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Beating the Thermodynamic Limit: Photo-Activation of n-Doping in Organic Semiconductors

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Molecular doping is of great importance to control the electronic and electrical properties of organic semiconductors, lower contact resistance, enhance bulk conductivity and carrier mobility, and create higher performance devices. We begin with an overview of doping mechanisms, and of the reducing or oxidizing power of a number of n- and p-type molecular dopants, respectively, and their effect on the electronic structure and conductivity of both vacuum- and solution-processed organic semiconductor films. We look at novel n-dopants that exhibit good ambient stability [1,2]. Specifically, we turn to very low electron affinity materials (EA ~ 2.0-2.1 eV), which are very important as ETL in OLEDs, but are notably difficult to n-dope. We look at phenyldi(pyren-2-yl)phosphine oxide (POPy2) with an EA = 2.1 eV doped with the air-stable dimer of (pentamethylcyclopentadienyl)(1,3,5-trimethylbenzene)ruthenium ([RuCp*Mes]2). We demonstrate that photo-activation of the cleavable dimeric dopant results in kinetically stable and efficient n-doping of the host semiconductor, whose reduction potential is beyond the thermodynamic reach of the dimer’s effective reducing strength [3]. This stability arises from the photo-assisted cleavage of the dopant, which ultimately leads to the resulting monomeric cationic organometallic species for which the reverse reaction sequence is kinetically hindered on a time scale of at least thousands of hours. We show that the ETL doped in this manner is used to fabricate high-efficiency organic lightemitting diodes with significantly improved performance relative to un-doped devices.

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