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Spotlights on Recent *JACS* Publications

BUILDING BIARYLS WITHOUT A CATALYST

Biaryls, in which two aromatic rings are connected by a covalent bond, are a common structure in pharmaceuticals, organic materials, and ligands for catalysts. Such molecules are typically made by connecting functionalized, and often activated, aromatic rings using a transition metal catalyst.

László Kürti and his colleagues have developed an aryl–aryl coupling reaction that does not require a transition metal catalyst (DOI: 10.1021/ja400897u). The reaction forms a 2-amino-2′-hydroxy-1,1′-biaryl or a 1-amino-1′-hydroxy-4,4′-biaryl, depending on the reaction mechanism.

Inspired by the Bartoli indole synthesis, the reaction combines a nitroarene with an aromatic Grignard reagent. Sequential addition of the aromatic anion to the nitro group initiates a sigmatropic rearrangement that forms the biaryl bond. The reaction tolerates a variety of halogen substitutions on the nitroarene and can be performed on the multigram scale.

This reaction builds structures that are currently difficult, or impossible, to construct using other aryl–aryl cross-coupling reactions, so it opens new avenues for those applications that utilize molecules with a biaryl motif. The halogenated biaryls from this reaction can be the starting points for other interesting heterocycles, like indoles, benzothiazoles, and benzofurans, that may be of broad interest in asymmetric catalysis, drug discovery, and materials science. **Melissae Fellet, Ph.D.**

SPHERICAL NANOCRYSTALS GROW LEGS

Blow a bubble from any starting shape, and it will always form a sphere. In our human, macro world, the sphere is a minimum energy geometry. But at the nanoscale, this rule does not always hold true.

Marijn van Huis and co-workers use a combination of computer modeling and experiment to show that spherical cadmium selenide (CdSe) nanocrystals branch into four-footed (tetrapod) and eight-footed (octapod) geometries when heated (DOI: 10.1021/ja401406q). Modeling confirms that the potential energy of a tetrapod is lower than that of a crystalline sphere with the same number of atoms. Surprisingly, the structural phase transformation within the nanocrystal does not proceed through common slip mechanisms, in which bonds are sequentially broken and re-formed, but through highly mobile vacancies on the cadmium atomic planes. Heating experiments in a high-resolution transmission electron microscope corroborate the simulation results.

CdSe nanocrystals demonstrate optical and electronic properties of interest for solar energy conversion, lasers, and biomedical imaging. Although this model system has been extensively studied, few reports have focused on the effect of temperature on CdSe nanostructures. This result points to new ways to synthesize branched nanostructures of CdSe and similar materials for use in optoelectronic devices. **Jenny Morber, Ph.D.**

HIGHLY EXTENDED POLYCYCLIC HYDROCARBONS WITH TUNABLE PROPERTIES

Polycyclic hydrocarbons with unique optical, electronic, and magnetic properties are a well-studied class of molecules that form the basis of many useful materials. However, highly extended forms of these molecules with an open-shell ground state, which may have potential for applications in nonlinear optics, organic electronics, and energy storage devices, are difficult to synthesize, isolate, and characterize due to their high reactivity and poor solubility.

Now, a research team led by Jishan Wu demonstrates the elegant synthesis of a class of highly extended polycyclic hydrocarbons and sheds light on their unusual optical properties (DOI: 10.1021/ja402467y). The π-conjugated systems they study are based on a building block known as *p*-quinodimethane, or *p*-QDM, and are of particular interest because of their low band gap and their open-shell biradical character.

The team demonstrates an efficient approach to the synthesis of soluble and stable extended *p*-QDMs and finds they can tune the ground state of a molecule, and other properties, by adjusting the chain length. The results of these studies are an important step toward better understanding the chemical and physical phenomena of highly extended polycyclic hydrocarbons based on *p*-QDM. **Christine Herman, Ph.D.**

NEW APPROACH TO UTILIZING LIGNIN

The irregular and complex structure of the biopolymer lignin, which surrounds cellulose and hemicellulose in plant cell walls, presents a challenge in trying to use the material as a bio-based chemical feedstock. In an effort to improve lignin processing, Shannon Stahl and co-workers have developed a selective method to oxidize the alcohol groups in lignin. This method provides the basis for selective cleavage of C–C and C–O bonds in the oxidized product to obtain valuable small aromatic compounds (DOI: 10.1021/ja401793n).

The researchers use an all-organic catalyst consisting of an acetamido derivative of the nitroxyl radical compound TEMPO, along with molecular oxygen and mineral acid co-catalysts, to convert select alcohol groups to carbonyl groups in a lignin model compound. The oxidation sets up the model compound for a subsequent peroxide-based oxidation process that generates the smaller aromatic products. The researchers demonstrate that the initial oxidation step also works well on lignin itself.

The next step for the team will be to develop improved cleavage methods to use on the oxidized lignin. They envision that the new process could serve as a platform for obtaining high yields of various aromatics from lignin by varying the reaction conditions of the stepwise oxidations. **Stephen Ritter** , *C&EN*

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