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# The interfaces of poly(*p*-phenylene vinylene) and fullerene derivatives with Al, LiF, and Al/LiF studied by secondary ion mass spectroscopy and x-ray photoelectron spectroscopy: Formation of AlF<sub>3</sub> disproved

W. J. H. van Gennip

*Dutch Polymer Institute, Eindhoven University of Technology, STW 3.48, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

J. K. J. van Duren

*Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

P. C. Thüne

*Dutch Polymer Institute, Eindhoven University of Technology, STW 3.50, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

R. A. J. Janssen

*Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

J. W. Niemantsverdriet

*Dutch Polymer Institute, Eindhoven University of Technology, STW 3.46, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

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Two mutually exclusive mechanisms have been proposed to explain the improved electron injection by the insertion of a LiF layer between the metal cathode and the active organic layer of organic photoelectronic devices: the dipole and the doping mechanism. The possibility of the doping mechanism was studied by investigating the interface of poly[2-methoxy-5-(3',7'-dimethyl-octyloxy)-1,4-phenylenevinylene] (MDMO-PPV) or 1-(3-(methoxycarbonyl)propyl)-1-phenyl[6,6]C<sub>61</sub> (PCBM) with Al, LiF, or Al/LiF. In this mechanism, Li dopes the organic layer, after liberation via the reaction  $\text{Al} + 3\text{LiF} \rightarrow \text{AlF}_3 + 3\text{Li}$ . If this reaction takes place, AlF<sub>3</sub> should be detectable at the surface. However, SIMS measurements showed that AlF<sub>3</sub> is not present at the Al/LiF/MDMO-PPV and Al/LiF/PCBM interfaces. This is evidence that the proposed reaction does not occur. Other evidence that the doping mechanism cannot be the general mechanism to explain the enhanced electron injection comes from the presence of LiF on both organic surfaces. XPS measurements indicate that there is a reaction of Al with the carboxylic oxygen of PCBM, and that a LiF layer between PCBM and Al prevents this reaction. © 2002 American Institute of Physics. [DOI: 10.1063/1.1498473]

## I. INTRODUCTION

Improving the electron injection into the active layer of polymer electronic devices, such as organic light emitting diodes and polymer solar cells, is one of the critical issues in their development. One way to improve the electron injection is to insert a thin layer of LiF between for example tris-(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>) and the metal cathode.<sup>1</sup> Such a layer is already effective at the equivalent layer thickness of 1 Å;<sup>2</sup> layers of seven nanometers or more, however, become detrimental to the electron injection.<sup>3</sup> The same beneficial effect of an inserted LiF layer was noted for several other devices, containing organic compounds such as 4-4'-bis(2,2-diphenylvinyl)-1,1'-biphenyl (DPVBi),<sup>4</sup> poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV)<sup>5</sup> and molecularly mixed layers of poly[2-methoxy-5-(3'-7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) and 1-[3-(methoxycarbonyl)propyl]-1-phenyl[6,6]C<sub>61</sub> (PCBM).<sup>6</sup>

Several mechanisms to explain the beneficial effect of a thin layer of LiF on the electron injection at the cathode have been suggested: The formation of a Li<sup>+</sup>polymer<sup>-</sup> or Li<sup>+</sup>molecule<sup>-</sup> charge transfer complex after the reaction of LiF with Al to AlF<sub>3</sub> and liberated Li,<sup>7-11</sup> tunneling injection,<sup>1,5</sup> formation of a dipolar layer,<sup>4,12</sup> and the protection of the organic layer from reaction with aluminum.<sup>4,8,9,13</sup>

The mechanism of electron injection enhancement by the formation of radical anions or charge transfer complexes, which could be responsible for the higher device efficiencies, was first suggested by Kido *et al.*<sup>14</sup> They showed that an organic layer at the cathode interface shows electron injection improvement upon the co-evaporation of a low-work-function metal and the organic layer, which suggests that doping takes place. However, when Le *et al.* used LiF instead of Li, they found that LiF alone does not decompose on Alq<sub>3</sub>, although a LiF layer also enhances the electron injection.<sup>8</sup> Hence, they suggested that Li is liberated in the presence of Al and reacts with Alq<sub>3</sub> to form the radical anion,

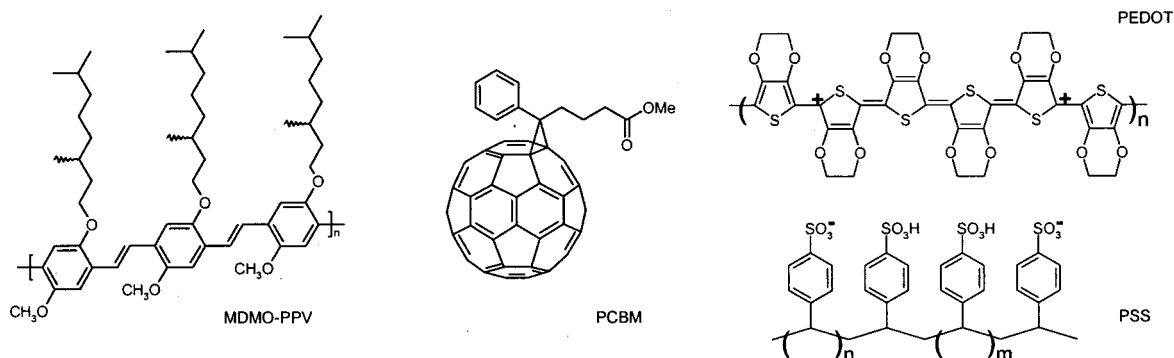


FIG. 1. Compounds used for semiconductive (MDMO-PPV:PCBM) and conductive (PEDOT:PSS) organic layers.

although they proposed no reaction scheme. Piromreun *et al.* claimed that Al reacts with CsF on MEH-PPV to form  $\text{AlF}_3$  and free Cs, which subsequently doped MEH-PPV.<sup>15</sup> Others claimed the same mechanism for LiF on  $\text{Alq}_3$ .<sup>7,11</sup> Al/CsF on poly(9,9-dioctylfluorene) (PFO) follows the same reaction scheme according to Greczynski *et al.*<sup>13</sup> However, these authors did not observe this for Al/LiF on PFO, which suggests that the proposed reaction scheme is not generally applicable. Also, Yang *et al.* noted that significant photoluminescence quenching should be expected if alkali metal ions diffuse into the active organic layer. However, when these authors measured the photoluminescence quantum efficiency of devices with and without an inserted LiF on MEH-PPV, they found essentially the same photoluminescence quantum efficiencies for both devices.<sup>16</sup>

The tunneling injection mechanism explains the improved electron injection only in terms of the backflow current reduction, caused by the reduction of the electrode metal image force on the organic molecules by the insulating layer of LiF. This mechanism was investigated by Yang *et al.* when they studied devices with LiF, CsF,  $\text{CaF}_2$ , and  $\text{BaF}_2$  layers stacked between different metal cathodes and a MEH-PPV layer. They found that tunneling through an insulating metal fluoride layer cannot be the correct mechanism because of the electron injection independence of the metal fluoride layer thickness and the strong performance dependence on the capping metals on top of the metal fluorides.<sup>16</sup> Masenelli *et al.*,<sup>17</sup> numerically modeling experimental data from Stöbel *et al.*,<sup>18</sup> confirmed that the reduction of the backflow current alone cannot explain the action of LiF, although it enhances the injection somewhat.

The aligned dipole mechanism explains the improved electron injection by the formation of a dipole in the LiF layer, which then lowers the work function of the metal cathode. Greczynski *et al.* showed that LiF deposited on a clean Al substrate shows weak dipole formation.<sup>19</sup> Masenelli *et al.* demonstrated good agreement between simulations of a dipolar LiF layer and experimental data.<sup>17</sup> Yang *et al.* found that devices with heavier metal fluorides exhibit less temperature dependence of the device lifetime. At an elevated temperature, thermal movement at the interface creates disorder, decreasing the orientation of the dipoles. Their interpretation was that since heavier metal fluorides show slower

thermal movement, a better lifetime is expected.<sup>16</sup> Baldo *et al.* remarked that an abrupt shift of approximately 1 eV in the vacuum level is observed at all metal cathode/ $\text{Alq}_3$  interfaces studied to date with photoelectron spectroscopy. This is evidence for charge separation near the metal, which results in dipoles at its interface with the underlying organic semiconductor. They suggested that LiF/Al cathodes improve injection by raising the Fermi energy and shifting the effective injection interface deeper into the organic film where the distribution of organic states is narrower and the hopping barrier to injection is reduced.<sup>12</sup>

Another mechanism is that LiF protects the active organic layer<sup>4,8,9,13</sup> from the hot impinging metal atoms. Several authors reported on chemical damage to the  $\text{Alq}_3$  layer upon deposition of the cathode material,<sup>20</sup> not only with Al,<sup>8</sup> but also with Mg,<sup>21</sup> although according to Mason *et al.* no bond breaking is caused by Mg, Na, Li, or K.<sup>9</sup> Nevertheless, according to Baldo *et al.*<sup>12</sup> chemical damage may explain the new gap states observed in ultraviolet photoelectron spectroscopy (UPS) in several studies upon deposition of the metal cathode. However, all authors seem to agree that this is a secondary reason.

Obviously the two most likely mechanisms for electron injection enhancement, dubbed the doping and dipole mechanism, are mutually exclusive, but conclusive evidence for any of these two models is hard to find, because of the complexity of the interface and because spectroscopic methods such as XPS (Ref. 22) and UPS (Ref. 23) cannot always give unequivocal information on this problem.

Knowledge about the presence or absence of the elements and compounds around the interface enables us to discriminate between the dipole and the doping model. Just as for the mixture of MDMO-PPV and PCBM, the same beneficial effect of LiF/Al has been observed for the pure compounds. Therefore, SIMS spectra were measured at the interface of the organic and the LiF layers to determine the chemical state of the LiF layer on the surfaces of MDMO-PPV and PCBM substrates (Fig. 1 shows the molecular formulas), taking into account the possible influence of aluminum. These spectra show that LiF does not dissociate or react with aluminum to  $\text{AlF}_3$  on both substrates, excluding the doping model for the explanation of enhanced electron injection in these substrates. Note that the validity of the

dipole mechanism has not been proved, but that the validity of the doping model has been disproved.

Furthermore, to study possible interactions between deposited aluminum and the underlying organic layer, x-ray photoelectron spectroscopy (XPS) measurements were performed using only relative shifts which indicated a reaction between aluminum and the carboxylic oxygen of PCBM. MDMO-PPV is resistant to a reaction with aluminum.

## II. EXPERIMENT

The materials used were poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) synthesized via the Gilch-route,<sup>24</sup> 1-[3-(methoxycarbonyl)propyl]-1-phenyl[6,6] $\text{C}_{61}$  (PCBM) generously provided by Rispens and Hummelen,<sup>25</sup> polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) from Bayer AG, LiF from Aldrich, Al from Engelhard-Clal, and anhydrous  $\text{AlF}_3$  from Aldrich. A glass plate covered with a 160 nm thick layer of indium tin oxide (ITO) was used as the substrate.

All samples were transported in a dry nitrogen atmosphere to a VG Ionex system equipped with a VG Clam II analyzer, Mg/Al  $K\alpha$  dual anode x-ray source, VG MIG-102  $\text{Ga}^+$  and VG FAB61 ion source, LEG 31F electron flood gun and M12-2s (<800 amu) quadrupole. The XPS measurements were carried out using the Al anode. All C 1s peaks corresponding to hydrocarbon were calibrated at a binding energy of 285.0 eV to correct for the energy shift caused by charging. The static SIMS measurements were performed with the electron impact gun (FAB 61) using Xe at 5 keV, while taking care to keep the total ion dose for each measurement within the static limit.

All samples were prepared as regular devices, except where mentioned otherwise. For this purpose the glass substrates were first cleaned by ultrasonic treatment in acetone, rubbing with soap, rinsing with demineralized water, refluxing with isopropanol, and finally UV ozone treatment. Subsequently, a layer of PEDOT:PSS was spin coated from an aqueous dispersion under ambient conditions on the cleaned substrates and the layer was dried by annealing the substrate. Then a layer of either MDMO-PPV or PCBM was spin coated from a chlorobenzene solution on top of the PEDOT:PSS layer and the sample was transferred to a  $\text{N}_2$  atmosphere glove box. Finally, for some samples LiF and/or aluminum layers were deposited by thermal evaporation under vacuum ( $5 \times 10^{-6}$  mbar, 1 ppm  $\text{O}_2$ , and <1 ppm  $\text{H}_2\text{O}$ ). The following samples were prepared:

- (1) Two reference samples of a 60 nm thick layer of Al or LiF deposited on a previously cleaned Si(100) wafer;
- (2) one reference sample of  $\text{AlF}_3$  powder pressed into indium foil;
- (3) two reference samples of pure MDMO-PPV or PCBM as the top layer of prepared-as-normal devices;
- (4) four samples with a 5 Å layer of Al or LiF deposited on top of either MDMO-PPV or PCBM as the top layer of prepared-as-normal devices;
- (5) two samples with a 5 Å layer of Al deposited on top of a

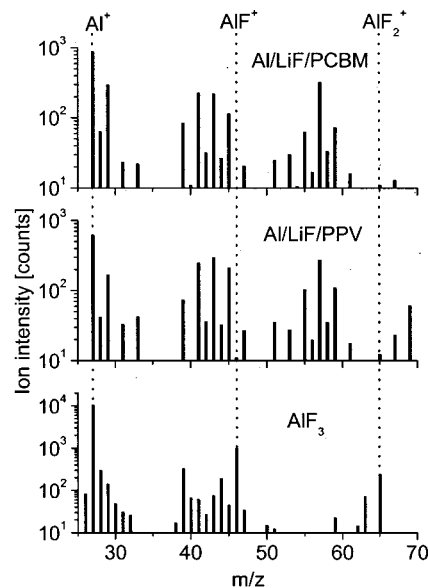


FIG. 2.  $\text{AlF}_3$  reference comparison with Al/LiF/MDMO-PPV or Al/LiF/PCBM. Note the logarithmic scale of the ion intensity axis.

5 Å layer of LiF on top of either MDMO-PPV or PCBM as the top layer of prepared-as-normal devices.

All samples were prepared in duplo, so that separate samples could be used for the SSIMS and XPS measurements.

## III. RESULTS AND DISCUSSION

A popular explanation of the improved electron injection by LiF is the doping of the active polymer by Li liberated by a reaction between LiF and Al deposited on top of this. Although the Gibbs free energy required to liberate Li was estimated at 112.8 kJ/mol, making it an endothermic and hence unfavorable reaction, Mason *et al.* suggested that this is only the case for bulk LiF and that the reaction might be exothermic in the case of small isolated clusters of LiF.<sup>9</sup>

Because the reaction would give rise to  $\text{AlF}_3$  on the surface of the organic layer, we have investigated the presence of  $\text{AlF}_3$ . Figure 2 shows the comparison between the SIMS spectra of a pure  $\text{AlF}_3$  reference sample and of the Al/LiF/MDMO-PPV and Al/LiF/PCBM interfaces. The peaks of interest of the  $\text{AlF}_3$  reference samples are  $\text{Al}^+$ ,  $\text{AlF}^+$ , and  $\text{AlF}_2^+$  at the  $m/z$  values of 27, 46, and 65 D. The  $\text{AlF}^+$  and  $\text{AlF}_2^+$  peaks should be present for the Al/LiF/MDMO-PPV and Al/LiF/PCBM samples, but they either have very low intensity or are completely missing. The low intensity of the  $\text{AlF}^+$  and  $\text{AlF}_2^+$  signals that are present are background signals caused by the underlying layers of MDMO-PPV and PCBM. Note that the drop in intensity for these peaks cannot be explained with the matrix effect, because then all signal intensities should drop by more or less the same amount, but the decrease in the Al ion signal is much less dramatic than that of the  $\text{AlF}^+$  and  $\text{AlF}_2^+$  signals.

Hence, the absence of  $\text{AlF}_3$  related signals in the SIMS spectra of the Al/LiF/MDMO-PPV and Al/LiF/PCBM samples is strong evidence that the proposed reaction between LiF and Al does not occur on MDMO-PPV or PCBM.

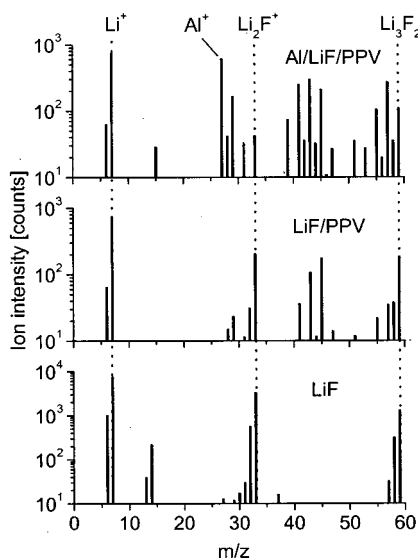


FIG. 3. Comparison of a LiF reference sample, a LiF/MDMO-PPV, and an Al/LiF/MDMO-PPV sample shows that LiF stays intact on the surface of MDMO-PPV, regardless of the presence of Al.

Greczynski *et al.*<sup>13</sup> claimed that CsF decomposes on PFO, based upon the ratio of CsF to the amount of Al needed to completely decompose CsF, and others have made the suggestion for LiF on Alq<sub>3</sub> based on rather indirect methods. However, Greczynski *et al.* showed with XPS that for the case of LiF on PFO no evidence can be found that LiF decomposes in the presence of Al.

Because all studied alkali and alkaline earth metal fluorides seem to improve the electron injection of the cathode,<sup>16</sup> a general mechanism is likely to exist. Our results indicate,

together with Greczynski *et al.*'s, that the proposed LiF/Al reaction to AlF<sub>3</sub> is *not* that general mechanism.

However, the reaction to AlF<sub>3</sub> was only proposed as a possible mechanism to obtain free Li atoms, which could subsequently dope the organic material. Kido *et al.* showed<sup>14</sup> that a Li-doped Alq<sub>3</sub> layer exhibited a luminance an order of magnitude higher than an Alq<sub>3</sub> layer without Li, suggesting that Li-doping of the organic layer may also occur for alkali and alkaline earth metal fluoride containing devices.

If Li is liberated on the surface of the organic material, by reaction with Al or in any other conceivable way, then LiF should no longer be visible on the surface of the organic material. Figure 3 shows a comparison between SSIMS spectra from a LiF reference sample, and of LiF on MDMO-PPV, with and without Al on top. The LiF panel at the top of Fig. 3 shows a clear ion cluster series of Li<sub>n</sub>F<sub>n-1</sub><sup>+</sup>, although only a small part is shown here. The LiF/MDMO-PPV panel in the middle clearly shows the same ion pattern for LiF. Unfortunately, an Al layer on top of the LiF layer attenuates the LiF cluster ion signals, as shown in the Al/LiF/MDMO-PPV panel. Identical results have been obtained for the PCBM samples.

Because of the small amount of LiF deposited, the presence of LiF on top of the organic layers indicates that no liberation of Li takes place in any way, as the ion cluster series of Li<sub>n</sub>F<sub>n-1</sub><sup>+</sup> can only be formed if there are large clusters of LiF on the surface, which is a rather unlikely occurrence if most of the LiF has reacted. Hence, a mechanism in which Li dopes the underlying organic layer is unlikely.

As mentioned before, one reaction that has been shown to occur is the reaction between Al and the underlying organic layer, for example with Alq<sub>3</sub> (Refs. 8 and 9) and

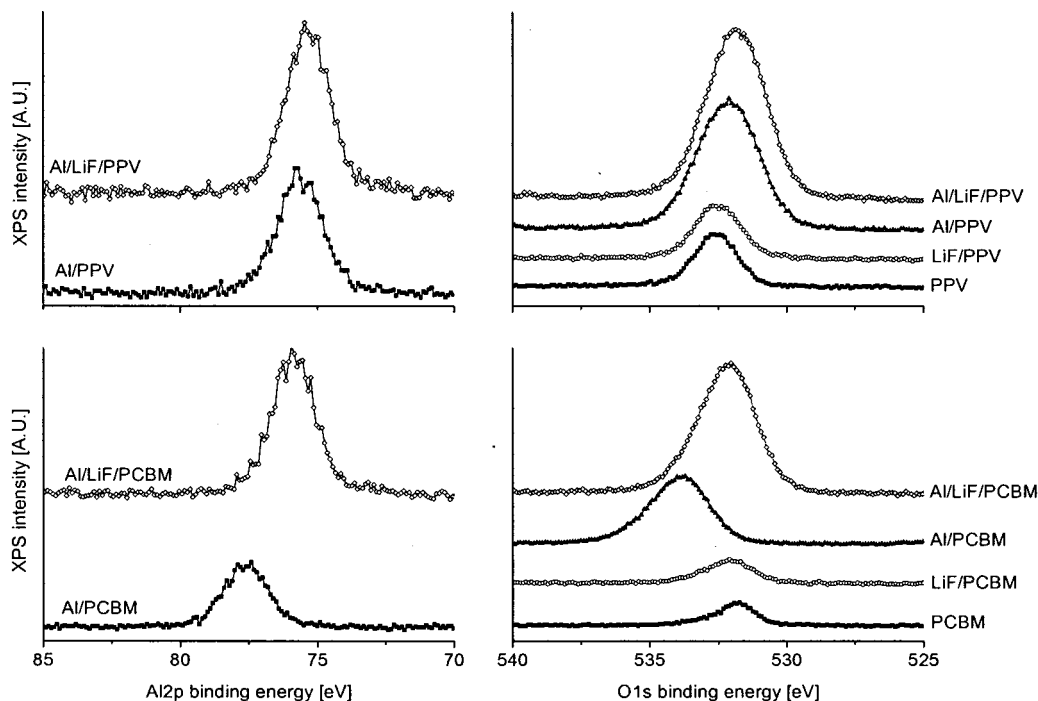


FIG. 4. Comparison of the Al 2*p* and O 1*s* regions of MDMO-PPV and PCBM samples suggests that PCBM reacts with Al upon adsorption if the PCBM layer is not protected by a thin layer of LiF. MDMO-PPV is insensitive to this reaction.



PFO.<sup>13</sup> In the case of  $\text{Alq}_3$ , Le *et al.*<sup>8</sup> calculated, using density-functional theory, that the first four angstrom<sup>9</sup> of incoming aluminum will bond directly to oxygen atoms on two of the three quinolate rings in the  $\text{Alq}_3$  molecule. Greczynski *et al.*<sup>13</sup> showed that only relatively small amounts of Al were needed in order to cause near complete degradation of the valence band, which suggests that Al–C complexes are formed, although the authors did not claim any specific site of reaction on PFO.

To investigate the possibility of a reaction of Al with MDMO-PPV and PCBM, XPS was used to systematically measure the C 1s, O 1s, and Al 2p core-level regions of MDMO-PPV and PCBM layers with or without LiF, Al, and Al/LiF layers on top. In the case of MDMO-PPV, shown in Fig. 4, all binding energies were within 0.1 eV of the reference values. However, in the case of Al/PCBM a large shift of 1.5 eV was observed for the O 1s peak originating from the oxygen in PCBM compared to the same peak seen for the sample with no Al on top. Upon the insertion of a thin LiF layer, this peak shifted back 1.8 eV to a lower binding energy. The same binding energy shift was found for the Al 2p peak. No difference in the C 1s region could be observed at all, indicating that carbon atoms were unaffected.

The fact that the O 1s and Al 2p peaks both shifted to higher binding energies by the same amount is a strong indication that the carboxylic oxygen interacts with the aluminum. The aluminum is probably not metallic but in the form of  $\text{Al}_x\text{O}$ , because of the extreme broadening of the O 1s peak upon adsorption of aluminum and the getter behavior of aluminum in vacuum. A possible reaction could be an acid–base reaction between the carboxylic group of PCBM and  $\text{Al}_x\text{O}$ , with methanol and an organometallic complex between the carboxylic group and the aluminum atom as reaction products. No comparison with literature values is possible, because a related complex could not be found in the literature.<sup>26,27</sup>

Unfortunately, verification of the proposed organometallic complex formation by SIMS is doubtful, because the most obvious peaks to look for, such as  $\text{AlO}^+$ , can also originate from  $\text{Al}_x\text{O}$ . Another consideration is that the nature of the carboxyl group bonds with the aluminum is not known, and these bonds may be too weak to survive the impact of the primary ions. Hence, DFT calculations should be performed to verify the probability of this reaction.

#### IV. CONCLUSIONS AND SUMMARY

Some relevant sandwich-type interfaces related to solar cell devices and polymer LEDs have been studied using secondary ion mass spectrometry and x-ray photoelectron spectroscopy, including Al/MDMO-PPV, LiF/MDMO-PPV, Al/LiF/MDMO-PPV, and similar interfaces containing PCBM instead of MDMO-PPV. SIMS measurements show that LiF does not react with aluminum to  $\text{AlF}_3$ , nor does it react in any other way to liberate Li as can be concluded from the detection of  $\text{Li}_n\text{F}_{n-1}^+$  ions. The doping of the organic layer by Li suggested by various authors is unlikely as a mechanism for the improvement of electron injection into the polymer layer.

Although MDMO-PPV seems to be stable towards the deposition of aluminum by evaporation, XPS data give evidence of a reaction between aluminum and PCBM at the carboxylic group present in PCBM, as shown by the shift of the O 1s carboxylic oxygen peak upon aluminum deposition. A thin layer of LiF is enough to undo this shift, evidence that the LiF layer protects the underlying PCBM from the aluminum atoms.

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