On the function of a bathocuproine buffer layer in organic photovoltaic cells

M. Vogel, S. Doka, Ch. Breyer, M. Ch. Lux-Steiner, and K. Fostiropoulos[a)]
Hahn-Meitner-Institut Berlin, Glienicker Str. 100, 14109 Berlin, Germany

(Received 7 July 2006; accepted 29 August 2006; published online 16 October 2006)

The role of bathocuproine (BCP) buffer layer inserted between active layer and Al contact in photovoltaic cells based on phthalocyanine (Pc) and C_{60} was investigated. Photoluminescence (PL) experiments show exciton quenching at the C_{60}–Al interface to be strongly reduced by inserting BCP. Current-voltage characteristics of photovoltaic cells with planar geometry front electrode/Pc/C_{60}/BCP/Al show that BCP dramatically improves electron transport out of the C_{60} film into the Al electrode. The tenfold increase in power conversion efficiency (η) with BCP can mostly be attributed to the latter effect. BCP does not improve η in photovoltaic cells with blend film geometry front electrode/Pc:C_{60}/Al. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2362624]

The vision of transferring the tremendous success of semiconductor devices to a potentially cheap technology on flexible substrates by the use of organic materials has attracted a steadily increasing number of researchers. Current active film thicknesses range in the order of 100 nm. Therefore device performance is governed by interface properties. In particular, the importance of the electronic transition between organic films and inorganic electrodes has been pointed out in numerous publications.[1–4] One solution has been to insert a so-called exciton blocking layer between electron transport layer and emissive layer in the case of organic light emitting device[5] or between electrode and acceptor materials in the case of organic photovoltaic cells.[6] It is the aim of this work to shed some light on the function of a bathocuproine (BCP) exciton blocking layer in organic photovoltaic cells. On this subject some evidence has been gathered by evaluation of device characteristics.[5–7] However, we would like to point out that the physics of multilayer systems is very elaborate. For this reason it is difficult to pin down physical effects taking device performance only into account. Therefore the problem is tackled by two approaches. Firstly by studying organic photovoltaic cells with and without BCP film in planar and in blend geometry we gather information about the effects of the buffer layer on charge transport. Secondly a photoluminescence experiment was carried out. Making use of this method enables us to disregard any charge transport effects and at the same time to greatly reduce the number of films and interfaces of the system. We thereby gather more direct evidence on the function of BCP films with regard to excitons. In addition we make use of theoretical calculations of electric field distribution and exciton diffusion to back conclusions from the experiments outlined above.

Photovoltaic cells were fabricated by thermal sublimation of phthalocyanine (Pc) (both CuPc and ZnPc were used, no significant differences could be observed), C_{60}, and the BCP buffer layer (all 99.9% purity, supplied by Covion AG) in vacuum. The front electrode consisted of commercial indium tin oxide (ITO) (supplied by PGO GmbH) cleaned with organic solvents, detergents, and de-ionized water. Prior to deposition of the active layer, ITO substrates were coated with a thin layer of poly(ethylene dioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS) or treated with phosphoric acid as described in a previous publication.[4] The Al back electrode was equally deposited *in situ* by thermal evaporation. Film thicknesses were monitored by means of quartz crystal microbalances. Device characteristics were measured after encapsulation in N_2 atmosphere. Simulated photovoltaic irradiation (AM 1.5 G, one sun) was supplied by a commercial source.

Samples for the photoluminescence (PL) experiment were produced on quartz substrates utilizing the same process as for photovoltaic cell fabrication. It is important to note that the evaporation steps were carried out within a few minutes in vacuum. The PL measurements were carried out in evacuated sample environment in reflection geometry. Sample temperatures were kept at 10 K by means of a He closed-cycle cryostat. Excitation light was supplied by an Ar-ion laser with 20 mW at 514 nm and a spot size of about 100 μm diameter. The photoluminescence was analyzed with a grating monochromator and detected with a liquid nitrogen cooled photomultiplier.

Figure 1 shows the photoluminescence spectra of C_{60}. Sample 1, consisting of quartz/30 nm C_{60}/100 nm Al, shows a low intensity spectrum, almost lacking characteristic features. Sample 2 (quartz/100 nm Al/30 nm C_{60}) yielded a spectrum more intense by up to one order of magnitude. According to Capozzi *et al.*[8] its characteristic features are typical of thin films of C_{60} on quartz and can be ascribed to the emission of C_{70} (1.90 eV), a self-trapped Frenkel exciton (1.71 eV) and its phonon replica at 1.62 and 1.53 eV. Similar values were also reported by Mochizuki *et al.*[9] According to Ref. 8, these features can also be observed somewhat broadened at room temperature. The most pronounced spectrum with the highest intensity is found for sample 3 (quartz/30 nm C_{60}/17 nm BCP/100 nm Al). It shows the four features described and therefore much resembles the spectrum of sample 2.

In Fig. 2 the *IV* curves of two photovoltaic cells with sequentially deposited phthalocyanine (30 nm) and C_{60} (30 nm) films are plotted. From these results a dramatic difference between the device without BCP (cell A) and the photovoltaic cell with 17 nm BCP (cell B) becomes apparent. The *IV* curve of cell A follows an s shape while the

[a)]Electronic mail: fostiropoulos@hmi.de

 © 2006 American Institute of Physics
Downloaded 30 Aug 2007 to 134.30.24.17. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

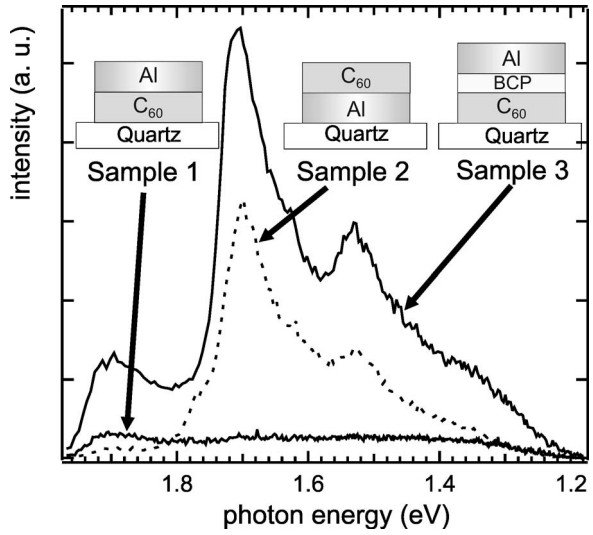

FIG. 1. Photoluminescence spectra of C_{60} films at 10 K with different interfaces to an Al electrode. The direction of excitation and PL is indicated in the inset sample schemes.

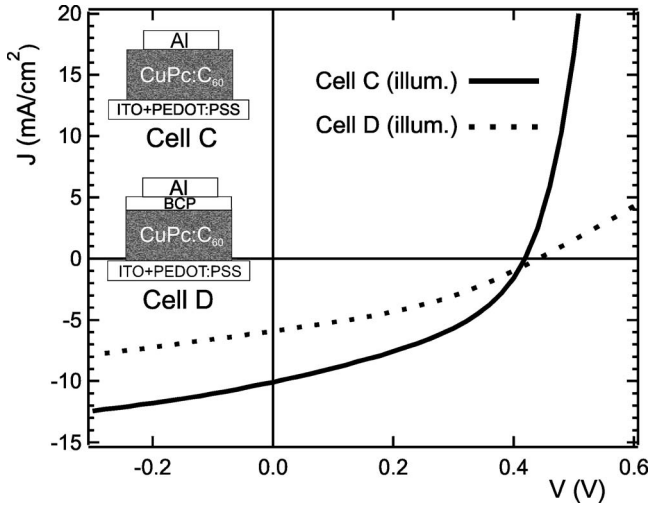

FIG. 3. Current density–voltage characteristics of photovoltaic cells with codeposited Pc–C_{60} blend film with and without BCP buffer layer. Photovoltaic cell parameters are the following. cell C: J_{sc}=10.1 mA/cm^2, V_{oc}=0.40 V, and FF=0.42, and η=1.7%; cell D: J_{sc}=5.9 mA/cm^2, V_{oc}=0.44 V, FF=0.36, and η=0.9%.

curve of cell B displays typical diode characteristics. The photovoltaic cell parameters of cell A are at least twice the value of cell B's parameters. The efficiency is higher by more than one order of magnitude.

In Fig. 3 the *IV* characteristics of photovoltaic cells with 80 nm phthalocyanine-C_{60} blend film as an active layer are shown. Cell C was produced without BCP buffer layer and cell D with 17 nm BCP. The ITO electrode is coated with a PEDOT:PSS. This additional film has proven necessary in our blend cells. Comparison of cells C and D clearly shows that the introduction of a BCP film in blend devices decreases the power conversion efficiency. The decrease is due to a reduction of the short circuit current density (J_{sc}) by about 40% and the fill factor by about 15%.

The interpretation of PL measurements is based on the following reasoning. Exciton lifetime is determined by both radiative and nonradiative recombination rates. By making the simple assumption that the radiative recombination (i.e., PL) rate of C_{60} films is an intrinsic property and therefore unaffected by its interfaces, we can conclude from PL on the nonradiative recombination (i.e., exciton quenching). By varying the C_{60}–Al interface we can therefore examine its influence on exciton quenching.

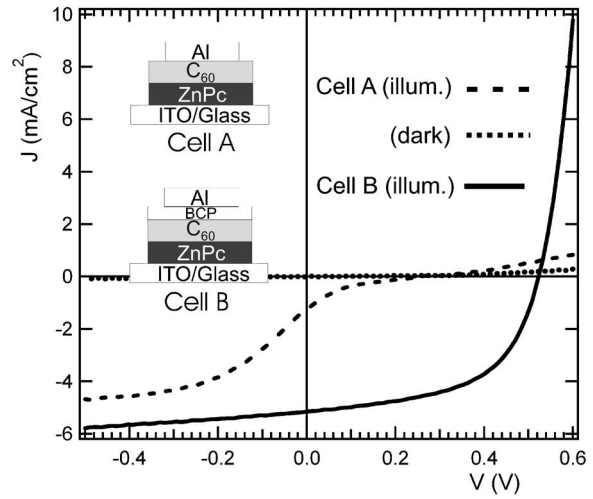

FIG. 2. Current density–voltage characteristics of photovoltaic cells with sequentially deposited ZnPc and C_{60} films with and without BCP buffer layer. Photovoltaic cell parameters are the following. cell A: J_{sc}=1.2 mA/cm^2, V_{oc}=0.12 V, fill factor (FF)=0.12, and η=0.0%; cell B: J_{sc}=5.2 mA/cm^2, V_{oc}=0.52 V, and FF=0.5, and η=1.5%.

In the case of sample 1, we conclude that in the absence of BCP nonradiative recombination at the Al–C_{60} interface is too fast to allow for strong photoluminescence. This exciton quenching effect is expected near a metal surface, since the oscillating dipole field of the excited molecules induces a field inside the metal. This interaction can result in excitations such as electron-hole pairs, phonons, or surface plasmons inside the metal and thus quench the molecular exciton.[10,11] In contrast to sample 1 significant PL is observed in sample 2, clearly showing the PL spectrum of C_{60}. Evidently the exciton quenching properties of the C_{60}–Al interface depend strongly on the deposition sequence. If Al is deposited on C_{60}, exciton quenching is much stronger than if C_{60} is deposited on Al. This can be explained by diffusion of Al during deposition into the C_{60} film, creating a highly structured interface, rendering interface induced exciton recombination more likely. Deposition related formation of Al clusters possibly also contributes to exciton quenching. An alternative explanation attributes the enhanced exciton recombination to chemical reactions, creating recombination centers at the interface. Those reactions may take place, when reactive Al atoms arrive at the C_{60} surface. Chemical interaction between molecules and metals can strongly enhance the quenching rate due to charge transfer processes.[11] It should be mentioned, however, that in the production process of sample 2 C_{60} is likewise deposited on top of a reactive, nonoxidized metal surface. Such recombination centers would therefore also be expected in sample 2. For this reason the explanation of exciton quenching by the structured Al surface due to Al diffusion is more likely.

Sample 3 with a BCP buffer layer between Al and C_{60} shows the strongest PL and consequently the lowest exciton quenching rate. We can conclude that BCP does indeed prevent exciton recombination at the Al–C_{60} interface. This can be achieved by simply increasing the distance d between

Downloaded 30 Aug 2007 to 134.30.24.17. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp

excited molecules and metal surface, since the exciton quenching rate is typically proportional to d^{-3} or even d^{-4}.[11,12] But does BCP serve as such a genuine exciton blocking layer or is it merely a protective film to avoid Al diffusion into C_{60} or chemical reactions due to the Al deposition process? Given the similarity of the PL spectra of sample 2 and sample 3 and the nearly completely quenched spectrum of sample 1, we tend to attribute the larger part of the improved interface properties to the function of BCP as a protective film.

By interpretation of the current-voltage (*IV*) characteristics of planar photovoltaic cells with and without BCP film (Fig. 2) conclusions on the effect of the buffer layer on electron transport from C_{60} into the Al electrode can be drawn. The reduction of the short circuit current density (J_{sc}) is reduced by more than 70% from 5.2 mA/cm^2 in cell B to 1.2 mA/cm^2 in cell A. In contrast at a bias of −0.5 V the photocurrent in cell A is only about 20% lower. This strong voltage dependence of the photocurrent shows that exciton quenching explains only a small part of the loss of photocurrent in cell A, since excitons are neutral and therefore independent of applied bias. Theoretical calculations of electric field distribution and exciton diffusion show that even complete quenching of excitons at the Al–C_{60} interface does not reduce the photocurrent by more than about 13% compared with an exciton reflecting interface. A detailed description of the model is found in Ref. 13. The larger part of the photocurrent increase in cell B must therefore be due to much more efficient electron transport from C_{60} into the Al electrode via BCP. Supporting evidence for this conclusion was found in literature,[14] stating that a blocking contact is formed upon deposition of Al on C_{60}. The most important function of BCP is consequently to establish an Ohmic contact between Al and C_{60}.

It has been proposed that BCP buffer layers can act as optical spacers[6] to optimize the electromagnetic field distribution in photovoltaic cells. We could show by the aforementioned simulation that BCP as spacer can increase J_{sc} by not more than ~10%. The optimal spacer thickness is around 10 nm.

In blend photovoltaic cells with no or very little phase separation between donor (here, Pc) and acceptor (C_{60}) as in the present case[15] excitons are always generated close to the Pc–C_{60} interface and therefore dissociate very quickly.[16] Accordingly the exciton density in the blend film is too low to account for significant nonradiative recombination. We therefore do not expect an exciton blocking layer to significantly improve J_{sc}. Indeed blend photovoltaic cells without BCP show ~60% higher J_{sc} than their counterparts with BCP buffer layer (Fig. 3). But how does the BCP film in blend photovoltaic cells influence charge transport into the Al electrode? Both cells C and D (Fig. 3) show diode behavior, unlike the *s*-shaped curve of the planar device without BCP (Fig. 2). We conclude that without BCP good electrical contact between blend film and Al is possible. In this regard the blend film differs from a pristine C_{60} film. As measurements by ultraviolet photoelectron spectroscopy have shown, there are significant differences in the electronic levels of C_{60} in blend films compared to pure C_{60} films[17] which may explain why a blocking contact is formed in the case of the C_{60}–Al interface and an Ohmic contact at the blend-Al interface. If the BCP film is needed neither for the prevention of exciton recombination at the blend-Al interface nor for the improvement of the electronic contact, it will only introduce an additional resistive layer and therefore lower the power conversion efficiency in the photovoltaic cell, as observed in Fig. 3.

In conclusion we could show that a BCP buffer layer reduces nonradiative recombination of excitons at the C_{60}–Al interface. In photovoltaic devices, however, its most important function is to establish an Ohmic contact between the C_{60} film and the Al electrode. In photovoltaic cells with a Pc–C_{60} blend as photoactive film devices without BCP buffer layer show superior performance. In this case an Ohmic contact at the blend-Al interface is formed without buffer layer and the exciton density in the blend is too low to account for significant nonradiative recombination at the blend-Al interface.

The authors gratefully acknowledge support of the German Ministry of Environment (Contract No. 0329927A) and helpful discussions with Marin Rusu.

[1] T. M. Brown, J. S. Kim, R. H. Friend, F. Cacialli, R. Daik, and W. J. Feast, Appl. Phys. Lett. **75**, 1679 (1999).
[2] L. S. Hung, C. W. Tang, and M. G. Mason, Appl. Phys. Lett. **70**, 152 (1997).
[3] P. Peumans and S. R. Forrest, Appl. Phys. Lett. **79**, 126 (2001).
[4] B. Johnev, M. Vogel, K. Fostiropoulos, B. Mertesacker, M. Rusu, M.-C. Lux-Steiner, and A. Weidinger, Thin Solid Films **488**, 270 (2005).
[5] D. F. O'Brien, M. A. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **74**, 442 (1999).
[6] P. Peumans, V. Bulovic, and S. R. Forrest, Appl. Phys. Lett. **76**, 2650 (2000).
[7] S. Heutz, P. Sullivan, B. M. Sanderson, S. M. Schultes, and T. S. Jones, Sol. Energy Mater. Sol. Cells **83**, 229 (2004).
[8] V. Capozzi, G. Casamassima, G. F. Lorusso, A. Minafra, R. Piccolo, T. Trovato, and R. Valentini, Solid State Commun. **98**, 853 (1996).
[9] S. Mochizuki, M. Sasaki, and R. Ruppin, J. Phys.: Condens. Matter **10**, 2347 (1998).
[10] R. R. Chance, A. Prock, and R. Silbey, J. Chem. Phys. **62**, 2245 (1975).
[11] Ph. Avouris and B. N. J. Persson, J. Phys. Chem. **88**, 837 (1984).
[12] G. Vaubel, H. Baessler, and D. Möbius, Chem. Phys. Lett. **10**, 334 (1971).
[13] Ch. Breyer, M. Vogel, M. Mohr, B. Johnev, and K. Fostiropoulos, Phys. Status Solidi B (in press).
[14] L. Ma, J. Ouyang, and Y. Yang, Appl. Phys. Lett. **84**, 4786 (2004).
[15] M. Vogel, J. Strotmann, B. Johnev, M. Ch. Lux-Steiner, and K. Fostiropoulos, Thin Solid Films **511-512**, 367 (2006).
[16] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science **258**, 1474 (1992).
[17] M. Vogel, dissertation, Freie Universität Berlin, 2005.

Downloaded 30 Aug 2007 to 134.30.24.17. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp