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Oxygen- and Water-Based Degradation in PCBM Films

Qinye Bao, Xianjie Liu, Slawomir Braun, and Mats Fahlman*

[*] Q. Bao, Dr. X. Liu, Dr. S. Braun and Prof. M. Fahlman
Division of Surface Physics and Chemistry
Department of Physics, Chemistry and Biology, IFM, Linköping University
SE-58183 Linköping, Sweden
E-mail: qinba@ifm.liu.se

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Organic semiconductors (OSCs), i.e. π -conjugated small molecules and polymers, exhibit optical and electronic properties suitable for applications in e.g. transistors, light emitting diodes and photovoltaic cells.¹⁻¹⁰ All such devices contain several interfaces, metal-organic and/or organic/organic, that effect significantly performance and functionality. Much effort consequently has been invested in describing the energetics governing charge injection/extraction at such heterojunctions.¹¹⁻²² To date, organic light emitting diodes (OLEDs) have found their way into commercial displays in e.g. cell phones and TVs, whereas organic transistors and photovoltaic cells are still waiting for a commercial breakthrough. The development of organic photovoltaics (OPVs) for solar energy harvesting has however intensified in recent years and energy conversion efficiencies of ~10% have been demonstrated.^{5, 23} Both small molecule and polymer based OPV technologies currently are being pursued, creating a large demand for new donor and acceptor type materials. For the polymer based OPV devices, however, fullerene derivatives, and in particular [6, 6]-phenyl-C61-butyric acid methyl ester (PCBM),²⁴ so far completely dominate in terms of choice of acceptor material.^{5, 25-27} In the field of polymer-PCBM bulk heterojunction photovoltaic cells, over 8% power conversion efficiency has been reported,^{5, 28} and the rate of improvement is rapid.⁵ The lifetime and stability for PCBM-based OPV devices historically have been

substantially lower than that of conventional inorganic solar cells,^{5, 29} however, and this may present an obstacle for commercialization.

Many OSCs indeed are sensitive to ambient atmosphere³⁰⁻³⁴ and may e.g. be oxidized (p-doped) when exposed to oxygen and/or water, a process typically accelerated by light exposure and elevated temperature. Absorption of water or other species from ambient air also may affect the electronic structure (and morphology) of an OSC film even if no doping or chemical modification occurs, by *e.g.* inducing increased film disorder and complexing with O₂ or water.^{30-32, 35} In fact, many OSC films display electron trap states at ~3.6 eV below the vacuum level, which is suggested to be caused by bishydrated-oxygen complexes created by water+O₂ uptake.³⁶ Hence, unless protected, the electronic and/or optical properties of OSC films in devices can degrade over time leading to loss in device performance. For OPVs such losses typically show up as decreases in short circuit current, open circuit voltage, fill factor and sometimes by the formation of an “S”-shaped current-voltage curve.³⁷⁻⁴⁰ Several studies have been carried out on the efficiency and lifetime degradation of OPV devices,^{25, 41-43} and the degradation mechanisms and stability of the OSC materials in OPVs themselves when exposed to different conditions have also been probed⁴⁴⁻⁴⁷ as an improved understanding of the fundamental degradation mechanisms of OSC materials in OPVs is expected to aid in future development of both materials (OSC and sealing materials) and in device design.

As PCBM is a common component in OPVs, it is of particular interest to probe the effects of oxygen and water vapor exposure on its electronic structure. Photoinduced chemical changes of PCBM films in ambient atmosphere have been demonstrated using a combination UV-vis and IR spectroscopy, showing a strong interaction between the oxygen and the C₆₀ cage of the fullerene.⁴⁶ In this paper, we further investigate the influence of ambient

atmosphere on PCBM films by controlled *in situ* exposure of O₂ gas and water vapor *separately*, and modifications to the chemical or electronic structure, if any, are probed by photoelectron spectroscopy. The *in situ* approach also ensures that the samples are shielded from the UV-part of sun light during O₂/H₂O exposure, which is the likely scenario in a real OPV cell/module. The origins of the measured effects for the two types of exposure are discussed and the expected effects on device performance are commented upon.

PCBM films were deposited onto various substrates chosen to feature a broad range of work functions so as to create PCBM/substrate interfaces spanning all three regimes of the integer charge transfer (ICT) model^{11-13, 48, 49}: (i) $\Phi_{\text{sub}} > E_{\text{ICT}+}$ - Fermi level pinning to a positive integer charge transfer state, resulting in a substrate-independent work function; (ii) $E_{\text{ICT-}} < \Phi_{\text{sub}} < E_{\text{ICT+}}$ - Vacuum level alignment, giving a substrate-dependent work function, slope = 1; (iii) $\Phi_{\text{sub}} < E_{\text{ICT-}}$ - Fermi level pinning to a negative integer charge transfer state, resulting again in a substrate-independent work function, see Fig. 1. From the results presented in Fig. 1, the PCBM $E_{\text{ICT-}}$ is determined to be 4.3 eV and the PCBM $E_{\text{ICT+}} = 5.3$ eV, the former in good agreement with previous results.⁵⁰⁻⁵² The achieved $E_{\text{ICT-}}$ ($E_{\text{ICT+}}$) value of PCBM corresponds to the largest energy gained from adding one electron (the smallest energy required to take away one electron) to (from) the PCBM molecule at the interface producing a fully relaxed state. When Φ_{sub} is smaller than $E_{\text{ICT-}}$ (is larger than $E_{\text{ICT+}}$) of PCBM, the spontaneous charge transfer occurs across the interface with the formation of downshift (upshift) dipole in reaching equilibrium, and the resulting $\Phi_{\text{PCBM/sub}}$ is constant with 4.3 eV of $E_{\text{ICT-}}$ (5.3 eV of $E_{\text{ICT+}}$). In the vacuum level alignment regime, predicted for the substrates with work function in between the PCBM $E_{\text{ICT+}}$ and $E_{\text{ICT-}}$ in absence of a dipole originating from the molecular film itself (ordering effect), the Φ_{sub} vs $\Phi_{\text{PCBM/sub}}$ points should all fall on the slope = 1 line without charge transfer, and indeed do for PCBM on ITO ($\Phi_{\text{sub}} = 4.7\text{eV}$)

and PEDOT:PSS ($\Phi_{\text{sub}} = 4.8 \text{ eV}$ and 5.0 eV , two different formulations), see Fig. 1. For PCBM coated onto SiO_x/Si ($\Phi_{\text{sub}} = 4.45\text{-}4.5 \text{ eV}$), the points sit $\sim 0.15 \text{ eV}$ above the slope = 1 line, indicating a dipole shift in a region where absence of charge transfer is expected according to the ICT model. The origin of this shift (reproduced for several samples) is thus not clear, but possibly related to partial ordering of the PCBM film at the SiO_x interface which would induce a dipole step through the molecular dipole moment of PCBM.

The PCBM/substrate work function subsequently was measured as a function of exposure time to O_2 gas, the corresponding results shown in Fig. 2a to 2e. Fig. 2a depicts the UPS spectral evolution of PCBM films on AlO_x/Al substrates as function of exposure time under the controlled oxygen gas pressure. The bottom spectrum corresponds to the pristine PCBM film, and its WF and the IP are estimated to be 4.3 eV and 6.2 eV , respectively. As the WF of AlO_x/Al substrate is 3.80 eV , the PCBM/ AlO_x/Al pins to the negative ICT (ICT^-) level, consistent with the previous reports.^{51, 52} Upon increasing exposure time from 30 to 180 min, a downward vacuum level shift of 0.16 eV is observed as the work function decreases from 4.31 to 4.15 eV , where it stabilizes. At the same time, the HOMO edge gradually shifts towards higher binding energy by 0.15 eV and finally locates at 2.07 eV below E_F level, i.e., the IP stays constant and is not affected by the oxygen exposure. Additionally, there is no observable broadening of spectral features and no additional features appear upon oxygen gas exposure. (Note that the applied exposure times are sufficient for complete diffusion of oxygen molecules through the PCBM film). Analogous results, exhibited in Fig. 2b, occur for the case of positive pinning illustrated by PCBM/ AuO_x/Au (UV-ozone cleaned gold) ($\Phi_{\text{sub}} = 5.6 - 5.8 \text{ eV}$) interfaces. Initially, the work function is pinned to the E_{ICT^+} value of PCBM, 5.3 eV , as $E_{\text{ICT}^+} < \Phi_{\text{sub}}$ for these substrates. Upon exposure, work function and HOMO shifts are induced reaching 0.13 eV and 0.12 eV , respectively, after 180 min exposure time. Again there is a saturating trend and no change in IP and no broadening of the spectral

features occur. Finally, Fig. 2c-e depict the cases of PCBM on ITO ($\Phi_{\text{sub}}=4.7\text{eV}$), SiO_x/Si ($\Phi_{\text{sub}}=4.45\text{ eV}$), and PEDOT:PSS ($\Phi_{\text{sub}}= 5.0\text{ eV}$). PCBM/ITO and PCBM/PEDOT:PSS undergo nearly an identical evolution of the work function and IP, saturating at a $\sim 0.15\text{ eV}$ downshift of work function and retaining an IP of $\sim 6.2\text{ eV}$ without broadening of the spectral features. Interestingly, the PCBM/ SiO_x/Si case also retains an IP of $\sim 6.2\text{ eV}$ and no broadening of the spectral features, but the work function downshifts $\sim 0.3\text{ eV}$, placing the resulting work function ~ 0.15 below the original ICT curve, just as for all the other points measured for O_2 exposure in region (i), (ii) and (iii), see Fig. 3.

To explore if the origin of the oxygen exposure effect, we performed a number of control experiments. A possible origin for the down shift in work function could be O_2 interaction with the substrates. The bare substrates were thus exposed to O_2 gas in a similar series as for the PCBM/substrate experiments and the work function evolution was monitored, see Fig. 4a. The bare substrates feature different surfaces than those of the PCBM/substrate samples where the surfaces are already covered by PCBM molecules prior to O_2 exposure and may thus behave differently, but nevertheless represent a useful comparison. As can be seen from the data presented in Fig. 4a, the work function evolution is indeed drastically different than for the corresponding PCBM-covered substrates, indicating that O_2 interaction with PCBM is responsible for the down shift in work function. To probe if the effect is related to O_2 interaction with the fullerene cage or with the substituent group of PCBM, studies on O_2 exposure of C_{60} films *in situ* deposited onto ITO substrates were carried out. The work function of the ITO used ensures that the C_{60}/ITO falls in region (ii) of the ICT model^{48, 53} just as the PCBM/ITO interface. The UPS spectra, depicted in Fig. 4b, show a similar behavior upon O_2 exposure as that for PCBM/ITO, with a work function downshift of 0.17eV at saturation and a constant IP with no broadening of the spectral features, suggesting that the

effect is not related to the PCBM substituent group. Finally, to test the strength of the O₂-PCBM interaction, post-exposure-series heating of samples were carried out. The original work function was recovered with no other change to the spectral feature or IP, suggesting a weak interaction (no covalent bonding). This was supported by XPS C(1s) and O(1s) core level spectra of PCBM films, pristine and after 180 min O₂ exposure, that show a slight uptake of oxygen (~8% increase) but no new features in the C1s and O1s core level spectra, see Fig 4c and d.

The interaction between water vapor and PCBM films differ significantly from the case of O₂ gas. Fig. 5a shows the UPS spectra evolution obtained of a pristine PCBM/AlO_x/Al film upon exposure to water vapor at the pressure of 6.5×10^{-6} mbar (exposure times depicted in the figure). With increasing water vapor exposure time, the frontier electron structure features undergo strong modification with extensive broadening even after very short exposure time. This observed bleaching of the features derived is direct evidence of a strong water-PCBM interaction. Simultaneously, the modification of the spectroscopic features is accompanied by a decrease of WF and IP. After 240 min exposure the WF is decreased by ~0.4 eV and the trend has not saturated. XPS C1s and O1s core level spectra of PCBM films, pristine and after 180 min water exposure, that show a significant uptake of oxygen (~18% increase) and a new feature in the C1s core level spectrum (broadening to the high energy side in the binding energy range of C-O bonds), see Fig 5b and c. Heating in vacuum did not recover the spectrum of pristine PCBM, also indicative of a strong water-PCBM interaction featuring covalent bonding. The same effects (unsaturated down shift of work function even after 240 min of exposure, extensive bleaching of the spectral features) were obtained for PCBM films on ITO substrates (not shown) in the unpinned case, region (ii), where no charged PCBM

species exist at the substrate interface. Hence, the results indicate that water molecules take a chemical interaction with PCBM, causing a decrease in IP and work function.

The results presented differ dramatically from what has been observed for PCBM films exposed to air, where $O_n(\text{PCBM})$ was formed, proposedly due to interaction with either ozone or hydroxide, yielding a deeper lying LUMO.⁴⁴ Such deeper lying LUMO states at the substrate interface are expected to shift the E_{ICT} to higher energy and hence upshift the work function for region (iii). This clearly does not happen for O_2 or water exposure in our experiments, and indeed we expect no significant amount of ozone to be present to form complexes as the samples are shielded from UV light during exposure. Furthermore, a modification of the E_{ICT} is not expected to create an upshift or down shift in region (ii), which we show does in fact occur for exposure under non-UV light conditions. Oxygen gas has been shown to create electron trap states in picene³⁰ and P(NDI2OD-T2)³¹, by forming non-covalently bonded O_2 -molecule/polymer complexes. A similar interaction does not seem likely for PCBM, however. If such trap states are empty, they are expected to lead to an increased E_{ICT} and a work function up shift, and if partially filled would induce a “band bending”-like effect, creating a thickness dependent upshift of the vacuum level (increase of work function). Again, this is not observed for either O_2 or water vapor exposure in our experiments. The formation of bishydrated-oxygen complexes introduces trap states closer to the vacuum level than the PCBM LUMO,³⁶ and hence such trap states could downshift the work function in region (iii), but again, would not induce the observed downshift in regions (i) and (ii). Simultaneous exposure to O_2 and water was nevertheless carried out but merely yielded a superposition of the two separate exposure effects (not shown). The mechanisms for the observed results thus remain an open question.

In conclusion, we present the effects of *in situ* oxygen/water exposure on the energetics of PCBM films. The results indicate that the modification of the spectroscopic features originates from interaction between the fullerene part of the PCBM molecules and the exposed O₂ or water molecules. Our results reveal that the degradation effects and mechanisms of PCBM induced by oxygen and water are completely different. Upon exposure to oxygen gas, the work function is downshifted by ~0.15 eV compared to the ideal ICT curve for pristine PCBM, which is incompatible with significant introduction of electron trap states or p-doping of the PCBM films. The IP and UPS spectral features of the PCBM films are not affected and the O₂ degradation is reversible by thermal treatment in vacuum, indicating a weak interaction between the O₂ and PCBM molecules. For water vapor exposure, we find that the occupied valence electron structure undergo irreversible strong modification illustrated by significant modification of the C1s and O1s core levels spectra, extensive broadening and bleaching of the UPS spectral features, as well as significant decreases of the IP and work function that do not saturate for the exposure times used. This suggests a degradation mechanism involving significant chemical interaction between PCBM and water. Our findings in this work can help us in understanding which molecules in atmosphere are very sensitive for PCBM and which are to be relatively insensitive so as to control of environment factors as need for application. Also, the degradation effects and mechanisms can provide the guidance for the design of electron acceptor materials for enhanced environmental stability in organic electronics.

Experimental

The PCBM used in the study was obtained from Solenne BV, and thin films (~20 nm) were spin-coated onto different conductive substrates from 15 mg/ml o-dichlorobenzene solutions in dark condition, then directly and quickly (~4 min) transferred using a container covered

with aluminum foil to shield from illumination, into the load lock chamber of the ultrahigh vacuum (UHV) system used for the experiments. All substrates were cleaned by sonication in acetone and isopropyl before spin coating. The photoemission experiments were done in an UHV surface analysis system, consisting of an entry chamber (base pressure $\sim 1 \times 10^{-7}$ mbar), a preparation chamber ($\sim 8 \times 10^{-10}$ mbar) and an analysis chamber ($\sim 2 \times 10^{-10}$ mbar). *In situ* exposure of PCBM film to oxygen and water vapor respectively was carried out in the preparation chamber under the pressure of 6.5×10^{-6} mbar controlled via a leak-valve. After each exposure step, the film samples were transferred to the analysis chamber without breaking UHV for measurements. Ultraviolet photoelectron spectroscopy, UPS, (HeI $h\nu = 21.22$ eV) and X-ray photoelectron spectroscopy, XPS, (monochromatized Al K α $h\nu = 1486.6$ eV) spectra were recorded with a Scienta-200 hemispherical analyzer, and calibrated by referencing to Fermi level and Au4f_{7/2} peak position of the Ar⁺ ion sputter-clean gold foil. UPS was performed to study the interfacial alignment and the frontier electronic structure features with an error margin of ± 0.05 eV. The work function is derived from the secondary electron cut-off and the vertical ionization potential (IP) from the frontier edge of the occupied density of states.^{14, 48} XPS was used to detect possible chemical reaction and element absorption in the films after exposure. All water/O₂ exposure and measurements were carried out in chambers shielded from UV light (by aluminum foil) and under near-dark conditions (ambient UHV chamber light). The samples were shielded from UV light during O₂/water exposure as OPV cells likely will be manufactured on glass or plastic (e.g. poly(ethylene terephthalate), PET) substrates, the latter typically featuring UV-absorbers as PET itself photo-degrades due to UV light.⁵⁴

Supporting information:

Supporting Information is available online from Wiley InterScience or from the author.

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References

- [1] C.J. Brabec, N.S. Sariciftci, and J.C. Hummelen, *Adv. Funct. Mater.* **11**, 15 (2001).
- [2] R.H. Friend, R.W. Gymer, A.B. Holmes, J.H. Burroughes, R.N. Marks, C. Taliani, D.D.C. Bradley, D.A.D. Santos, J.L. Brédas, M. Lögdlund, and W.R. Salaneck, *Nature* **397**, 121 (1999).
- [3] M. Hiramoto, H. Fujiwara, and M. Yokoyama, *Appl. Phys. Lett.* **58**, 1062 (1991).
- [4] M. Hiramoto, H. Fujiwara, and M. Yokoyama, *J. Appl. Phys.* **72**, 3781 (1992).
- [5] G. Li, R. Zhu, and Y. Yang, *Nature Phot.* **6**, 153 (2012).
- [6] C.W. Tang, *Appl. Phys. Lett.* **48**, 183 (1986).
- [7] C.W. Tang and S.A. Vanslyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- [8] Y. Wang, O. Acton, G. Ting, T. Weidner, S. P. J, H. Ma, F.S. Ohuchi, D.G. Castner, and A.K.-Y. Jen, *Org. Electron.* **11**, 1066 (2010).
- [9] J. Zaumseil and H. Sirringhaus, *Chem. Rev.* **107**, 1296 (2007).
- [10] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, and A.J. Heeger, *Science* **270**, 1789 (1995).
- [11] M. Bokdam, D. Cakir, and G. Brocks, *Appl. Phys. Lett.* **98**, 113303 (2011).
- [12] M. Fahlman, A. Crispin, X. Crispin, S.K.M. Henze, M.P.d. Jong, W. Osikowicz, C. Tengstedt, and W.R. Salaneck, *J. Phys.: Condens. Matter* **19**, 183202 (2007).
- [13] M.T. Greiner, M.G. Helander, W.M. Tang, Z.B. Wang, J. Qiu, and Z.H. Lu, *Nature Mater.* **11**, 76 (2011).

- [14] H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater.* **11**, 605 (1999).
- [15] H. Fukagawa, S. Kera, T. Kataoka, S. Hosoumi, Y. Watanabe, K. Kudo, and N. Ueno, *Adv. Mater.* **19**, 665 (2007).
- [16] S. Braun, M.P. de Jong, W. Osikowicz, and W.R. Salaneck, *Appl. Phys. Lett.* **91**, 202108 (2007).
- [17] L. Ley, Y. Smets, C.I. Pakes, and J. Ristein, *Adv. Funct. Mater.* **23**, 794 (2013).
- [18] N. Koch, *Journal of Physics-Condensed Matter* **20**, 12 (2008).
- [19] H. Vázquez, W. Gao, F. Flores, and A. Kahn, *Phys. Rev. B* **71**, 041306R (2005).
- [20] S. Braun, X. Liu, W.R. Salaneck, and M. Fahlman, *Org. Electron.* **11**, 212 (2010).
- [21] G. Brocks, D. Cakir, M. Bokdam, M.P. de Jong, and M. Fahlman, *Org. Electron.* **13**, 1793 (2012).
- [22] D. Cakir, M. Bokdam, M.P. de Jong, M. Fahlman, and G. Brocks, *Appl. Phys. Lett.* **100**, 4 (2012).
- [23] M.A. Green, K. Emery, Y. Hishikawa, W. Warta, and E.D. Dunlop, *Prog. Photovolt: Res. Appl.* **20**, 12 (2012).
- [24] J.C. Hummelen, B.W. Knight, F. Lepeq, F. Wudl, J. Yao, and C.L. Wilkins, *Journal of Organic Chemistry* **60**, 532 (1995).
- [25] O. Armbruster, C. Lungenschmied, and S. Bauer, *Phys. Rev. B* **86**, 235201 (2012).
- [26] J. Peet, J.Y. Kim, N.E. Coates, W.L. Ma, D. Moses, J.H. A, and D.C. Bazan, *Nature Mater.* **6**, 497 (2007).
- [27] J. Shinar, Z.V. Vardeny, and Z.H. Kafafi, in *Optical and Electronic Properties of Fullerenes and Fullerene-based Materials*. 1999, Marcel Dekker: New York.
- [28] Z. He, C. Zhong, X. Huang, W.-Y. Wong, H.B. Wu, L.W. Chen, S.J. Su, and Y. Cao, *Adv. Mater.* **23**, 4636 (2011).

- [29] M.A. Green, K. Emery, Y. Hishikawa, and W. Warta, Prog. Photovolt: Res. Appl. **17**, 320 (2009).
- [30] Y. Wang, S.D. Motta, F. Negri, and R. Friedlein, J. Am. Chem. Soc. **133**, 10054 (2011).
- [31] R.D. Pietro, D. Fazzi, T.B. Kehoe, and H. Sirringhaus, J. Am. Chem. Soc. **134**, 14877 (2012).
- [32] K.Z. Xing, M. Fahlman, M. Lögdlund, D.A.D. Santos, V. Parenté, R. Lazzaroni, J.L. Brédas, R.W. Gymer, and W.R. Salaneck, Adv. Mater. **8**, 971 (1996).
- [33] K.Z. Xing, N. Johansson, G. Beamson, D.T. Clark, J.L. Brédas, and W.R. Salaneck, Adv. Mater. **9**, 1027 (1997).
- [34] A. Vollmer, O.D. Jurchescu, I. Arfaoui, I. Salzmänn, T.T.M. Palstra, P. Pudolf, J. Niemax, J. Pflaum, J.P. Rabe, and N. Koch, Eur. Phys. J. E **17**, 339 (2005).
- [35] T. Sueyoshi, H. Kakuta, M. Ono, K. Sakamoto, S. Kera, and N. Ueno, Applied Physics Letters **96**, 093303 (2010).
- [36] H.T. Nicolai, M. Kuik, A.H.W. G. B.d. Boer, C. Campbell, C. Risko, J.L. Brédas, and P.W.M. Blom, Nature Mater. **11**, 882 (2012).
- [37] J. Bhattacharya, R.W. Mayer, M. Samiee, and V. L.Dalal, Appl. Phys. Lett. **100**, 193501 (2012).
- [38] M. Hermenau, M. Riede, K. Leo, S.A. Gevorgyan, F.C. Krebs, and K. Norrman, Sol. Energy Mater. Sol. Cells **95**, 1268 (2011).
- [39] M. Jørgensen, K. Norrman, and F.C. Krebs, Sol. Energy Mater. Sol. Cells **92**, 686 (2008).
- [40] A. Seeman, T. Sauermann, C. Lungenschmied, O. Armbruster, S. Bauer, H.-J. Egelhaaf, and J. Hauch, Sol. Energy **85**, 1238 (2011).
- [41] A. Guerrero, P.P. Boix, L.F. Marchesi, T. Ripolles-Sanchis, E.C. Pereira, and G. Garcia-Belmonte, Solar Energy Materials and Solar Cells **100**, 185 (2012).

- [42] N. Grossiord, J.M. Kroon, R. Andriessen, and P.W.M. Blom, *Org. Electron.* **13**, 432 (2012).
- [43] J.A. Hauch, P. Schilinsky, S.A. Choulis, S. Rajioelson, and C.J. Brabec, *Appl. Phys. Lett.* **93**, 103306 (2008).
- [44] M.O. Reese, A.M. Nardes, B.L. Rupert, R.E. Larsen, D.C. Olson, M.T. Lloyd, S.E. Shaheen, D.S. Ginley, G. Rumbles, and N. Kopidakis, *Adv. Funct. Mater.* **20**, 3476 (2010).
- [45] S. Chambon, M. Manceau, M. Firon, S. Cros, A. Rivaton, and J.L. Gardette, *Polymer* **49**, 3288 (2008).
- [46] S. Chambon, A. Rivaton, J.L. Gardette, and M. Firon, *Solar Energy Materials and Solar Cells* **91**, 394 (2007).
- [47] Q.D. Yang, T.-W. Ng, M.-F. Lo, F.Y. Wang, N.B. Wong, and C.-S. Lee, *J. Phys. Chem. C* **116**, 10982 (2012).
- [48] S. Braun, W.R. Salaneck, and M. Fahlman, *Adv. Mater.* **21**, 1450 (2009).
- [49] C. Tengstedt, W. Osikowicz, W.R. Salaneck, I.D. Parker, C.-H. Hsu, and M. Fahlman, *Appl. Phys. Lett.* **88**, 053502 (2006).
- [50] R.J. Davis, M.T. Lloyd, S.R. Ferreira, M.J. Bruzek, S.E. Watkins, L. Lindell, P. Sehati, M. Fahlman, J.E. Anthony, and J.W.P. Hsu, *J. Mater. Chem.* **21**, 1721 (2011).
- [51] P. Sehati, S. Braun, L. Lindell, X.J. Liu, L.M. Andersson, and M. Fahlman, *IEEE J. Sel. Top. Quantum Electron.* **16**, 1718 (2010).
- [52] Z. Xu, L.M. Chen, M.H. Chen, G. Li, and Y. Yang, *Appl. Phys. Lett.* **95**, 013301 (2009).
- [53] W. Osikowicz, M.P.d. Jong, and W.R. Salaneck, *Adv. Mater.* **19**, 4213 (2007).
- [54] G.J.M. Fechinec, M.S. Rabellob, R.M.S. Maiora, and L.H. Catalani, *Polymer* **45**, 2303 (2004).

Fig. 1 Three regimes of the integer charge transfer plots between $\Phi_{\text{PCBM/sub}}$ and Φ_{sub} : (i) $\Phi_{\text{sub}} > E_{\text{ICT}^+}$, (ii) $E_{\text{ICT}^-} < \Phi_{\text{sub}} < E_{\text{ICT}^+}$, and (iii) $\Phi_{\text{sub}} < E_{\text{ICT}^-}$. E_{ICT^+} and E_{ICT^-} of the pristine PCBM are determined to be 5.3 eV and 4.3 eV, respectively.

Fig. 2 UPS spectra evolution at the secondary electron region (work function) and the frontier electronic structure region (HOMO) of PCBM coated on (a) AlO_x/Al , (b) AuO_x/Au (UVO), (c) ITO, (d) PEDOT:PSS, and (e) SiO_x/Si substrates as function of *in situ* exposure time under the controlled O_2 gas pressure of 6.5×10^{-6} mbar versus a base UHV of 1.0×10^{-9} mbar.

Fig. 3 The resulting ICT plots of PCBM after saturated O_2 exposure.

Fig. 4 (a) work function evolution of the bare substrates as function of O_2 exposure time. (b) UPS spectra of C60 film *in situ* deposited onto ITO substrate when exposed to O_2 . (c) and (d) XPS $C1s$ and $O1s$ core level spectra of PCBM film before and after 240 min O_2 exposure.

Fig. 5 (a) UPS spectra evolution obtained of a pristine PCBM/AlOx/Al film as function of *in situ* water vapor exposure time at the pressure of 6.5×10^{-6} mbar versus a base UHV of 1.0×10^{-9} mbar, (b) and (c) XPS $C1s$ and $O1s$ core level spectra of a PCBM/AlOx/Al film before and after 240 min water vapor exposure.

The table of contents entry: Effects of *in situ* oxygen/water exposure on the energetics of PCBM films are presented. For oxygen exposure, WF is downshifted by ~ 0.15 eV compared to the ideal ICT curve for pristine PCBM, which is incompatible with significant introduction of electron trap states or p-doping. Water induces HOMO structure undergoing irreversible strong modifications accompanied by a chemical interaction with PCBM.

Keywords: electronic structure; integer charge transfer; oxygen/water exposure; degradation; photoelectron spectroscopy.

Qinye Bao, Xianjie Liu, Slawomir Braun, and Mats Fahlman*

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Oxygen- and Water-Based Degradation in PCBM Films

By Qinye Bao, Xianjie Liu, Slawomir Braun, and Mats Fahlman*

[*] Q. Bao, Dr. X. Liu, Dr. S. Braun and Prof. M. Fahlman
Division of Surface Physics and Chemistry
Department of Physics, Chemistry and Biology, IFM, Linköping University
SE-58183 Linköping, Sweden
E-mail: qinba@ifm.liu.se

To test the effect of short air exposure (~4 minutes) prior to pump down to UHV conditions (~ 1 hour), PCBM films were spin coated on Al (Sample1: S1) and Au(UVO) (Sample 3: S3) substrates in a glove box, transferred using a N₂-containing sealed container and finally inserted into the load lock chamber under a N₂ environment, thus shielding the samples from air exposure. Sample 2 (S2) and 4 (S4) were PCBM films spin coated on Al and Au(UVO) substrates and transferred to the load lock in air. As evidence from the UPS spectra shown in Fig. S1, the WF, ionization potential, and spectral features show no change between S1 and S2, and between S3 and S4, respectively, and the O/C ratios from XPS are equal to the theoretical value. There is hence no measurable difference between the two types of preparation/transfer procedures, *i.e.*, they yield identical samples from a spectroscopy perspective.

Fig. S1: UPS spectra of PCBM coated on Al (S1, S2) and Au(UVO) (S3, S4). S1 and S3 are pristine films protected with N₂, S2 and S4 have no N₂ protection on the transfer way.

Fig. S2: Work function, HOMO and IP plots of PCBM film as function of *in situ* O₂ exposure time. WF shows a down shift and HOMO has an upward shift, but IP keeps constant.

Fig. S3: Work function, HOMO and IP plots of PCBM film as function of *in situ* water vapor exposure time. All of WF, HOMO and IP show down shifts.

Fig. S4: XPS C1s core level spectra fitting of PCBM film before and after oxygen (a, b) and water vapor exposure (c, d) by Gaussian/Lorentzian mixing functions and the least-square peak. Dashed lines represent the fitting results.