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Energetics of organic semiconductor interfaces: enhancing injection via chemical doping[1]

ANTOINE KAHN, Princeton University

Chemical doping of organic molecular films is a powerful way to improve charge injection and transport in organic devices, and to enhance device functionality. The formation of narrow depletion regions at doped organic-conductor interfaces facilitates injection via carrier tunneling through the barrier, and allows the use of moderate work function and non-reactive metals as efficient contacts. P-doping with the electronegative molecule, tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ), has been used on a number of hole-transport materials. N-type doping is more challenging, often hindered by the energetic requirements of transferring an electron from the dopant HOMO to the host low lying LUMO. We recently demonstrated efficient n-doping of the electron transport material tris2,5-bis(3,5-bis-trifluoromethyl-phenyhl)-thieno[3,4-b,h,n]-1,4,5,8,9,12-hexaazatriphenylene (THAP), which has a 4.59 eV electron affinity (EA), with cobaltocene (CoCp, IE = 4.07 eV). We now introduce a stronger n-dopant, i.e. decamethylcobaltocene ($CoCp^*_2$), and demonstrate n-doping of copper phthalocyanine (CuPc, EA = 3.25 eV). $CoCp^*_2$ is found to have a remarkably low IE of 3.30 eV. N-doping is evidenced by a large upward swing of the Fermi-level in the gap of CuPc, and confirmed by current-voltage (I-V) measurements. A 10^4- to 10^7-fold increase in current density of the interface-doped device a compared to the undoped CuPc device is due to enhanced injection. An additional 10^3-fold increase in current density is observed for the uniformly doped device and is attributed to enhanced conductivity of the bulk film. The application of p- and n-doping of CuPc to an organic homojunction p-i-n diode with a 1.47 eV built-in potential is demonstrated.

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