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Spotlights on Recent *JACS* Publications

HYBRID METAL–ORGANIC CRYSTALS PROVIDE TUNABLE CATALYSIS

Metal–organic frameworks (MOFs) are materials composed of metal ions or clusters linked together, in an orderly fashion, by organic molecular "ropes". MOFs can be thought of as porous supercrystals, and their applications include gas storage and separation, drug delivery, and catalysis.

M. Ángeles Monge and colleagues synthesize and explore MOFs with identical structures but different metal ions in equivalent crystallographic sites (DOI: 10.1021/jacs.5b02313). After studying the effect of aluminum, gallium, and indium separately, the team creates "solid solution" MOF compounds in which In and Ga are both present within the MOF in equivalent crystallographic sites.

By tuning the ratios of the metal ions in these MOF solid solutions, the researchers find that they can control the MOF's catalytic activity in a common one-pot reaction for the formation of amino acids. Here, the MOF acts as a heterogeneous catalyst that allows precise tuning for desired products. The results demonstrate for the first time that the activity of a mixed-ion MOF catalyst can be controlled by varying the ratios of metals occupying the same crystallographic positions, revealing an entirely new strategy for multicomponent catalytic reactions.

Jenny Morber, Ph.D.

NANOSHEETS FOR GREENER NITROGEN FIXATION

Every living thing needs nitrogen. The air is filled with nitrogen, but the incredibly strong native triple bond renders the molecule in this form unusable for most organisms. Converting nitrogen in the atmosphere into an active state that living organisms can use—called nitrogen fixation—is one of chemistry's most kinetically challenging reactions.

The nitrogen fixation process currently employed to create crop fertilizers has helped to sustain a booming human population, but it requires high temperatures and pressures and iron catalysts, consumes 1–2% of the world's annual energy supply, and produces more than 2 tons of carbon dioxide per year. Yet plants easily fix nitrogen in the soil every day.

Inspired by Nature, Lizhi Zhang and colleagues present a nitrogen fixation approach that can proceed at room temperature and atmospheric pressure, in water, using visible light and very thin sheets of bismuth oxybromide (BiOBr) (DOI: 10.1021/jacs.5b03105). Oxygen vacancies within the layered BiOBr sheets provide binding sites for atmospheric nitrogen molecules. The vacancies, together with photoexcited electrons on the nanosheets, activate and reduce adsorbed nitrogen into reactive ammonia. Though the authors predict that this mild photocatalytic reduction is unlikely to replace traditional methods at present, the study may launch a less expensive, more environmentally friendly means to wrest usable nitrogen from the atmosphere.

Jenny Morber, Ph.D.

SOLID-STATE NMR HELPS SCIENTISTS GET THE FLU

Modern medicine still lacks drugs that directly treat the influenza virus, in part because scientists have not nailed down the molecular details of infection and replication. Now, Mei Hong and co-workers have figured out how one key molecule—the influenza M2 protein—shuttles protons into a virus, thereby lowering the internal pH and jumpstarting the viral replication machinery (DOI: 10.1021/jacs.5b02510).

The influenza M2 protein consists of three parts: the ectodomain, a cytoplasmic domain, and a transmembrane domain. In previous studies of the transmembrane domain, researchers analyzed the structure and function of histidine-37, which is responsible for ushering protons, and only protons, through the channel. However, compared to this fragment, the full-length protein has twice the proton shuttling capacity.

To understand this discrepancy, the researchers use solid-state NMR spectroscopy to measure the pK_a of histidine-37 in a construct that includes the transmembrane and cytoplasmic domains. The cytoplasmic domain boosts the pK_a of histidine-37, increasing its affinity for protons, which explains the enhanced shuttling. These results demonstrate that the cytoplasmic domain is an essential component of the shuttling mechanism and may be important in the development of drugs that target the influenza M2 protein.

Erika Gebel Berg, Ph.D.

BIOMIMETIC MOLECULAR SYSTEM THAT COUNTS PROTONS

Many biological molecules can recognize specific signals and respond to them by changing conformation. These reversible shape-shifts kick off an information relay through a series of other molecules. In a similar vein, researchers are interested in creating chemical mimics of shape-shifting biological molecules. The challenge in creating these chemical mimics, called foldamers, is making them as sophisticated as their biological counterparts in picking out and responding in a reversible fashion to specific signals in a complex mixture.

Now Jonathan Clayden and colleagues describe a helical foldamer that interacts with particular ligands in a mixture and shifts its shape as a result (DOI: 10.1021/jacs.5b03284). Depending on the surrounding pH and the ligands' pK_a values, the foldamer binds non-covalently to one specific ligand out of the choice of several.

The investigators demonstrate that the foldamer's selective interactions with its chosen ligand cause its helical structure to undergo a global conformational change. The foldamer keeps switching back and forth between its two helical conformations as it binds to different ligands at different pHs. The switching is detectable by NMR spectroscopy. The researchers say that the foldamer and its ligands represent a biomimetic chemical system that can act as a tunable and reversible molecular proton counter.

Rajendrani Mukhopadhyay, Ph.D.

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