

On doping of fullerene derivatives in photovoltaic and thermoelectric devices

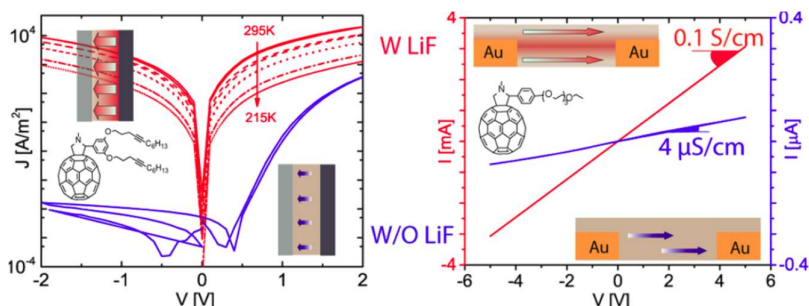
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During our search for new organic semiconductors with increased dielectric constant, we discovered that LiF is everything but innocent towards fullerene derivatives in thin film devices, as in devices made for capacitance measurements to derive dielectric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

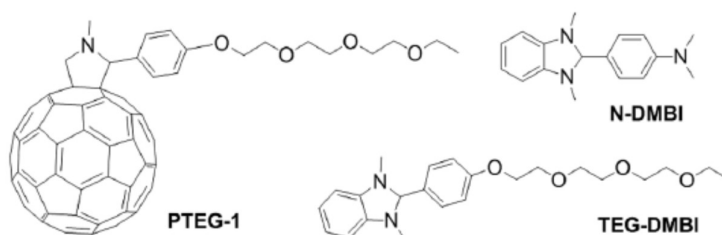
We have studied the role of LiF cathode interlayers as a doping agent in fullerene-based devices. We perform current-voltage (J-V) and capacitance-voltage characterization of capacitors out of fullerene derivatives capped with LiF/Al versus Ba/Al and Al top contacts. The effective dielectric constants 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. 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.



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.

During our studies on *intentional* doping of fullerene derivatives, mainly for thermoelectric applications, we found that the polarity of fullerene derivatives can be tailored to enhance the miscibility between the host and dopant molecules. A fullerene derivative with a hydrophilic triethylene glycol type side chain (PTEG-1) was used as the host and (4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)phenyl) dimethylamine n-DMBI) as the dopant. Thereby, the doping efficiency was greatly improved to around 18% (<1% for a nonpolar reference sample) with optimized electrical conductivity of 2.05 S cm⁻¹, which represents the best result for solution-processed fullerene derivatives.

Next, we tailored both the fullerene derivative and the dopant for better miscibility. By introducing the polar triethylene glycol (TEG) side chain onto both fullerene host (PTEG-1) and dopant (TEG-DMBI) materials, the TEG-DMBI doped PTEG-1 films obtained through solution processing provide a better miscibility compared with films doped with commercially available N-DMBI (bearing a dimethylamino group instead of TEG), as determined by phase imaging AFM (atomic force microscopy) measurements and coarse-grain molecular dynamics simulations, leading to high doping efficiency up to 18% at 20 mol% doping concentration and thus high carrier density and mobility, which are critical to the electrical conductivity. Therefore a record power factor of 19.1 $\mu\text{W m}^{-1} \text{K}^{-2}$ is obtained with an electrical conductivity of 1.81 S cm⁻¹, one of the highest values reported for solution processable fullerene derivatives as n-type organic materials for thermoelectric applications to date.



Similarly, we found that molecular n-doping of a donor–acceptor (D–A) copolymer yielded a 200-fold enhancement of electrical conductivity, by rationally tailoring the side chains without changing the D–A backbone. Instead of the traditional alkyl side chains for poly {[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl](NDI)-alt-5,5'-(2,2'-bithiophene)} (N2200), polar triethylene glycol type side chains were utilized, resulting in a high electrical conductivity of 0.17 S cm⁻¹ after doping with (4-(1,3-dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)phenyl) dimethylamine. This is the highest reported value for n-type D–A copolymers.

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