

Despite the success of p- and n-doped organic semiconductors in commercially available OLEDs, molecular doping efficiency remains low compared to the inorganic counterpart and critically the fundamental mechanism of the doping process is still debated. 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's ionisation potential (IP), such that it is energetically favourable for one electron transfer from the host's HOMO to the dopant's LUMO. This mechanism is described as integer charge transfer. An alternative mechanism to integer charge transfer has been proposed in which the frontier molecular orbitals of the host and dopant hybridise. The anti-bonding orbital then acts as the effective dopant level. A consequence of this complex formation is that a strong dopant, one with an EA far greater than the IP of the host, may dope less efficiently than expected. It is therefore crucial for dopant design and host-dopant pairing that the doping mechanism can be predicted. Here, 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.