



Nano Focus

Click coupling conjugated polymers to semiconductor nanorods

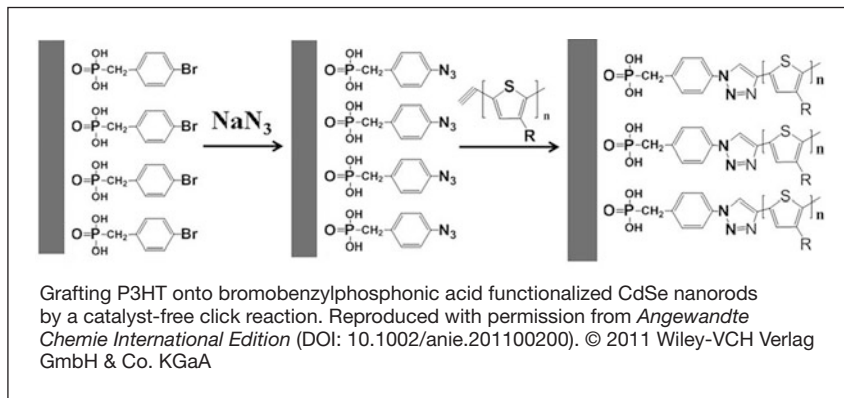
Conjugated polymers combine flexibility and ease of processing with good optoelectronic properties which make them ideal for organic devices such as solar cells. Introducing quantum dots as electron acceptors in such devices can improve electron mobility, but blends with polymers are often hampered by phase separation and slow charge transfer at the inorganic–organic interface. In the April edition of *Angewandte Chemie International Edition* (DOI: 10.1002/anie.201100200; p. 3818), Z. Lin and co-workers at Iowa State University and Georgia Institute of Technology describe a simple “click” reaction for chemically bonding these two materials and facilitating the electronic interaction between them.

Their research employs the widely studied conjugated polymer poly(3-hexylthiophene) (P3HT), and semiconductor nanorods of cadmium selenide. Elongating one dimension of quantum dots to form nanorods has proved to be beneficial in many device applications because of reduced electron conduction pathways and an extended range of absorbed wavelengths. The researchers promote the growth of their CdSe

particles into 40-nm long rods by using bromobenzylphosphonic acid as a surface passivating ligand. The acid group binds to the crystal surface while the terminating bromines are left available for further reaction with NaN_3 to convert them to azides. These groups can then be coupled to ethynyl-terminated P3HT through a Huisgen cycloaddition reaction which belongs to the direct, catalyst-free, bond-forming reactions

charge transfer between the two materials is evident from almost complete quenching of the polymer fluorescence and much faster fluorescence lifetime for the chemically bound composite.

The use of a cycloaddition to couple conjugated polymers to the surface of a nanocrystal provides an effective alternative to more established ligand-exchange methods, and results in over twice the density of attached polymers. Chemi-



of click chemistry. The success of this step was confirmed by proton nuclear magnetic resonance of the coupled ligand and polymer after detaching them from the crystal surface.

Electron microscopy of the resulting composite reveals that there is no phase separation, and therefore a much larger interface than for an equivalent physically blended material. Efficient

cal bonding appears to considerably enhance charge separation at the material interface, and is therefore promising for hybrid solar cells. This research demonstrates the potential of click chemistry when applied to materials, allowing even further scope for chemical tailoring to device applications.

Tobias Lockwood

Study helps explain superconducting behavior of metallic, insulating pnictides

Researchers Q. Si and R. Yu of Rice University and J.-X. Zhu of Los Alamos National Laboratory have offered one of the first theoretical explanations of how two dissimilar types of high-temperature superconductors behave in similar ways.

Reporting in the May 6th issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.106.186401), the research team describes how the magnetic properties of electrons in two dissimilar fami-

lies of iron-based pnictides could give rise to superconductivity. One of the parent families of pnictides is a metal— $(\text{Ca}, \text{Ba}, \text{Sr})\text{Fe}_2\text{As}_2$ —and was discovered in 2008; the other is an insulator— $(\text{K}, \text{Tl})_{1-x}\text{Fe}_{2-x}\text{Se}_2$ —and was discovered in late 2010. Experiments have shown that each material, if prepared in a particular way, can become a superconductor at roughly the same temperature. This has left theoretical physicists scrambling to determine what might account for the similar behavior between such different compounds.

Lead author Q. Si said that the explanation is tied to subtle differences in the way iron atoms are arranged in each

material. The pnictides are laminates that contain layers of iron separated by layers of other compounds. In the newest family of insulating materials, iron atoms are selectively removed, leaving behind an orderly pattern of vacancies in the iron layer.

Si suspected that the explanation for the similar behavior between the new and old compounds could lie in the collective way that electrons behave in each compound as they are cooled to the point of superconductivity. His prior work had shown that the arrangement of the iron atoms in the older materials could give rise to collective behavior of the magnetic moments, or spins, of electrons.

These collective behaviors, or quasi-localizations, have been linked to high-temperature superconductivity in both pnictides and other high-temperature superconductors.

“We found that ordered vacancies enhance the tendency of the electrons to lock themselves some distance away from their neighbors in a pattern that physicists call ‘Mott localization,’ which gives rise to an insulating state,” Yu said. “This is an entirely new route toward Mott localization.”

By showing that merely creating ordered vacancies can prevent the mate-

rial from being electrical conductors like their relatives, the researchers concluded that even the metallic parents of the iron pnictides are close to Mott localization.

“What we are learning by comparing the new materials with the older ones is that these quasi-localized spins and the interactions among them are crucial for superconductivity, and that’s a lesson that can be potentially applied to tell experimentalists what is good for raising the transition temperature in new families of compounds,” Zhu said.

One impediment to the broader use of high-temperature superconductors has

been the struggle to precisely explain what causes them to become superconductors in the first place. The race to find that has been called the biggest mystery in modern physics.

“The new superconductors are arguably the most important iron-based materials that have been discovered since the initial discovery of iron pnictide high-temperature superconductors in 2008,” Si said. “Our theoretical results provide a natural link between the new and old iron-based superconductors, thereby suggesting a universal origin of the superconductivity in these materials.”

Quantum phase transition revealed in ultrathin films

Like atomic-level bricklayers, I. Božović from Brookhaven National Laboratory, G. Dubuis from Ecole Polytechnique Federale de Lausanne, and their colleagues are using a precise atom-by-atom layering technique to fabricate an ultrathin transistor-like field effect device to study the conditions that turn insulating materials into high-temperature superconductors. The technical break-through, which is described in the April 28th issue of *Nature* (DOI: 10.1038/nature09998; p. 458), could lead to advances in understanding high-temperature superconductivity.

“Understanding exactly what happens when a normally insulating copper-oxide material transitions from the insulating to the superconducting state is one of the great mysteries of modern physics,” said Božović, lead author on the study.

One way to explore the transition is to apply an external electric field to increase or decrease the level of doping and see how this affects the ability of the material to carry current. But to do this in copper-oxide (cuprate) superconductors, one needs extremely thin films of perfectly uniform composition—and electric fields measuring more than 10^9 V m^{-1} .

Božović’s group has employed molecular beam epitaxy (MBE) to uniquely

create such perfect superconducting thin films one atomic layer at a time, with precise control of each layer’s thickness. Recently, they have shown that in such MBE-created films, even a single cuprate layer can exhibit undiminished high-temperature superconductivity.

Now, the researchers have applied the same technique to build ultrathin superconducting field effect devices that allow them to achieve charge separation, and thus electric field strength, for these critical studies.

These devices are similar to the field-effect transistors (FETs) that are the basis of modern electronics, in which a semiconducting material transports electrical current from the source to a drain electrode. FETs are controlled by a gate, positioned above the source–drain channel—separated by a thin insulator—which switches the device on or off when a particular gate voltage is applied to it.

But because no known insulator can withstand the high fields required to induce superconductivity in the cuprates, the standard FET scheme does not work for high-temperature superconductor FETs. Instead, the researchers used electrolytes to separate the charges.

In this setup, when an external voltage is applied, the electrolyte’s positively charged ions travel to the negative electrode and the negatively charged ions travel to the positive electrode. But when the ions reach the electrodes, they abruptly stop, as though they have hit a

brick wall. The electrode “walls” carry an equal amount of opposite charge, and the electric field between these two oppositely charged layers can exceed the 10^9 V m^{-1} goal.

The result is a field effect device in which the critical temperature of a prototype high-temperature superconductor compound (lanthanum-strontium-copper-oxide) can be tuned by as much as 30 K, which is about 80% percent of its maximal value—almost 10 times more than the previous record.

The researchers have now used this enhanced device to study some of the basic physics of high-temperature superconductivity.

One key finding is that as the density of mobile charge carriers is increased, their cuprate film transitions from insulating to superconducting behavior when the film sheet resistance reaches 6.45 k Ω . This is exactly equal to the Planck quantum constant divided by twice the electron charge squared. Both the Planck constant and electron charge are atomic units—the minimum possible quantum of action and of electric charge, respectively, established after the advent of quantum mechanics early in the last century.

“It is striking to see a signature of clearly quantum-mechanical behavior in a macroscopic sample (up to millimeter scale) and at a relatively high temperature,” Božović said. Most people associate quantum mechanics with character-