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Spotlights on Recent *JACS* Publications

WIZARD HAT-SHAPED MOLECULE SIGNALS PROMISE TOWARD "WARPED" GRAPHENES

Spheres, tubes, hemispheres, and saddles are all well-known morphologies of nanographenes, which are made of polycyclic aromatic compounds. Their strained structures and curved π-surfaces often yield unusual and useful properties. Scientists have been interested in creating nanographenes through precisely controlled chemical synthesis, which allows modifying the electronic properties in a predictable manner. Now, researchers led by Hak-Fun Chow and Dietmar Kuck report the synthesis of a new curved polycyclic aromatic compound with an unprecedented wizard hat shape (DOI: 10.1021/jacs.6b05820).

The molecule, which is composed of a nonplanar tribenzotriquinacene derivative bearing three inner five-membered rings and three outer seven-membered rings, is created via a nonconventional Scholl-type oxidative cyclization, which is traditionally used to create six-membered rings. The team uses various analytical techniques to determine the molecule's crystallographic packing modes and both its optical and electronic properties. The hat-shaped molecule, which presents methoxy groups on its rim, has the potential to serve as a key intermediate in the synthesis of other extended cone-shaped nanographenes. The work demonstrates a significant step toward "warped" graphenes that may have intricate properties for applications in nanoscale electronics.

Christine Herman, Ph.D.

APPLICATIONS IN BIO-NANO SCIENCE: LOST IN TRANSLATION?

Bio-nano science is an area burgeoning with exciting discoveries, many of which carry promise for new medical treatments. However, as Frank Caruso and co-workers point out in a new Perspective, there is more that can be done to facilitate translation of research into real world applications and treatments (DOI: 10.1021/jacs.6b08673).

In the authors' opinion, research in this field should focus on clinical problems that need solving, in addition to developing new technologies. Focusing on advances in a stepwise manner by building research cumulatively could bring discoveries to the clinic more quickly. To accelerate discoveries, the authors advocate for more transparent science, including making sure that research is reliable and reproducible. Similarly, "dark data"—data generated through well-performed studies that are never published—should be made public. Finally, they suggest that bio-nano science research would benefit from a set of common standards on what details to report and a set format for doing so. These suggestions, the authors add, will lead to better fundamental knowledge in this field as well as improved clinical outcomes.

Christen Brownlee

FIRST SUCCESSFUL SYNTHESIS OF POLYBENZENE-LIKE MOF

Seventy years ago, a hypothetical purely carbon-based structure known as "cubic graphite" was proposed by J. Gibson, portraying the polymorph of three-coordinated (sp^2) carbon as both plausible and very stable (*J. Chem. Soc.*, DOI: 10.1039/JR9460000456). Since then, numerous efforts have been made to synthesize various forms of the material, but the first successful demonstration has only recently been reported by Pantelis Trikalitis, Mohamed Eddaoudi, and co-workers (DOI: 10.1021/jacs.6b08176).

The researchers take advantage of the precision of reticular chemistry—which uses secondary building units to direct the assembly of ordered frameworks—to bring about the assembly of hexagonal-shaped molecular organic and inorganic building blocks into crystals of a polybenzene–metal–organic framework, termed pbz-MOF-1. They find that the resulting material is highly porous, offering high gravimetric and volumetric methane uptake. These qualities highlight the material's potential for applications in gas storage and separation, catalysis, sensing, and drug release. The authors attribute this long-awaited success to the judicious selection of the proper primary and secondary building units and say that having the crystal structure information for this new generation of porous solids will provide new insights into how the material's structure correlates with its properties.

Christine Herman, Ph.D.

UNDERSTANDING THE MECHANISM OF CO_2 METHANATION

The main issue with fossil fuel combustion is the release of carbon dioxide into the atmosphere, which contributes to global warming. Recycling CO_2 into a fuel is a promising way to reduce the net production of CO_2. By reacting CO_2 with hydrogen obtained by, for example, light-driven water-splitting, one can produce methanol, methane, and syngas. These fuels can in turn power cars without generating additional CO_2, since the released CO_2 had previously been taken out of the atmosphere. The nickel-catalyzed Sabatier reaction, in which hydrogen reacts with CO_2 at moderate temperature, ~150 °C, is viewed as a promising route to alternative CO_2 utilization. However, how this catalyst works has eluded researchers up to now.

Miquel Salmeron and co-workers focus on the interaction of CO_2 with a nickel crystal surface (DOI: 10.1021/jacs.6b06939). Using X-ray photoelectron spectroscopy, they find that CO_2 first dissociates into CO and atomic oxygen on the Ni(111) surface, which is the crucial step for the hydrogenation. CO then is reduced to atomic carbon, followed by its hydrogenation to form methane.

Alexander Hellemans

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SIMILAR STRUCTURES, BIG DIFFERENCE IN PROPERTIES

Propynylidene (HC_3H) is one of the smaller and simpler hydrocarbons containing a conjugated chain of three carbon atoms linked to two hydrogen atoms at each end of the chain. Found as an intermediate in the combustion of hydrocarbons, and closely related to molecules observed in interstellar space, research has established that its geometry is close to a linear carbon chain whereby the central carbon atom is linked to the CH moieties by either two double bonds or one single and one triple bond. Both structures contribute in nearly equal amounts to the schizophrenic character of this molecule.

Robert McMahon and co-workers, who have previously investigated the geometric structure of propynylidene, now focus on dimethylpropynylidene ($CH_3C_3CH_3$ or MeC_3Me), where the two hydrogens in HC_3H have been substituted by methyl groups (DOI: 10.1021/jacs.6b07444). Computational methods and spectroscopic studies show that the molecule exists, just like its parent, HC_3H, in a quasilinear form. Electron paramagnetic resonance spectroscopy further reveals that the methyl substituents cause an unexpectedly large degree of spin polarization in the carbon chain. The molecule is less likely to form cyclic compounds in photochemical reactions than its parent because, upon irradiation with UV light, one of the methyl hydrogen atoms migrates to an adjacent carbon atom, precluding cyclization. The work offers valuable insight into the structure and behavior of small, highly unsaturated hydrocarbons relevant to astrochemistry and combustion.

Alexander Hellemans

LETTING THE SUNSHINE IN ON LOW-BANDGAP PEROVSKITE SOLAR CELLS

Yanfa Yan, Ren-Gen Xiong, Dewei Zhao, and co-workers report fabrication of novel low-bandgap tin−lead perovskite solar cells (PVSCs) with a power conversion efficiency (PCE) of 15% (DOI: 10.1021/jacs.6b08337).

Research on organic−inorganic lead halide PVSCs has led to steady improvement in the PCEs of these materials, giving them enormous promise in low-cost solar energy conversion. Tandem solar cells—stacks of one high-bandgap cell on top of a low-bandgap one—offer further efficiency improvement toward the capture of a broad range of the solar spectrum; however, most recent research and development has focused primarily on high-bandgap materials, leaving low-bandgap PVSCs under-explored. Yan, Xiong, Zhao, and their colleagues report a breakthrough in this area. They synthesize thin films that act as absorbers by combining formamidinium tin iodide with methylammonium lead iodide at different molar ratios. Perovskite cells using this material demonstrate low bandgap with high efficiency and high reproducibility. Moreover, the cells contain 60% less lead than traditional lead-based non-tandem PVSCs. The reduction in lead content and improved efficiency for a low-bandgap cell represent a significant step toward practical and "greener" tandem solar cells with inexpensive halide perovskite materials.

Christen Brownlee

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