

Spotlights on Recent JACS Publications

ORGANIC PIGMENTS DO MORE THAN LOOK NICE

Though economies once depended on plant-based colorants like indigo, synthetic pigments are now ubiquitous and cheap. Synthetic pigments are used in printer ink, cosmetics, and food, and recently researchers have discovered that many pigments exhibit interesting semiconductor properties. Unfortunately, the same chemistry that keeps pigments stable in the printer and on a face makes them difficult to process into transistors and photovoltaic devices. With a series of clever chemical changes Wolfgang Heiss and colleagues transform insoluble commercial pigments into a solution of micro and nanocrystals ready for use in optical and electronic devices (DOI: 10.1021/ ja5073965).

Key to the process is the sequential addition and removal of chemical protecting groups and other small molecular components to selectively control solubility and the size and shape of the final crystals. Tests have shown that the products are stable and possess a range of useful optical and electronic properties. All of the pigments used in this work can be purchased at low cost from industrial suppliers, highlighting the method as a cheap, nontoxic, and environmentally friendly alternative to traditional techniques. The authors predict that this work might jumpstart a new generation of solution processed organic electronics.

Jenny Morber, Ph.D.

CATALYTIC PHAGE FINDING

Rein V. Ulijn, Hiroshi Matsui, and co-workers devise a method for creating phage—a type of virus that infects bacteria—that are capable of catalyzing the condensation and hydrolysis of amide bonds in water (DOI: 10.1021/ja509393p). This fundamental chemical transformation proceeds with a half-life of 300 years in the absence of a catalyst; thus methods to identify practical and efficient catalysts are needed.

The authors construct a phage display library of 10^9 dodecapeptides, wherein each virus displays five copies of a unique dodecapeptide sequence on its surface. Addition of nonself-assembling amino acid derivatives as reaction substrates enables screening for phage that can catalyze their condensation and hydrolysis. Key to the approach is that the product of the reaction spontaneously self-assembles, forming an insoluble aggregate that accumulates on the phage tip. This aggregation allows separation from noncatalytic phage by centrifugation. Catalytic phage can be amplified through infection of *E. coli*, enabling mass production.

This clever strategy has led to the discovery of seven phages capable of catalyzing the hydrolysis of amide bonds in aqueous solution. The dodecapeptides that distinguish the phages have no sequence homology, supporting this approach as a general method for the nonbiased discovery and production of phage with catalytic abilities.

ALKANE SOLVENTS: SMALL CHANGES CAN HAVE HUGE EFFECTS

Owing to their ability to stabilize or destabilize chemical species, solvents play a key role in a wide variety of thermodynamic and chemical events. A solvent's properties, including its polarity, acidity, and ability to form hydrogen bonds, determine the nature of solvent—solute interactions. Since aliphatic hydrocarbons, i.e., alkanes, interact minimally with their solutes, switching from one alkane solvent to another does not usually cause significant changes in the outcome of a chemical event.

Helical macromolecular scaffolds, however, are different from most solutes in their ability to amplify small local energy differences. To further investigate this phenomenon, researchers led by Michinori Suginome set out to create a helical scaffold that would be sensitive to otherwise unnoticeable solvent effects. In their new study, the team reports that a simple switch from a linear to a cyclic alkane solvent induces a solvent-dependent helix inversion in the polymer backbone of a class of molecules composed of poly(quinoxaline-2,3-diyl)s (DOI: 10.1021/ja509531t).

The solvent switch even causes the outcome of a highly enantioselective metal-catalyzed organic transformation asymmetric hydrosilylation—to be completely reversed with respect to the chirality of the final product. The researchers plan to next explore the origin and mechanism underlying this solvent-dependent helix inversion.

Christine Herman, Ph.D.

CARBON-FLUORINE FOR NITROGEN REPLACEMENT MAKES ORGANIC ELECTRONIC DEVICES MORE ROBUST

Organic electronic devices, such as field-effect transistors or photovoltaics for solar cells, must maintain their performance under various environmental conditions. Materials for such devices have traditionally been designed to optimize charge carrier mobilities and solar power conversion efficiencies, ahead of thermal stability. However, the manufacture and application of these materials also require that they keep their bulk functionality over a large temperature range for long-term durability.

With the goal of increasing the thermal stability of such materials, Guillermo Bazan and co-workers take a conjugated donor-acceptor molecule that they have previously shown performs well as an organic semiconductor, and swap out some of its nitrogen atoms with carbon-fluorine moieties (DOI: 10.1021/ja510088x). In four molecules of two different lengths, the researchers find that a higher degree of fluorination corresponds with greater bulk stability to temperature changes. This observation holds as the researchers incorporate their new molecules into thin-film field-effect transistor devices, where the longer and more fluorinated molecules result in materials that

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are both more thermally resistant and better functioning for charge transport.

These fluorinated materials, and especially the correlation between the degree of fluorination and performance, hold promise for the future design of improved organic solar cell devices.

Leigh Krietsch Boerner, Ph.D.

REPORTER MOLECULE SENSES STRESS WHERE POLYMERS AND NANOPARTICLES MEET

A mechanophore—a molecule activated by stress or strain can be useful when studying mechanical or chemical phenomena like friction, lubrication, and degradation. With an understanding of these properties, researchers can predict or engineer the "weakest link" to break selectively and eventually apply the knowledge to functional design. To this end, mechanophores are typically placed between twin polymer chains. Now, Jeffrey Moore and his team use a known mechanophore to investigate stresses at an organic—inorganic interface (DOI: 10.1021/ja509949d).

The researchers note that despite the prevalence of composite materials in industrial applications, which include aircraft bodies, solar panels, medical equipment, and many more, the chemical and mechanical interactions at these interfaces are largely unexplored. The team anchors a small, stress-activated molecule between a silica nanoparticle and a linear polymer chain. They find that this interfacial mechanophore behaves similarly to traditionally placed molecular sensors between polymer chains.

This work represents an important early step in directing and sensing stress in composite materials and serves as an entryway into the study of mechanochemical events in these materials. In addition to the clear basic science benefits, a potential application of this work is in the design and construction of self-sensing, self-repairing composite materials. Jenny Morber, Ph.D.