

# The Effect of Energy Levels on Doping processes in Organic Semiconductors

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Molecular p- and n-doping of organic semiconductors has been key for the successful commercialisation of OLEDs and been used also to improve the performance of organic solar cells and transistors. The advantage of using a doped transport layer in a device is that the voltage losses can be reduced through an increase in conductivity. Furthermore, an increase in the charge carrier density reduces the barrier for tunnel injection at the metal contacts. 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.

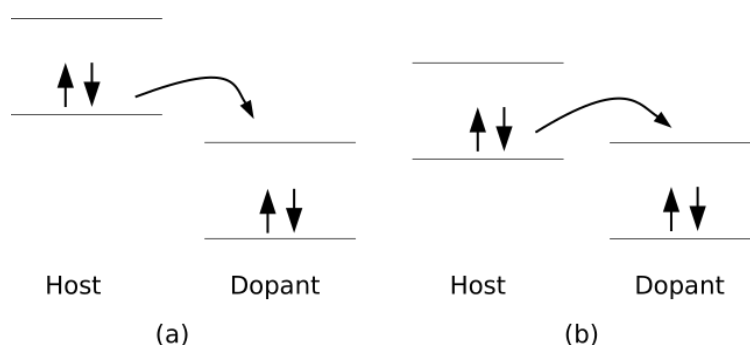


Figure 1. A simple schematic illustrating the common assumption of a host and dopant pair with (a) favourable (b) unfavourable energetic offset for p-type doping.

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. [1]

In this contribution we present the effect of the energy-level offset from favourable to the unfavourable case, as shown in figure 1b, on the efficiency of charge transfer between the host and dopant. We used zinc phthalocyanine (ZnPc) and its fluorinated derivatives Fx-ZnPc, x= 4, 8, 16, as host semiconductor and co-evaporated it with the p-type dopant F6-TCNNQ. We probed the effects of doping via electron paramagnetic resonance, photo thermal deflection spectroscopy and conductivity measurements and observe how the doping efficiency changes as function of the energy level of the host. We compare our experimental data to a statistical model based on work by Tietze et al. [2] in order to unravel how the doping process depends on energetic offset and improve the current understanding of how doping in organic semiconductors works.

[1] I. Salzmann, G. Heimel, M. Oehzelt, S. Winkler, N. Koch, *Acc. Chem. Res.*, **49**, 370–378 (2016)

[2] M. Tietze, J. Benduhn, P. Pahner, B. Nell, M. Schwarze, H. Kleemann, M. Krammer, K. Zojer, K. Vandewal, K. Leo, *Nat. Comms*, **9**, 1182 (2018)