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Spotlights

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Spotlights on Recent *JACS* Publications

GROWING MOLECULES IS LIKE CHILD'S PLAY

Imagine that you have built a repeating crystal-like structure out of tinker toys. At every corner is a round junction piece, and in between each of these is a slender red stick. Now imagine that you replace each of the shorter red sticks with a longer green stick. The spaces between the junctions grow, and the new structure has become a larger copy of its predecessor.

Nathaniel Rosi and colleagues perform a similar manipulation with molecules (DOI: 10.1021/ja403810k). In these crystal-like structures called metal−organic frameworks (MOFs), each "junction piece" is a metal ion, and each "stick" is an organic ligand. MOFs are useful for applications including catalysis, sensing, and gas storage because periodic spaces between the atoms make ideal storage compartments. Using a simple soak-and-bake technique, the authors build a MOF and then twice exchange smaller ligands with longer molecules to create progressively larger pores.

This "ligand exchange" strategy represents a potentially universal method for increasing MOF porosity and can create thermodynamically unfavorable structures that may be inaccessible by other methods. The MOFs created here contain interconnected mesoporous channels and, according to the authors, are some of the most porous MOFs ever recorded. **Jenny Morber, Ph.D.**

PUSHING THE LIMITS OF POLYMER ARCHITECTURES

A new class of self-assembling polymeric materials takes macromolecular design research to the next level. Researchers led by E. W. Meijer, Krzysztof Matyjaszewski, and Sergei S. Sheiko report the synthesis of a copolymer that self-assembles into a series of three-dimensional polymer architectures (DOI: 10.1021/ja400890v).

Initial reports of polymeric architectures involved the creation of relatively simple structures. Decades of progress in synthetic methods have now made it possible for researchers to exert more control over the size and shape of resulting structures. The team, wanting to see how far they could push the synthetic limits of controlling polymer architectures, prepares a series of polymer architectures composed of a new class of polymeric materials known as brush-nanoparticle block copolymers. The approach combines multiple previously reported polymerization techniques and deprotection strategies to generate structures with unique architectural features, observable with atomic force microscopy.

This study represents a significant advancement on the frontiers of polymer synthesis, molecular analysis, and three-dimensional polymer architectures, while simultaneously shedding light on the limitations of complex polymer architectures. **Christine Herman, Ph.D.**

MOLECULES SHAPE UP TO DETECT POLYOLS

Noninvasive techniques for imaging metabolites *in vivo* could lead to the development of improved disease diagnostics. Boronic acids are compounds with inherent affinity for polyhydroxylated compounds, or polyols, most notably for the detection of glucose in monitoring devices. To date, boronic acid-based metabolite sensing systems have relied on fluorescence quenching as a readout, which presents challenges for *in vivo* applications.

Now, researchers led by Jeffrey Bode demonstrate the first boronic acid-based sensor array for the noninvasive detection of metabolites (DOI: 10.1021/ja404981q). The team functionalizes a class of shape-shifting molecules, known as bullvalenes, with boronic acids. The resulting molecules undergo rapid structural remodeling rearrangements to yield a combinatorial mixture of hundreds or thousands of structural isomers. With this single synthetic modification, the team produces a multitude of structurally related sensors that have the ability to recognize and covalently bind to a wide scope of polyols, including carbohydrates, flavanols, and sialic acid. Upon binding, the equilibrium population of the bullvalene isomers shifts, which can be detected by ^{13}C NMR and visualized by an easy-to-recognize "barcode". Since NMR is a noninvasive technique with the potential for high-resolution imaging *in vivo*, this approach may lead to the development of new tools for medical imaging and diagnostics. **Christine Herman, Ph.D.**

SURPRISE! IONIC LIQUIDS DISRUPT ORDERED FILMS

A new report reveals surprising interactions between ionic liquids and polymerized films that were previously believed to be stable under all conditions. Researchers led by Bjorn Winther-Jensen discover that phosphonium ionic liquids disrupt and expand the ordered structure of in situ-polymerized films of poly(3,4-ethylenedioxythiophene), or PEDOT (DOI: 10.1021/ja405032c).

Thin films of conducting polymers, such as those that coat electrodes in electrochromic devices and dye-sensitized solar cells, are known to be highly ordered and presumed to be stable in the presence of various solvents. But the interactions between conducting polymer electrodes and the ionic liquid solutions that provide electrolytes had not been explored until now.

The team observes a distinctive swelling behavior that is accelerated in composites containing poly(ethylene glycol) and gives the material a boost in both $\pi-\pi^*$ absorption and capacitance without a change in resistance. The present study is limited to a small fraction of available ionic liquids but nonetheless reveals a need to develop more suitable and less disruptive ionic liquids for PEDOT and other conjugated polymers where significant swelling is not desirable. **Christine Herman, Ph.D.**

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