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N-doping of electron transport layers in organic light-emitting diodes studied by combining TOF-SIMS and XPS

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With the introduction of p-i-n structures in the early 2000s, the performance of organic electronic devices has considerably improved, making them competitive with their inorganic counterparts. Doping aims to increase the charge-carrier conductivity as well as achieving an Ohmic contact with the electrodes. Compared to P-doping, N-doping is more difficult as it requires dopants with low ionization energy that are very reactive. A widely used approach consist of using alkali or alkaline earth metals/compounds. However, such materials are easily oxidized and may diffuse in the organic stack. In 2019, Bin *et al* reported the use of Ag, an air-stable metal, to dope phenanthroline-based organic materials [1]. The formation of complexes between Ag ions and the nitrogen of the molecule induces a reduction of the electron injection barrier when compared to Cs doping. Multiple articles compare this doping with various elements: Li, Cs or Cs_2CO_3 . However, no study compares Ag with Ca that has been shown to be an efficient n-dopant for OLEDs [2].

Here, we present a comparative study of the doping of phenanthroline-based organic material (Bphen) with Ca or Ag atoms. First, the formation of [Bphen(Ag)] complexes is verified using tandem time-of-flight secondary ion mass spectrometry (ToF-SIMS) : characteristic peaks of the organic molecule, dopant and the complex are present in the mass spectrum. Then, a range of doping is studied by X-ray / ultraviolet photoelectron spectrometry (XPS / UPS) to trace core-level / Fermi-level shift. At low doping (4%), a similar shift is observed for both elements. As expected, the main advantages using Ag instead of Ca resides in its stability. The reactivity of these layers in electron only devices was studied by aging electrically or exposing to air electron only devices. Electric I-V curves as well as ToF-SIMS and XPS profiles and spectra demonstrated that Ag-doped layers are more stable under these conditions.

[1] Z. Bin et al, Nature Communications, 10(1), 866 (2019) [2] D. Shelhammer et al, Organic Electronics, 84, 105799 (2020)