LiF as a surprisingly non-innocent intermediate layer in fullerene-based electronic devices

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During our search for new organic semiconductors with increased dielectric constant, we discovered that LiF is everything but innocent towards fullerene derivatives in thin film devices, as in devices made for capacitance measurements to derive dielectric constants.

A low work function contact is desirable for the cathode interface in organic electronic devices. Low work function metals however, are prone to rapid oxidation and corrosion. Therefore, Al is used along with interlayers inserted at the Al/organic interface. These interlayers improve the function of Al as an electron extracting/injecting contact and impede Al-organic bonding. Amongst these interlayers, LiF has proved its significant role in providing enhanced electron extraction in organic solar cells. Nevertheless, it is still important to disentangle the extrinsic effects of LiF that potentially influence the properties of the active organic compound when deposited as the cathode interlayer.

We have studied the role of LiF cathode interlayers as a doping agent in fullerene-based devices. The chemical structures of the two new compounds used in this study are shown in Figure 1. We perform current-voltage (J-V) and capacitance-voltage characterization of capacitors out of fullerene derivatives capped with LiF/Al versus Ba/Al and Al top contacts. The effective dielectric constants extracted from fullerene/LiF/Al capacitors were significantly higher than the pristine values while other capacitors retrieved the pristine values indicating that LiF dopes the fullerene layer.

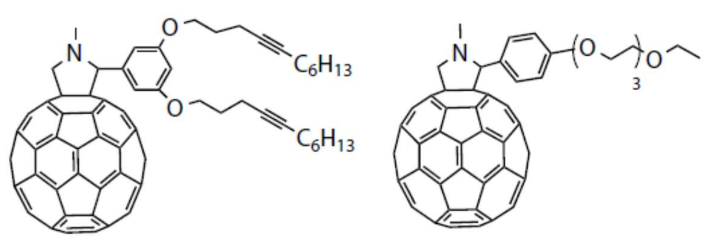

Figure 1: Chemical structures of the fullerene derivatives F2M (left) and PTEG-1 (right)

Cathode	d [nm]	$\varepsilon_{r-eff} \pm 0.3$	N_D $[10^{21} m^{-3}]$
Ba/Al	345	3.9	0.4
Ba/Al	276	4.1	7
Ca/Al	345	4.6	-
LiF/Al	280	6.8	60
LiF/Al	228	8.4	160
Al	95	3.3	-
Al	231	3.7	-

Figure 2: The apparent doping desnity and the effective dielectric constants of F2M in combination with different electrod materials.

In addition, high doping densities as determined from Mott-Schottky analysis and increased current densities close to Ohmic regime were observed as a signature of doping effect of LiF. In bulk-heterojunction solar cells with LiF/Al cathodes, devices with 4:1 ratios of fullerene:polymer showed distinct doping changes with respect to 1:1 ratios. While in the case of the pristine polymers, LiF did not impose any doping effect. Our J-V measurements proved that LiF should not necessarily be capped with Al in order to be able to dope the fullerenes films. This was shown in a nexperiment depicted in Figure 3, where a thin layer of LiF was put between two layers of PTEG-1, in a device without aluminum.

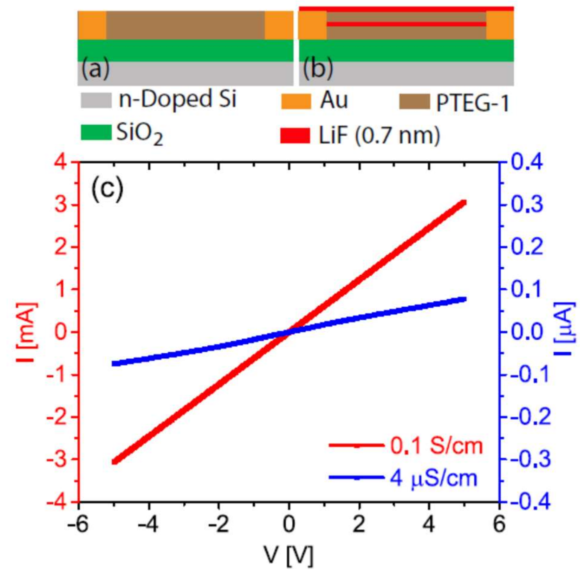

Figure 6: Cross sections of in-plane capacitors/diodes of (a) pristine PTEG-1, (b) doped PTEG-1. (c): *I-V* curves of pristine (blue) and doped PTEG-1 (red) after annealing to 115 ºC for 10 minutes. The legend shows the corresponding conductivity values

The intercalation of LiF into films of fullerene derivatives upon evaporation seems to give rise to alkali metal-doping of these molecular semiconductors. Therefore the more openly packed fullerene derivatives are more influenced by the doping. Such doping effect cannot be explained merely with formation of a thin n-doped layer adjacent to the cathode to facilitate charge injection/extraction, as accepted within the organic electronic community. In conclusion, even though many scenarios promote LiF as a modifying interlayer for organic electronic devices, one can hardly disentangle the doping effect of LiF in fullerene based devices. Therefore, properties such as mobility, conductivity, built-in voltage and the dielectric constant, extracted from the devices in which monolayers of LiF have been used, will be dubious in conveying the correct values. LiF doped fullerene derivatives, however, can be applied as electron extracting buffer layers in organic or perovskite solar cells or find suitable applications in organic thermoelectrics.

S. Torabi, J. Liu, P. Gordiichuk, A. Herrmann, L.Qiu, F. Jahani J. C. Hummelen, and L.J. A. Koster, Deposition of LiF on films of fullerene derivatives leads to bulk doping, *ACS Appl. Mater. & Interfaces* 8, (34), 2016, 22623-8 (2016)