SCIENTIFIC HIGHLIGHT

Beating the thermodynamic limit with photo-activation of n-doping in organic semiconductors using "hyper-reductants"

Doping of semiconductors is a key process for controlling the materials' charge carrier density, which directly impacts the electrical conductivity. Electronic and optoelectronic devices used in information, communication, energy conversion, and energy storage technologies rely on precise and efficient doping, i.e., the admixture of a small amount of a doping agent into the semiconductor.

However, n-type doping of organic semiconductors – electron transfer from the dopant to the semiconductor – is notoriously difficult as the molecular dopants employed presently are highly sensitive to ambient exposure, upon which they react with water and oxygen and are rendered inactive.

In an article that just appeared in *Nature Materials*, a team of researchers from the Georgia Institute of Technology, the Helmholtz-Zentrum Berlin, Humboldt-Universität zu Berlin, and Princeton University demonstrates a new approach towards n-doping of organic semiconductors, which allows bypassing the dopant sensitivity to the ambient and simultaneously enables doping organic electron transport materials that have been out of reach for n-doping so far.

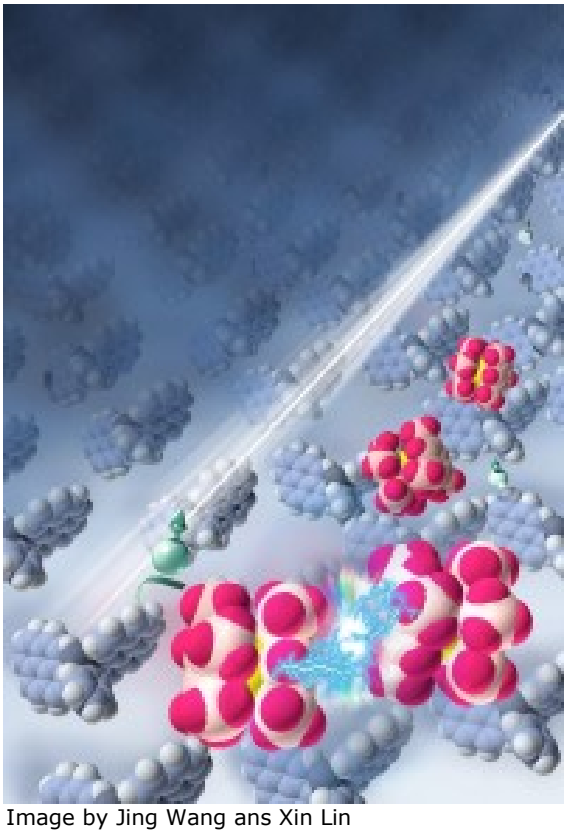

Image by Jing Wang ans Xin Lin

The first step of innovation lies in chemically connecting two organometallic molecular dopants in a dimer that is stable even in air, with reduced ability to dope organic electron transport semiconductors. Consequently, when mixing these into the organic semiconductor, nothing happens at first.

The revolutionary step now involves illuminating the mixture with light. A dimer and a semiconductor molecule in immediate proximity absorb a photon, the dimer can dissociate and unfold the full doping power

of each dopant in a multi-step process. "By this optical activation of dopants, we could enhance the conductivity of organic electron transport materials by five orders of magnitude. This boosts the efficiency of organic light emitting diodes and solar cells, using rather simple and technologically relevant processing." says Prof. Antoine Kahn from Princeton University, who coordinated the project.

The choice of the article's title is explained by Prof. Seth Marder from Georgia Tech: "This doping is actually beyond the thermodynamic limit of what the dopant should be able to do, thus once the light is turned off one might naively expect the reverse reaction to occur (rapidly, within seconds perhaps) and the conductivity increase to disappear. However, this is not the case. The reason for this is that the doping process involves multiple steps, and the back-reaction to the starting system involves many uphill intermediate steps creating a kinetic barrier, thus the reverse reaction is extremely slow." Indeed, no indications of a loss in conductivity upon light-activation after hundreds of hours were found. For these reasons, the compounds are referred to as "hyper-reductants".

The fact that the team demonstrated the beneficial effect of their doped electron transport semiconductors in highly efficient light emitting diodes underlines the huge potential of this approach in device applications. "We believe that our work enables simple processing of n-doped organic semiconductors in numerous device architectures, where the critical step - doping activation - can take place after standard device encapsulation. This will contribute substantially to improved device lifetime and in some case simplify device fabrication." notes Prof. Norbert Koch from Humboldt-Universität, member of **IRIS Adlershof**. The work was part of a project within the strategic partnership program of Princeton University and Humboldt-Universität.

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