

Spotlights on Recent JACS Publications

■ BUBBLE, BUBBLE, TOIL AND TROUBLE, NANOCRYSTALS ON THE DOUBLE

Researchers use tiny crystalline materials called nanocrystals in applications that include electronics, solar energy, and medicine. These tiny tools can be created almost like a soup, with carefully mixed and heated ingredients swirling in a liquid. To get just the right shape and composition, researchers need to ensure that specific crystal faces grow while others stay dormant. While adding components to “seal off” certain faces has worked to a degree, the nanocrystal soups could be of higher quality if researchers had a better idea of exactly how each variable affects growth. Kevin Ryan and colleagues perform experiments to tease out the contributions from each variable (DOI: 10.1021/ja501591n).

The team focuses on a crystal that contains copper, tin, and selenium as it is an important photovoltaic material and also because this material can easily adopt two different crystalline structures. The results show that fine-tuning the selection of ingredients, how they are combined, and the reaction temperatures greatly affects the shape and structure of the resulting particles. Much like a master chef laying out a recipe for the perfect dish, the researchers create a set of best protocols to obtain each crystal phase and shape composition.
Jenny Morber, Ph.D.

■ SMALL BONDS A BIG DEAL IN PEROVSKITE SOLAR CELLS

Inorganic–organic perovskites have attracted tremendous attention recently due to their interesting and technologically important properties, especially as new multiferroic and photovoltaic materials. Therefore, chemists have carefully studied these materials and learned that their properties are highly tunable, depending on their chemical composition and exact structure. A new type of perovskite material based on metal–organic frameworks (MOFs) has shown greater tunable properties than the more conventional metal oxides.

Now Zheshuai Lin, Anthony Cheetham, and co-workers probe the structures even further and find that two analogous MOF perovskites show markedly different properties, depending on how they hydrogen-bond (DOI: 10.1021/ja500618z). Both of the perovskites have similar $[\text{Mn}(\text{HCOO})_3]^-$ framework structures and are charge-balanced by guanidinium $[(\text{NH}_2)_3\text{C}]^+$ and azetidinium $[(\text{CH}_2)_3\text{NH}_2]^+$, respectively. The guanidinium compound (**1**) has six hydrogen bonds per amine cation, while the azetidinium compound (**2**) has two. As a result, compound **1** is more rigidly constrained, and this material is about twice as stiff and hard as compound **2**. However, **1** has lower thermal expansion and atomic displacement than **2**.

This work shows how small structural details can significantly influence the mechanical properties of hybrid perovskites (including important photovoltaic perovskite halides), which can in turn help chemists to better design and direct the physical properties of these important materials.

Leigh Krietsch Boerner, Ph.D.

■ BRINGING A NEW TWIST TO NANORIBBONS

While Moore’s law, the gold standard that predicts the improvement of performance in microprocessors, is reaching its limit with current manufacturing technology, molecular electronics may provide the means for continued improvement. Nanoribbons, predicted to be compatible with a larger and more diverse number of electronic applications than graphene, are promising molecular building blocks to fabricate various nanoscale semiconductor devices.

Now, Shengxiong Xiao, Fay Ng, Michael L. Steigerwald, Colin Nuckolls, and co-workers develop a novel bottom-up synthetic approach to electron-deficient nanoribbons from perylene-3,4,9,10-tetracarboxylic diimide (PDI), a five-ring polycyclic aromatic hydrocarbon derivative (DOI: 10.1021/ja503533y). Through careful design of precursors, the researchers are able to synthesize helical nanoribbons as PDI dimers, trimers, and tetramers in good yields with precise control.

Experimental and computational studies reveal the unique yet multifaceted attributes of these nanoribbons, including optical, electronic, and charge-transport properties. This work not only demonstrates a class of desirable nanomaterials for organic light-emitting diode and solar cell applications but also opens an avenue whereby a variety of graphene ribbons can be designed and developed.

Xin Su, Ph.D.

■ TRANSITION METAL COMPLEXES FOR QUANTUM COMPUTING

Although the notion of quantum computation has existed for four decades, successful implementation remains in its preliminary stages. Quantum computers use quantum-mechanical phenomena to perform calculations, such as the simulation of quantum behavior in chemical systems and factoring large semiprime numbers. Quantum computers also possess many advantages over classical computers; for example, they can achieve certain types of computations orders of magnitude faster. While digital computers encode data into binary digits known as bits, quantum computers use quantum bits, or qubits, and chemists are stepping up to create molecular candidates to fill this role.

Researchers led by Stephen Hill and Danna Freedman looked to empirically derive design principles for electronic spin-based qubits. Their team has analyzed two series of simple transition metal complexes to develop a set of design principles that should help guide the future development of an electron spin-based molecular qubit (DOI: 10.1021/ja5037397). As a proof-of-concept, it is notable that one of the complexes exhibits slow decoherence, which minimizes the chance of information loss, and rare Rabi oscillations, a phenomenon that is essential for establishing the viability of a species as a qubit. The aggregate of this research demonstrates one of the complexes, $[\text{Ru}(\text{C}_2\text{O}_4)_3]^{3-}$, to be a molecular qubit candidate and presents a beginning to a set of design principles that will

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help guide the synthetic development of electron spin-based molecular qubits for applications in quantum computing.

Christine Herman, Ph.D.

■ SOLAR CELL ABSORBS IN NEAR-IR, PUSHES THEORETICAL EFFICIENCY HIGHER

Perovskite solar cells are a promising type of photovoltaic cell—a device or material able to convert the energy of light into electricity—because they are inexpensive and easy to make and have a high conversion efficiency. Recent versions of these devices have conversion efficiencies of over 15% with high open-circuit voltages, a measure of the amount of power that is available from a solar cell. Theoretically, perovskite photovoltaic cells can have over 30% conversion efficiencies if they can utilize more of the electromagnetic spectrum, from the ultraviolet to the infrared. However, existing cells do not absorb well over 780 nm because they have larger band gaps, a property that correlates directly with electrical conductivity of a material.

To address this problem, Mercuri Kanatzidis and co-workers synthesize two perovskite solid solutions—methylammonium tin iodide and its lead analogue—that can efficiently absorb into the near-IR at 1050 nm (DOI: 10.1021/ja5033259). The researchers are able to achieve this result because the energy band gaps of mixed Pb/Sn compounds do not follow the expected linear trend. Instead, they have a narrower band gap of less than 1.3eV, which allows the low-energy absorption. The scientists study a series of the devices using different ratios of tin to lead and identify a perovskite material with the broadest light absorption, showing that near-IR absorption is possible and that higher efficiency solar cells could be achieved in the near future.

Leigh Krietsch Boerner, Ph.D.