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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Spotlights on Recent *JACS* Publications

2D π-CONJUGATED POLYMERS: LARGER SIZE, SMALLER BAND GAP

A new computational study brings researchers one step closer to designing tailor-made polymers with desirable electronic properties. The study, performed by Rico Gutzler and Dmitrii Perepichka, sheds light on the relationship between the size of planar two-dimensional π-conjugated polymers and their semiconducting potential (DOI: 10.1021/ja408355p).

Due to a growing interest in 2D materials and their electronic properties, chemists are increasingly exploring new synthetic routes to create semiconducting organic analogues to graphene. To assist in this pursuit, the researchers performed density functional theory calculations to determine the structures and electronic properties of both theoretical and experimentally realized 2D π-conjugated polymers.

The team reports that, compared to their linear, 1D counterparts, 2D polymers that are grown in two directions as planar sheets have smaller band gaps, a quality that is favorable for most electronic device applications. Additionally, the band gap in 2D polymers decreases faster with the number of molecular repeat units in 2D than in 1D polymers. This information may help researchers in the field of band gap engineering design functional organic materials with desirable semiconducting and luminescent properties for applications ranging from optoelectronics to sensing.

Christine Herman, Ph.D.

SHINING A LIGHT ON PROTEIN DYNAMICS

Light can provoke changes in protein structure, which in turn can affect a cell's movement or gene expression. Now a team led by Peter J. Tonge and Stephen R. Meech uses high-speed spectroscopy to reveal how certain proteins change their structure on time scales ranging from 100 fs to 1 ms after the short pulse of light arrives (DOI: 10.1021/ja407265p).

Light is a useful tool for studying protein dynamics because its arrival at the protein is easier to control than other stimuli, such as small molecules. And unlike well-established X-ray studies, infrared observations do not require the proteins to be in crystalline form, so they offer a more natural glimpse of how proteins change their shape in real time.

In this study, the researchers bombard a bacterial protein that naturally responds to light and changing oxygen levels with pulses of blue light. Using a tool called time-resolved multiple probe spectroscopy, the team identifies a hierarchy of activity in the protein's structural changes: residues close to the site of light absorption respond first and then activate more remote parts of the protein. In a mutant version of the protein, the team finds that the response to light is short-circuited. The ability to observe a protein's dynamics across multiple time domains will help test and improve models of protein function and lead to the development of new tools for controlling gene expression with light, the authors say.

Lucas Laursen

NEW CLASS OF HYDROGELS FALLS APART WITH LIGHT

"Smart" biomaterials, which undergo a physical change in response to external stimuli, are of enormous interest to researchers in cellular and biomolecular engineering. A new class of photoresponsive hydrogels, designed by Yan Zhang and co-workers, represents a significant step toward the goal of controlling both the structure and assembly of cellular microenvironments (DOI: 10.1021/ja409000b).

The team synthesizes peptides modified with a small-molecule phototrigger, known as a biaryl-substituted tetrazole. The peptides self-assemble to form a hydrogel that can be used to culture cells in either a 2D or 3D environment. In the presence of UV light, the tetrazole-based phototrigger undergoes an intramolecular ligation that causes the hydrogel to partially disassemble, presumably because the new slightly tilted ring system interrupts the hydrophobic $\pi-\pi$ stacking.

To demonstrate the utility of the light-responsive hydrogels in biological applications, the researchers show that they can control the differentiation of a model cell line by using UV light to release a differentiation-inducing protein from within the hydrogel. Efforts to create photopatterned channels that induce different biological behaviors of cultured cells are currently underway, the researchers say.

Christine Herman, Ph.D.

BREAKING DNA, TWICE

A compelling therapeutic strategy for diseases characterized by out-of-control cell growth, like cancer and rheumatoid arthritis, is to kill the cells by inducing DNA damage. Numerous compounds damage DNA by breaking a single strand of the DNA double helix, but molecules that break both strands are more efficient damaging agents. Toward the design of compounds capable of inducing such double strand breaks, Marisa Taverna Porro and Marc Greenberg delineate a chemical pathway that leads to this deadly alteration (DOI: 10.1021/ja409513q).

The authors determine that, in the presence of oxygen, formation of a highly reactive free radical at a particular location within the DNA double-helix structure leads to a double strand break. Specifically, they find that the radical triggers breakage of the first strand, which generates a second radical. This second radical triggers the removal of a hydrogen atom from the double helix, which initiates breakage of the second strand.

These findings provide a starting point for the design of molecules that can produce double strand breaks for potential therapeutic applications. In addition, they may offer insight into the mechanisms by which certain natural products cause double strand breaks in DNA.

Eva J. Gordon, Ph.D.

Published: November 13, 2013

dx.doi.org/10.1021/ja411266n | *J. Am. Chem. Soc.* 2013, 135, 16745−16745