Negative Polaron in n-Doped Organic Semiconductors: Energy Levels and Hubbard U Interactions

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Doping organic semiconductors leads to the formation of polarons, positive in the case of p-doping and negative for n-doping. The released carrier polarizes neighboring molecular sites and induces intra- and inter-molecular relaxation. In the traditional picture, prevalent in the literature since the 1980's, the formation of a negative polaron results in two localized levels within the gap. The addition of the electron to the LUMO/CBM leads to a gain in energy equal to the electron affinity of the neutral molecule. The ensuing molecular relaxation stabilizes the excess charge, resulting in a singly occupied level below the LUMO/CBM, and a doubly occupied level which relaxes upwards above the HOMO/VBM. Conversely, the formation of a positive polaron results in an empty level below the LUMO/CBM and a half-occupied level above the HOMO/VBM. Recent experimental and theoretical studies have challenged this original interpretation. [1-3] In the case of an added electron (hole), the new picture points to a half-occupied (empty) level below the semiconductor LUMO/CBM, split from an unoccupied (half-occupied) level positioned above (below) the LUMO/CBM (HOMO/VBM). The split corresponds to the intra-molecular Coulomb interaction, also known as Hubbard interaction U. In this work, we investigate n-doping of two organic semiconductors, the polymer P(NDI2OD-T2) and the small molecule C60, with the n-dopants [RhCp*Cp]2, [N-DMBI]2 and Cs for P(NDI2OD-T2) and [N-DMBI]2 for C60. We use ultra-violet and inverse photoemission spectroscopy (UPS, IPES) aided by EPR measurements and DFT computations. The UPS data show that the n-dopants induce the growth of a (partially) occupied DOS in the former empty gap of the organic material, while IPES shows an additional empty DOS in the unoccupied band above the LUMO. In agreement with the above-mentioned new interpretation, the additional DOS in the gap and above the LUMO are assigned to the formation of the singly occupied and unoccupied levels, respectively. These experimentally determined features allow a direct estimation of the Hubbard U, equal to ~1.1-1.3 eV in the polymer, in good agreement with theory. [4] Initial experimental results lead to a Hubbard U value of ~1.4 eV in C60. [5]

References:

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