

Nano Focus

Molecular ordering phenomenon found at interface between liquids and solids

As part of the quest to form perfectly smooth single-molecule layers of materials for advanced energy, electronic, and medical devices, researchers at Brookhaven National Laboratory have discovered that the molecules in thin films remain frozen at a temperature where the bulk material is molten. Thin molecular films have a range of applications extending from organic solar cells to biosensors, and understanding the fundamental aspects of these films could lead to improved devices.

The study, which appears in the April 1st issue of *Physical Review Letters* (DOI: 10.1103/PhysRevLett.106.137801), is the first to directly observe “surface freezing” at the buried interface between bulk liquids and solid surfaces.

“In most materials, you expect that the surface will start to disorder and

eventually melt at a temperature where the bulk remains solid,” said physicist Ben Ocko, who collaborated on the research with scientists from the European Synchrotron Radiation Facility (ESRF), in France, and Bar-Ilan University, in Israel. “This is because the molecules on the outside are less confined than those packed in the deeper layers and much more able to move around. But surface freezing contradicts this basic idea. In surface freezing, the interfacial layers freeze before the bulk.”

In the early 1990s, two independent teams made the first observations of surface freezing at the vapor interface of bulk alkanes, organic molecules similar to those in candle wax that contain only carbon and hydrogen atoms. Surface freezing has since been observed in a range of simple chain molecules and at various interfaces between them.

“The mechanics of surface freezing are still a mystery,” said Bar Ilan scientist Moshe Deutsch. “It’s puzzling why alkanes and their derivatives show this unusual effect, while virtually all other materials exhibit the opposite, surface melting, effect.”

In the most recent study, the researchers discovered that surface freezing also occurs at the interface between a liquid and a solid surface. In a temperature-controlled environment at Brookhaven’s National Synchrotron Light Source and the

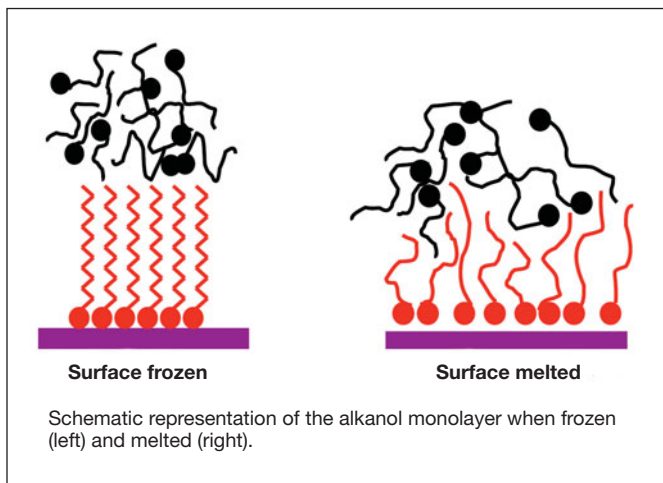
ESRF, the research group made contact between a piece of highly polished sapphire surface and a puddle of liquid alkanol. The researchers shot a beam of high-intensity x-rays through the interface and by measuring how the x-rays reflected off the sample, the group revealed that the alkanol molecules at the sapphire surface behave very differently from those in the bulk liquid.

According to ESRF scientist Diego Pontoni, “Surprisingly, the alkanol molecules form a perfect frozen monolayer at the sapphire interface at temperatures where the bulk is still liquid.” At sufficiently high temperatures, about 30°C above the melting temperature of the bulk alkanol, the monolayer also melts.

The temperature range over which this frozen monolayer exists is about 10 times greater than what is observed at the liquid-vapor interfaces of similar materials. According to Alexei Tkachenko, a theoretical physicist who works at Brookhaven’s Center for Functional Nanomaterials, “The temperature range of the surface-frozen layer and its temperature-dependent thickness can be described by a very simple model that we developed. What is remarkable is that the surface layer does not freeze abruptly as in the case of ice, or any other crystal. Rather, a smooth transition occurs over a temperature range of several degrees.”

Ocko said, “These films are better ordered and smoother than all other organic monolayer films created to date.”

Deutsch said, “The results of this study and the theoretical framework which it provides may lead to new ideas on how to make defect-free, single molecule-thick films.”



Energy Focus

Why strongly photoluminescent polymers make poor solar cells

At first glance, the semiconducting polymers used in organic light-emitting diodes and photovoltaics may seem to require similar properties, and yet materials which work well for one

application are often unsuitable for the other. Highly photoluminescent polymers such as polyfluorenes have long exciton lifetimes which should aid charge separation in an organic solar cell, but instead tend to give poor efficiencies. Recent work by Y.W. Soon and J.R. Durrant of Imperial College London and their co-workers suggests that one cause of this discrepancy may be a fast

energy transfer mechanism which competes with electron transfer to the acceptor material.

The group’s article in the online edition of *Chemical Science* (DOI: 10.1039/c0sc00606h) compares the photophysics of photovoltaic devices made from blends of the electron acceptor [6,6]-phenyl C61 butyric acid methyl ester (PCBM) and either of two indenofluorene-based poly-

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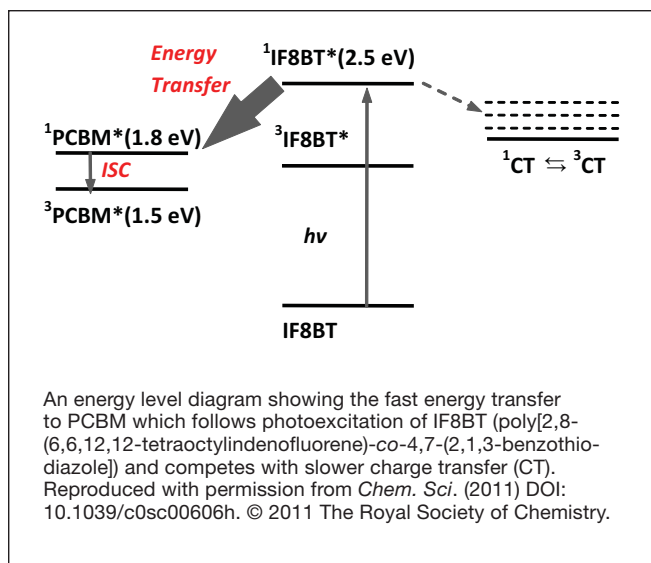
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mers. One of the polymers (an indenofluorene analogue of F8BT) shows no photovoltaic activity, while the other achieves reasonable power conversion efficiencies of up to 1.9%. The photoluminescence spectrum of the ineffective blend shows emission from a PCBM singlet exciton which is not present for

the latter superior polymer and suggests that energy transfer to the acceptor material is taking place. Given the strong photoluminescence from this polymer and its larger degree of overlap with the absorption spectrum of PCBM, there should indeed be fast Förster resonant energy transfer

PCBM exciton which, instead of generating a current, either relaxes to the ground state or crosses to a triplet state. A photocurrent could nonetheless be generated from this process if, in reverse fashion, the hole generated in the highest occupied molecular orbital (HOMO) of the PCBM were to hop to the HOMO of the polymer. For this polymer it seems that there is not enough energy remaining in the PCBM exciton to drive this process, but it is likely that hole transfer is responsible for photocurrents generated in other polymers which show strong photoluminescence toward the blue end of the spectrum.

The research goes a long way toward explaining the difficulties of using intensely photoluminescent polymers in organic solar cells and provides an important clue for designing photovoltaics that absorb blue light. Polymers for this purpose would benefit from having weakly emissive excitons that do not favor the wasteful energy transfer.

Tobias Lockwood

between the two materials.

For a photocurrent to be generated in the blend, an electron excited in the polymer has to be transferred to the PCBM and from there to an electrode. In the poorly performing poly-indenofluorene this process is slow compared to a transfer of the electron's energy to create a

Nano Focus

Organic ligands encapsulating catalytic nanoparticles improve monodispersity of vertically aligned carbon nanofibers

Regular arrays of vertically-aligned carbon nanofibers are actively sought: Due to their anisotropy and high surface area-to-volume ratio, they could be useful in many areas in nanotechnology. They can be grown from catalyst nanoparticles deposited on a substrate. Fibers with monodisperse diameters above 100 nm can be grown from dewetted catalyst thin films. For diameters below 100 nm, electron beam lithography is very successful, but the cost of this technique is an obstacle for commercialization. Alternatively, for these sizes, chemically synthesized nanoparticles can be used as seeds for nanofiber growth. M.F. Sarac, R.M. Wilson, A.V. Melechko, J.B. Tracy from North Carolina State University, K.L. Klein from the National Institute of Standards

and Technology, and their colleagues show the influence of the ligands capping Ni catalyst nanoparticles for obtaining monodisperse, regular arrays of vertically-aligned nanofibers with diameters up to 100 nm.

As reported in the March 16th online edition of *ACS Applied Materials & Interfaces* (DOI: 10.1021/am101290v),

the researchers compared nanofibers grown by plasma-enhanced chemical vapor deposition. The seeds were Ni catalyst nanoparticles, either capped by organic ligands (trioctylphosphine and oleylamine), or after ligand removal with UV-ozone treatment. The fibers obtained from ligand-capped nanoparticles are monodisperse of diameter and

