ORGANIC SEMICONDUCTORS

Beyond 100% doping efficiency

A single dopant molecule can exchange more than one charge with the hosting polymer semiconductor, doubling the maximum doping efficiency achievable.

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Adding impurities to semiconductors to control their electronic properties – a process known as doping – is a key ingredient that contributed to the rapid development of integrated circuits that we witnessed in the last decades. In fact, most of the electronic and optoelectronic devices based on inorganic or organic materials, from silicon based transistors to organic light-emitting diodes[1], rely on stacks of materials having an excess of negative or positive charges (called n- and p-doped materials, respectively) to optimize their performance. When doping inorganic and organic semiconductors, both seem to follow very similar fundamental principles, but are remarkably different in their microscopic details. One of the most impressive consequences of such differences is now described in a recent article by David Kiefer and co-workers in *Nature Materials:*[2] in organic semiconductors, a single dopant (the impurity added to the material) can contribute more than one charge carrier to the host semiconductor, reaching a doping efficiency higher than 100%.

Ever since their early days, polymer or molecular semiconductors were doped.[3] Whereas first doping experiments were performed by exposing the semiconductor to oxidizing or reducing gases, using larger molecular dopants resulted in a doped semiconductor with a much higher stability.[4] However, surprisingly, the doping efficiency observed in these systems was low – often in the range of only 5-10%.[5] The reason for the low doping efficiency remained nebulous. It was argued that the dopant is readily ionized and will easily transfer a charge carrier to the host semiconductor. Still, Coulomb interactions will keep the ionized dopant and the oppositely charged electron/hole together, meaning that the generated charge carrier is not free and does not contribute to charge transport.

More recently, a consistent and complete understanding of organic doping began to emerge,[6–8] leading also to increases in the observed doping efficiency, reaching values close to 100%.[9] Still, although not explicitly stated, it was always assumed that every dopant can only contribute one charge carrier to its host. This assumption is in line with inorganic semiconductors, where Coulomb repulsion between two equal charges localized on the same dopant will increase the activation energy of doping to high enough levels that make a double ionization of the dopant impossible.

Kiefer and colleagues have now shown that this assumption is not correct for the p-doping of polymer semiconductors (Fig.1a). In fact they demonstrated that, as long as the ionization energy (IE in Fig.1b) of the host polymer is smaller than the electron affinity of the already negatively charged dopant EA^-, forming dianions — that is, accepting a second negative charge in the dopant — becomes energetically favorable. This corresponds to an ionization efficiency of 200%. Not only are almost all the dopants doubly ionized, but also most of the generated charge carriers contribute to charge transport, leading to a doping efficiency of 170% at low doping concentrations. In fact, using results from Monte-Carlo simulations,[8] the researchers argued that the separation of the doping process in two distinct steps – ionization and separation of the oppositely charged dopant/hole pair – is an oversimplification. At large doping concentrations, the “free” holes are never truly free, but are always within the capture radius of the Coulomb potential of the dopant molecule. Nevertheless, a large fraction of these holes contributes to charge transport.

Kiefer and colleagues systematically investigated a series of dopant/host combinations. As expected, they found that bithiophene-thienothiophene based copolymers with an IE of less than 5 eV, e.g. the polymer p(g42T-TT),[10] work well, whereas similar polymers with a larger IE (for instance the widely studied PBTTT, having IE~5.2 eV) do not allow dianion formation. Examples for dopants used in the experiments are F6TCNNQ (EA^-=4.8 eV) and F4TCNQ (4.7 eV), which both have an EA^- large enough to dope p(g42T-TT) twice. In contrast, F2TCNQ has a much lower EA^- and is not able to receive two electrons from the host materials.

Looking forward, we can expect that these new design rules may be applied to other classes of organic semiconductors - in particular to small molecular semiconductors. These results also suggest that dianions might have already been formed in previously studied systems, which will make it necessary to revisit some of the earlier data.

Most importantly, reaching a higher doping efficiency will allow researchers to reduce the concentration of dopants in the semiconductor. Adding impurities to the organic semiconductor almost inevitably disturbs the nanostructure of the semiconductor, usually reducing the charge carrier mobility. Being able to minimize the disruption of the host material crystallinity by halving the density of dopant atoms will therefore present an important step toward the use of doping not only in organic optoelectronic devices such as OLEDs or organic solar cells, but in organic field-effect transistors, organic thermoelectrics and organic bioelectronics as well.

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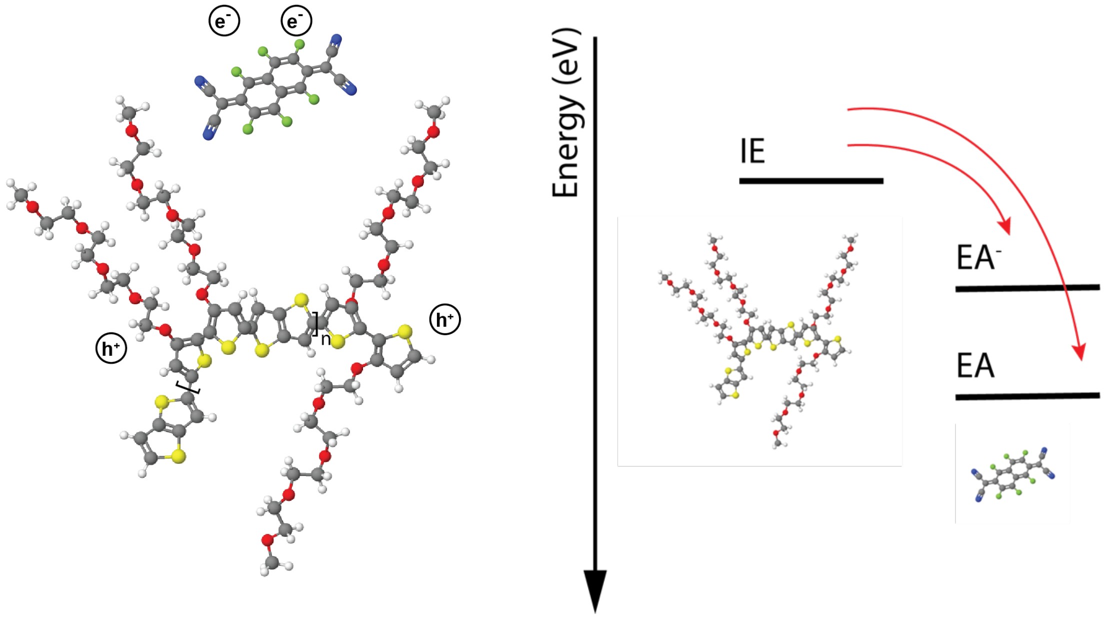

Figure 1. Double p-doping. **a.** Dopants, represented by the F6TCNNQ molecule on top are mixed into the organic semiconductor to accept electrons e^- and generate holes h^+ in the host material. As example, a segment of the polymer p($g_4$2T-TT) is shown here. **b.** Energy diagram of the dopant-host system. If the electron affinity EA of the dopant and the electron affinity of the already ionized dopant EA^- are larger than the ionization energy (IE) of the semiconducting host, two holes per dopant molecule can be generated. Gray, green, blue, red, yellow and white spheres in the sketch represent, respectively, C, F, N, O, S, and H atoms.