

Molecular p- and n-doping of organic semiconductors has been key for the successful commercialisation of OLEDs, and for improvements in performance of organic solar cells and transistors. Advantages of using doped transport layers include reduced voltage losses across the device, through an increase in conductivity, and better injection at the metal/organic interface, from an increase in charge carrier density. Despite the success of dopants in OLEDs, the doping efficiency remains very low as compared to the inorganic counterpart and critically the fundamental mechanism of the doping process is still under debate.

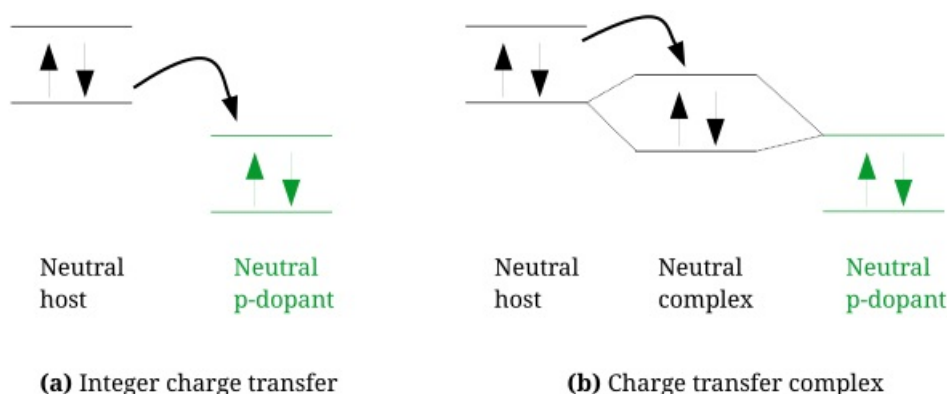


Figure 1. A simple schematic illustrating the two mechanisms of electron transfer in host and dopant pairs: (a) integer charge transfer, and (b) charge transfer via a ground-state charge transfer complex.

The prevailing practice for pairing hosts and dopants is based on favourable energy-level alignment. For p-doping, this involves introducing a molecule with an electron affinity (EA) greater than that of the host molecule's ionisation potential (IP) such that it is energetically favourable for one electron transfer from the host's highest occupied molecular orbital (HOMO) to the dopant's lowest unoccupied molecular orbital (LUMO), as shown in figure 1a. This mechanism is described as integer charge transfer or ion-pair formation. An alternative mechanism to integer charge transfer for doping has been proposed which involves the formation of a ground-state charge transfer complex as shown in figure 1b. The frontier molecular orbitals of the host and dopant form hybridised energy levels with an occupied bonding orbital and an empty anti-bonding orbital. The anti-bonding orbital then acts as the effective dopant level.

A consequence of this second mechanism is that a strong dopant - one with an EA far greater than the IP of the host - may dope less efficiently than expected if it forms a complex with the host. It is therefore crucial for dopant design and host-dopant pairing that the doping mechanism can be predicted. In this contribution, we present calculations of the relevant energy levels and the transfer integrals between the host and dopant molecules for a variety of p- and n-type doped systems. The transfer integrals are calculated using a projection-based method with a counterpoise basis set, allowing us to avoid basis set superposition error. By comparing the calculations to the experimentally probed doping efficiency, via electron paramagnetic resonance, we offer a step toward understanding efficient doping of organic semiconductors.