

ORGANIC SEMICONDUCTORS

No more breaks for electrons

In semiconducting polymers, the mobility of negative charges is typically much smaller than that of positive charges. Identification of a universal electron-trap level that is associated with water complexation now clarifies this difference and provides guidelines for the design of improved organic semiconductors.

Anna Köhler

The development of plastic electronics allows designers to dream of a future with windows that may double as lighting panels, wallpaper with built-in display screens, rollable solar cells, and even smart fabrics that contain sensors or display elements. Whether these are energy-saving or simply fun items, they will require significant improvements in today's organic semiconductor devices, such as organic light-emitting diodes (OLEDs), organic solar cells (OSCs) and organic field-effect transistors (OFETs). Organic semiconductors are hydrocarbon-based molecular or polymeric π -conjugated compounds in which single positive and negative charges, that is, holes and electrons, can be transferred between the π orbitals of adjacent molecular units. The performance of organic electronic devices, which rely on macroscopic charge transport, is intimately coupled to the understanding of this fundamental process.

Regarding charge transport, there is a basic enigma that has been puzzling scientists for a long time. In traditional inorganic semiconductors such as crystalline silicon or germanium, the mobility of electrons and holes differs by less than a factor of five, even at low doping levels that approach

the intrinsic case. In contrast, organic semiconductors typically show highly asymmetric electron and hole mobilities, even though there is no fundamental reason why these should be different. Most organic semiconductor materials are intrinsically p-type, that is, the hole mobility exceeds the electron mobility by orders of magnitude. Writing in *Nature Materials*, Nicolai and co-workers now clarify the origin of this low electron mobility¹. They show that the transport of electrons in a wide range of semiconducting polymers is limited by trapping, and that the trap states in all these materials are similar. They are able to rule out a number of possible traps and identify an oxygen–water complex as the most likely universally present trap at an energy level of about -3.6 eV versus vacuum.

With this finding, Nicolai and co-workers address an issue that is almost as old as the field of organic semiconductors. When molecular crystals from naphthalene, anthracene or pentacene were first investigated in the 1960s, it was not immediately clear whether charge transport would take place in delocalized bands, as in inorganic semiconductor crystals, or whether hopping transport would prevail.

A well-ordered, symmetric material with electronically interacting units should, in principle, show coherent band-like transport, at least at low temperatures. Experimentally, however, the charge mobility usually decreased on cooling, implying temperature activated incoherent transport. This issue could only be resolved when purification methods improved due to the pioneering work of Norbert Karl in the 1980s². It turned out that band transport prevailed, as theoretically expected, in ultrapure crystals, whereas in less pure samples charge mobility was limited by trapping. Electrons were more susceptible to trapping than holes, turning the verification of band transport for electrons into a challenge.

This issue re-appeared in the 1990s with the fabrication of OFETs, OLEDs and OSCs from amorphous films of organic semiconductors. Although there were plenty of materials suited to make p-type transistors, materials for n-type transistors were rare. Similarly, for the design of OLEDs and OSCs it was well known that holes generally travel faster and further than electrons, and that this needs to be compensated for in the device architecture. When combining the work of Nicolai and colleagues with previous insights^{3–4}, the reason for this apparently mysterious 'breaking of charge conjugation symmetry' becomes clear.

Holes move by incoherent transfer between the highest occupied molecular orbitals (HOMOs) of adjacent molecules, whereas electrons hop between the lowest unoccupied molecular orbitals (LUMOs), as illustrated in Fig. 1. As there is no fundamental difference in the electronic coupling between neighbouring LUMOs or HOMOs, similar transfer rates for electrons and holes would be expected. However, both carriers differ strongly in their sensitivity to trapping at defects or impurities. Trapping and subsequent thermally activated release reduces the mean mobility of a charge carrier, just like frequent breaks reduce the mean travel speed of a car on a highway journey. The different susceptibility of electrons and holes to trapping results from the dissimilar energies of the HOMO and LUMO. For most organic semiconductors,

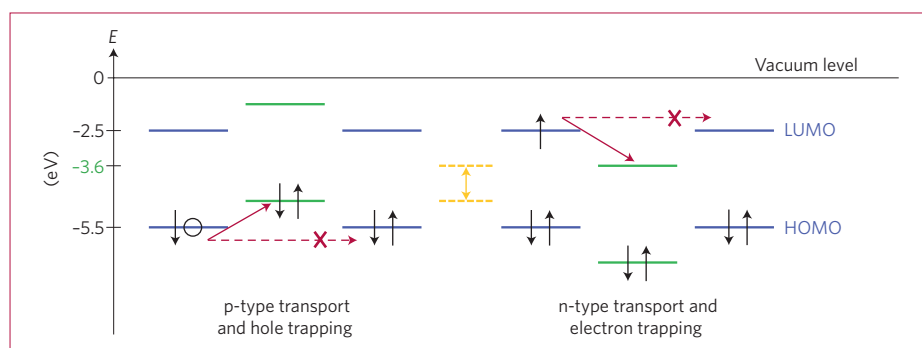


Figure 1 | Energy level diagram illustrating hole and electron trapping in organic semiconductor films. In the case of p-type transport (left), a hole (black circle) can be localized by a higher-lying filled defect level (shown in green) instead of being transferred between the HOMOs of two adjacent molecules (shown in blue). n-type transport (right) requires the transfer of an excess electron (black arrow) between the LUMOs of two molecules (shown in blue). An empty lower-lying defect level (shown in green) can trap the electron for some time until it is released by thermal activation. Trap-free high-mobility transport of both electrons and holes may therefore require materials with a small HOMO–LUMO gap (shown in yellow). In the work reported in ref. 1, a universal empty trap level at -3.6 eV is identified that limits the electron mobility for a wide range of π -conjugated polymers.

the HOMO is located around -5 to -6 eV versus vacuum, whereas the LUMO ranges from about -2 to -3 eV. As illustrated in Fig. 1, defects or impurities frequently have empty orbitals below -3 eV that can take up an electron. Filled orbitals above -5 eV (suitable for accepting holes) are more elusive. The way to obtain similar mobilities for electrons and holes is hence clear: eliminate the electron traps.

A beautiful example of this approach was reported by Chua and co-workers for OFETs (ref. 4). They found that electronegative hydroxyl groups at the interfaces between organic semiconductors and gate dielectrics are responsible for electron trapping. When they used dielectric materials that were free of hydroxyl groups, electron transport was uninhibited and n-type transistors could be realized, even with materials that were originally thought to be p-type semiconductors. This opened the way to ambipolar and light-emitting transistors. The Blom group^{1,3} applied this principle to semiconducting polymers used in OLEDs and OSCs, where charge transport proceeds through the bulk of the semiconductor film.

In 2010, Zhang and co-workers validated that the electron and hole mobility were indeed equal for the prototypical semiconducting polymer (poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene) when the electron traps were filled up by doping³. The present work from Nicolai and colleagues now shows that this approach may be generalized and applied to a wide range of semiconducting polymers¹. Their results also explain the paradox that electron and hole mobility appear equal in microwave conductivity measurements⁵, but not in measurements with other, macroscopic techniques⁶. When the conductivity is measured by analysing the absorption of microwave radiation, charges are accelerated and decelerated by the electromagnetic field only over a short section of a polymer chain where trapping effects do not take place, in contrast to the macroscopic transport over many chains.

The result by Nicolai and co-workers is a major advance in two ways. For those interested in the application of organic semiconductors, it can guide the design of p-type or n-type materials and the

development of more efficient organic electronic devices. At the same time, their finding implies that ambipolar high-mobility materials for bulk film applications need to have small HOMO–LUMO gaps, as is the case for many solar-cell materials — for large gaps, either electrons or holes will be susceptible to trapping. To those interested in fundamental charge transfer processes in π -conjugated materials, these results provide a clear understanding of the limitations of electron transport. With this knowledge, a quantitative and unified description of the current flow in organic semiconductors has become possible. □

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MECHANICAL PROPERTIES

Overcoming old barriers

Dislocation motion is crucial to the deformation of materials. The discovery that at least at lower temperatures quantum effects play an important role in this process considerably improves quantitative predictions of mechanical properties.

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When metals such as iron and steel deform, they do so via the movement of dislocations through the crystal. These long, one-dimensional line defects don't move easily, which is the reason why iron can be hard to deform. The stress required to overcome this resistance to motion, the so-called Peierls stress, depends on the crystal structure. In face-centred cubic (fcc) materials it generally is low, increasing with temperature, whereas in body-centred cubic (bcc) materials it is higher, but thermal fluctuations have a stronger influence so that the Peierls stress drops as temperature rises.

It is believed that the rate-limiting step is the nucleation of a kink-pair: two steps on the dislocation line, which once created move easily along the line moving it forwards. However, there has been a longstanding discrepancy between theory and experiment regarding the behaviour

of dislocations at low temperatures in iron and other bcc metals. Across a range of materials, calculations based on the classical transition-state theory applied to kink-pair creation, generally overestimate the energetic barrier involved. Many explanations have been put forward to explain the reduced barriers seen in experiments. Defects for example might assist the nucleation. Writing in *Nature Materials*, Laurent Proville and colleagues have now performed calculations on dislocation movements in iron that suggest that the classical transition-state theory itself is at fault: quantum effects must be invoked to describe the system¹.

Transition-state theory has been such a central part of understanding reaction rates that its fundamental tenets typically go unchallenged. In an approach first formulated by Eugene Wigner², to transit from one macrostate to another required the

free-energy barrier to be defined: we must consider a thermally averaged 'transition state'. This state corresponds to the barrier, and is treated as a macrostate distinguished from the initial and final states. Practically, it may seem odd that modes with frequencies much lower than the time corresponding to the barrier crossing should be included in the calculation, because how can some vibration that doesn't have time to happen enter into the calculation? However, in the classical case it turns out to be fine, but in a quantum picture this is more troublesome (Fig. 1).

In the classical case such approximations are appropriate, because transition-state theory is usually applied to chemical reactions at high temperatures and reaction rates at low temperatures are negligible. In direct molecular dynamics simulations, the atoms are therefore treated classically and quantum effects such as tunnelling and