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Spotlights

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# Spotlights on Recent *JACS* Publications

## DECONSTRUCTING METAL−MOLECULE INTERACTIONS USING RAMAN SPECTROSCOPY

Interactions between metals and molecules are critical to determining the properties of materials, actions of catalysts, and behaviors of molecular electronic devices. To better understand metal−molecule interactions, researchers often use surface-enhanced Raman spectroscopy (SERS) because this spectroscopic method is highly sensitive and works in the hard-to-analyze infrared region of the electromagnetic spectrum. However the geometry and electronic properties of substrates used to study metal−molecule interactions by SERS can be unpredictable and difficult to control.

Now Katsuyoshi Ikeda and colleagues systematically analyze how geometric and electronic features influence metal−molecule interactions and SERS measurements (DOI: 10.1021/ja502008t). The investigators construct self-assembled monolayers of an organic molecule on platinum substrates that include various structural features on atomic and nanometer scales. They then analyze the SERS spectra from these features.

From their analyses, Ikeda and colleagues find, for example, that the SERS spectra are influenced by the metal crystal's orientation; the spectra show how atomic surface arrangements alter the adsorption geometries of the organic molecule to the platinum surface. Usually, such detailed information is nearly impossible to obtain from conventional SERS because the values from different surface structures are typically averaged. The investigators say their work will help researchers understand the individual contributions of geometric and electronic substrate effects on metal−molecule interactions.

**Rajendrani Mukhopadhyay,** Ph.D.

## DENDRIMER DNA TREE LIGHTS ITSELF UP

Feng Xuan and I-Ming Hsing report a new, nonlinear method for designing fluorescent dendritic nanostructures of DNA through a self-sustained, branching growth mechanism (DOI: 10.1021/ja502904s).

DNA dendrimers are branched nanostructures that are promising building blocks for use in nanotechnology and biomedical and materials science. Making them is complicated, though. So far their synthesis has required a sequential ligation of structural subunits. Hybridization chain reaction is a linear approach to initiate the successive assembly of DNA hairpins into polymeric DNA nanowires. Now Xuan and Hsing pioneer a nonlinear version of hybridization chain reaction to grow dendritic DNA nanostructures that has exponential growth kinetics similar to that of real-time polymerase chain reaction.

In the hairpin-free system, a trigger DNA initiates the progressive assembly of quenched double-stranded DNA substrates into a fluorescent dendrimer structure by continually branching growth. The dendrimer's fluorescence intensifies as it grows. The researchers verify the structure's morphology using atomic force microscopy. The method could be applied to make DNA dendrimers more efficiently for use in microarrays, biosensors, and drug delivery, among other applications.

**Deirdre Lockwood,** Ph.D.

## BETTER SILICON FOR SUN

Silicon is a nearly ideal material for solar cells. It is stable, durable, abundant, nontoxic, and easily manipulated. It would be perfect, if only it were better at converting energy from the sun. Today's commercial silicon solar cells suffer efficiencies barely topping 15−20%. This shortfall is largely due to the indirect band gap as well as differences between the solar energies that are best at popping out silicon's electrons, and those that the sun provides.

Julong He and colleagues develop six theoretical forms of silicon with direct or quasidirect band gaps that would more efficiently absorb and use solar energy (DOI: 10.1021/ja5035792). The researchers find that these structures should be stable at high temperatures and exhibit better optical properties than forms of silicon in current use. Because their proposed crystals absorb different frequencies, the authors envision stacked layers within solar cells to absorb wide-spectrum sunlight.

If such structures can be created, greater efficiencies would likely translate into solar energy at lower cost, and therefore wider adoption of solar to meet the world's energy needs. Currently, cost is a primary obstacle to large-scale acceptance of this clean, renewable energy source.

**Jenny Morber,** Ph.D.

## PROBING PROTEIN STRUCTURE WITH UVPD

Top-down proteomics studies characterize proteins by iterative fragmentation and analysis via mass spectrometry. Different fragmentation techniques have their own strengths and weaknesses, and ultraviolet photodissociation (UVPD) offers the benefit of relatively consistent fragmentation along the protein backbone. Kevin Pagel, Gert von Helden, and colleagues show the technique also can distinguish subtle structural differences (DOI: 10.1021/ja502994b).

The researchers use ion mobility mass spectrometry to resolve two distinct conformations of the +11 charge state of the model protein, ubiquitin. UVPD fragmentation of those conformations, which are identical in sequence and charge, reveals significantly different fragmentation patterns and efficiencies, mostly around proline-19, a difference the authors attribute, using both spectral data and molecular dynamics simulations, to cis−trans isomerization of the peptide bond N-terminal to that residue.

The data, the authors say, suggest UVPD is sensitive to protein structural variation. "Seen from a broader perspective, these data furthermore demonstrate the potential of conformer-selective UVPD to serve as tool for the structural analysis of proteins in the gas phase," they conclude.

**Jeffrey M. Perkel**

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