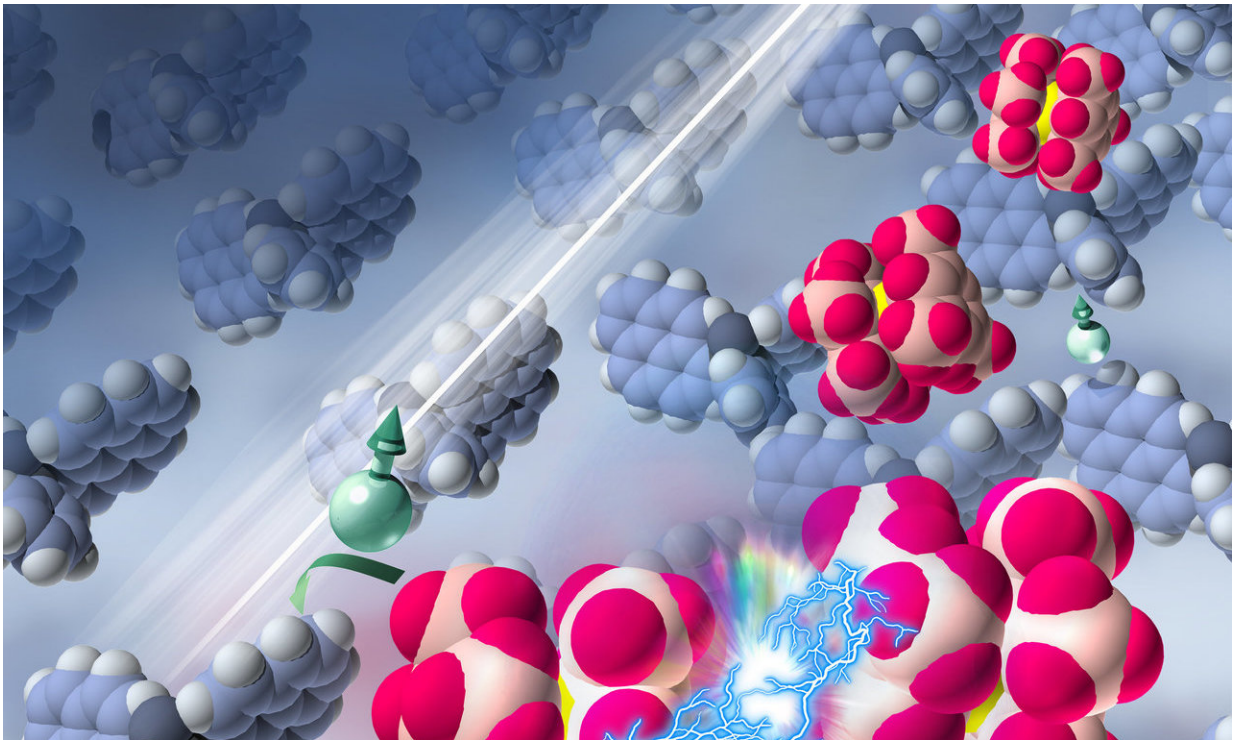


Breakthrough could launch organic electronics beyond cell phone screens

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Researchers used ultraviolet light to excite molecules in a semiconductor, triggering reactions that split up and activated a dopant Credit: Jing Wang and Xin Lin

A discovery by an international team of researchers from Princeton University, the Georgia Institute of Technology and Humboldt University in Berlin points the way to more widespread use of an

advanced technology generally known as organic electronics.

The research, published Nov. 13 in the journal *Nature Materials*, focuses on organic semiconductors, a class of materials prized for their applications in emerging technologies such as flexible electronics, [solar energy conversion](#), and high-quality color displays for smartphones and televisions. In the short term, the advance should particularly help with [organic light-emitting diodes](#) that operate at high energy to emit colors such as green and blue.

"Organic semiconductors are ideal materials for the fabrication of mechanically flexible devices with energy-saving low temperature processes," said Xin Lin, a doctoral student and a member of the Princeton research team. "One of their major disadvantages has been their relatively poor electrical conductivity, which leads to inefficient devices with a shorter operating lifetime than required for commercial applications. We are working to improve the electrical properties of organic semiconductors to make them available for more applications."

Semiconductors, typically made of silicon, are the foundation of modern electronics because engineers can take advantage of their unique properties to control electrical currents. Among many applications, semiconductor devices are used for computing, signal amplification and switching. They are used in energy-saving devices such as light-emitting diodes and devices that convert energy such as solar cells.

Essential to these functionalities is a process called doping, in which the semiconductor's chemical makeup is modified by adding a small amount of chemicals or impurities. By carefully choosing the type and amount of dopant, researchers can alter semiconductors' electronic structure and electrical behavior in a variety of ways.

In their recent *Nature Materials* article, the researchers describe a new

approach for greatly increasing the conductivity of organic semiconductors, which are formed of carbon-based molecules rather than silicon atoms. The dopant, a ruthenium-containing compound, is a reducing agent, which means it adds electrons to the [organic semiconductor](#) as part of the doping process. The addition of the electrons is the key to increasing the semiconductor's conductivity. The compound belongs to a newly-introduced class of dopants called dimeric organometallic dopants. Unlike many other powerful reducing agents, these dopants are stable when exposed to air but still work as strong electron donors both in solution and solid state.

Seth Marder and Steve Barlow from Georgia Tech, who led the development of the new dopant, called the ruthenium compound a "hyper-reducing dopant." They said it is unusual, not only its combination of electron donation strength and air stability, but in its ability to work with a class of organic semiconductors that have previously been very difficult to dope. In studies conducted at Princeton, the researchers found that the new dopant increased the conductivity of these semiconductors about a million times.

The ruthenium compound is a dimer, which means it consists of two identical molecules, or monomers, connected by a chemical bond. As is, the compound is relatively stable and, when added to these difficult-to-dope semiconductors, it does not react and remains in its equilibrium state. That posed a problem because to increase the conductivity of the organic semiconductor, the ruthenium dimer needs to split and release its two identical monomers.

Lin, the Princeton doctoral student who was lead author of the Nature Materials article, said the researchers looked for different ways to break up the ruthenium dimer and activate the doping. Eventually, he and Berthold Wegner, a visiting graduate student from the group of Norbert Koch at Humboldt University, hit upon adding energy by irradiating with

ultraviolet light, which effectively excited molecules in the semiconductor and initiated the reaction. Under exposure to the light, the dimers split into monomers, and the conductivity rose.

After that, the researchers made an interesting observation.

"Once the light is turned off, one might naively expect the reverse reaction to occur" and the increased conductivity to disappear, Marder said in an email. "However, this is not the case."

The researchers found that the ruthenium monomers remained isolated in the semiconductor _ increasing conductivity _ even though thermodynamics should return the molecules to their original configuration as dimers. Antoine Kahn, a Princeton professor who leads the research team, said the physical layout of the molecules inside the doped semiconductor provides a likely answer to this puzzle. The hypothesis is that the monomers are scattered in the semiconductor in such a way that it is very difficult for them to return to their original configuration and re-form the ruthenium dimer. To reform, he said, the monomers must be facing in the correct orientation, but in the mixture they remain askew. So, even though thermodynamics shows that dimers should reform, most never snap back together.

"The question is why aren't these things moving back together into equilibrium," said Kahn, the Stephen C. Macaleer '63 Professor in Engineering and Applied Science. "The answer is they are kinetically trapped."

In fact, the researchers observed the doped [semiconductor](#) for over a year and found very little decrease in the electrical conductivity. Also, by observing the material in [light-emitting diodes](#) fabricated by the group of Barry Rand, an assistant professor of electrical engineering at Princeton and the Andlinger Center for Energy and the Environment, the

researchers discovered that doping was continuously re-activated by the light produced by the device.

The light activates the system more, which leads to more light production and more activation until the system is fully activated, Marder said. "This alone is a novel and surprising observation."

More information: Xin Lin et al, Beating the thermodynamic limit with photo-activation of n-doping in organic semiconductors, *Nature Materials* (2017). [DOI: 10.1038/nmat5027](https://doi.org/10.1038/nmat5027)

Provided by Princeton University

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