE NEAR-IMPOSSIBLE WITH H⁻

Metal oxides that incorporate anions such as N^{3-} , F^- , or OH^- have attracted recent attention due to their interesting electronic and photochemical properties. But, synthesizing these compounds has thus far required harsh conditions involving high temperatures and sometimes high pressures. Hiroshi Kageyama and co-workers now show that using a titanium perovskite oxyhydride (BaTiO_{2.5}H_{0.5}) starting material can moderate the reaction conditions needed to produce these intriguing compounds by introducing hydride (H⁻) as a labile ligand available for exchange reactions (DOI: 10.1021/jacs.Sb10255).

By reacting nitrogen with this oxyhydride precursor, the researchers are able to form the oxynitride $(BaTiO_{2.5}N_{0.2})$ at temperatures between 400 and 600 °C because of a ligand exchange with H⁻, overcoming nitrogen's typically inert nature. Hydride's reactivity with oxidizing agents and acids also make it possible to obtain mixed compositions of $BaTi(O, H, F)_3$ and $BaTi(O, F)_3$ by treating the precursor with HF at 150 °C under mild pressure, even though the latter compound usually requires high pressure during synthesis. By further exchanging the F⁻ ion with OH⁻, the researchers prepare $BaTi(O^{2-}, H^-, OH^-)_3$, a compound that allows the thermodynamically unlikely coexistence of both H⁺ and H⁻. The authors suggest that the use of other oxyhydrides as precursors could eventually lead to easier synthesis of other mixed anion oxides.

Christen Brownlee

ACS Publications © 2015 American Chemical Society

Published: December 8, 2015