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Faster holes by delocalization

Zhigang Shuai

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Terahertz photoconductivity measurements coupled with theoretical modelling reveals that thermal transient excitations to more delocalized states enhances hole mobility in organic molecular semiconductors.

Carrier transport in organic materials, characterized by mobility (in units of $cm^2 V^{-1} s^{-1}$), governs optoelectronic performance. The room-temperature mobility in silicon single crystals, carbon nanotubes and graphene is around $600 cm^2 V^{-1} s^{-1}$, $10^5 cm^2 V^{-1} s^{-1}$ and $3 \times 10^5 cm^2 V^{-1} s^{-1}$, respectively. By contrast, the mobility in organic semiconductors is much smaller, typically on the scale of a few tens of $cm^2 V^{-1} s^{-1}$. In recent years, the mobility of the molecular material didodecyl[1]benzothieno[3,2-b][1]1benzothiophene (BTBT) was found to reach above $100 cm^2 V^{-1} s^{-1}$ (ref. [1]), a remarkable improvement in organic semiconductors. Although the transport mechanism in silicon is well understood by band structure theory, the mechanism has long been under scrutiny for organic materials.

The complexity for organic materials lies in the competition of the localization and delocalization of the thermally accessible states of the system, in contrast to silicon or carbon nanotubes where delocalized carriers surfing extended states dominates. In addition to static disorder and impurities, two types of intrinsic localization mechanism have been proposed, namely, intramolecular electron–phonon coupling (Holstein polaron) and intermolecular coupling (Su–Schrieffer–Heeger type). The latter is often termed as non-local dynamic disorder. In 1985, Munn and Silbey found that the non-local dynamic disorder in the small polaron limit tends to increase carrier mobility[2]. This behaviour was termed phonon-assisted current. Instead of the mobility being hindered through scattering, which was demonstrated by a theory for localized carriers, fluctuations in intermolecular transfer integrals (ΔV) can enhance mobility[3]. By contrast, the recent so-called transient localization theory emphasizes the timescale τ for wavepacket relaxation of carriers from 'wave-like' to 'particle-like' diffusive behaviour. The transient localization theory could also be amended to describe a band-like limit with reduced dynamic disorder[4]. In brief, the transient localization theory is a (non-local) dynamical localization correction to the band transport picture. Although the original formulation of the transient localization theory has been successfully applied to understand many features of charge carrier transport in organic semiconductors, some subtleties of the transport mechanism could only be clarified using explicit numerical non-adiabatic dynamic simulations[5] that relaxed some approximations made in the analytical transient localization theory formulation[6]. The general transient localization scenario emerged from the standard transient localization theory, and non-adiabatic dynamics has gained a lot of attention not only for carrier transport but also for exciton transfer[7].

Experimentally, a method to measure the microwave photoconductivity for the intrinsic mobility of a single molecule, polymer chains and organic thin films has been demonstrated. The advantage of such a
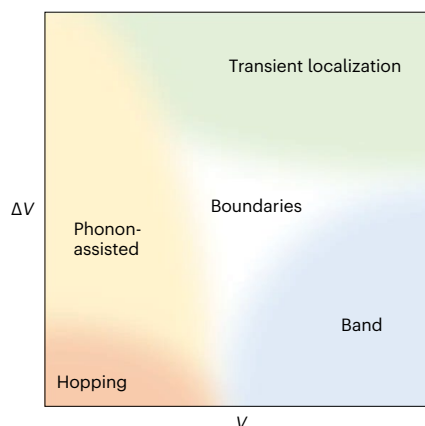

Fig. 1 | Schematic sketch of a phase diagram for carrier transport. V is the intermolecular transfer integral and ΔV is the non-local dynamic disorder. Figure adapted from ref. [9], under a Creative Commons licence CC BY 4.0.

method is that device-contact-related complexities are avoided[8]. Now, writing in *Nature Materials*, Giannini et al. report[5] a theory–experiment collaborative investigation on the carrier transport mechanism in dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]-thiophene (DNTT) and its alkylated derivative C8-DNTT-C8. The measurement was done with terahertz spectroscopy for polycrystalline centimetre-scale samples from room temperature down to 78 K. It was found that the C8-DNTT-C8 presents larger room-temperature mobility and more pronounced (decreasing) temperature dependence than DNTT. The most striking feature of the work is that it reveals rich physics behind the carrier transport in organic semiconductors, supported by surface-hopping non-adiabatic dynamics simulations, and in the context of the recent transient localization scenario[6].

Giannini et al. found that for both systems, the transport behaviour is band-like with a temperature dependence T^{-n} ($n = 1.5$ for pure band-like). According to their numerical simulations based on an updated surface-hopping dynamics algorithm, the alkylated DNTT presents a larger polaron size than DNTT, with $n = 1$ for alkylated DNTT and $n = 0.5$ for DNTT, indicating that there are more delocalized carriers in C8-DNTT-C8 than in DNTT owing to the side-chain-mediated intraplane stacking that leads to more isotropic and favourable electronic interactions in alkylated DNTT. The authors also revealed that differences in the specific electronic band structure and interactions network of these two chemically similar semiconductors lead to a different delocalization of the states as a function of energy. Thermal transient excitations to more delocalized states as a function of temperature enhances hole mobility in C8-DNTT-C8 compared with DNTT. Thus, such a transient (de)localization framework provides a general transport paradigm, beyond traditional hopping or band-like limits.

It should be noted that transport in organic semiconductors is indeed complicated. A recent communication indicated[9] that

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transient localization is fundamentally different from (dynamical disorder) phonon-assisted current, with the former derived from dynamic-disorder-limited transport behaviour, in contrast to the latter. Such a difference can be distinguished by photoelectron spectroscopy. Figure 1 shows a general phase diagram for carrier transport in organic semiconductors. In fact, within the hopping regime, the quantum nuclear tunnelling effect could also lead to a 'pseudo-band-like'[10] behaviour that has been demonstrated in a negative isotope-effect experiment. Thus, a number of bridges have been found between semi-classical hopping and full quantum coherent band-like effects: quantum nuclear tunnelling, phonon-assisted current and transient localization.

So far, both theory and numerical simulations have focused on single-carrier diffusion with phonon scattering, assuming that the carrier density is low enough to avoid carrier–carrier scattering. In fact, in field-effect transistors, the carriers concentrate in just a few molecular layers adjacent to the substrate. The carrier density could be high. Electron correlation effects could be important and deserve careful investigation. A recent work indicated that a heavily p-doped conjugated polymer manifests n-type transport, a plausible electron correlation effect to alter the carrier polarity[11].

Zhigang Shuai ⓘ ✉

School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen, People's Republic of China.
✉e-mail: shuaizhigang@cuhk.edu.cn

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Competing interests

The author declares no competing interests.