

Ambipolar Blends of Cu-Phthalocyanine and Fullerene: Charge Carrier Mobility, Electronic Structure and their Implications for Solar Cell Applications

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Summary: Ambipolar transport has been realised in blends of the molecular hole conductor Cu-phthalocyanine (CuPc) and the electron conducting fullerene C₆₀. Charge carrier mobilities and the occupied electronic levels have been analyzed as a function of the mixing ratio using field-effect transistor measurements and photoelectron spectroscopy. These results are discussed in the context of photovoltaic cells based on these materials.

Keywords: ambipolar transport; organic semiconductor blends; organic solar cells

Introduction

In recent years organic semiconductors have attracted considerable interest due to their growing potential as active materials in electronic and optoelectronic devices. A long-standing paradigm, however, has been seen in their unipolar transport of electrical charges. Thus multi-layer structures comprising different organic materials with spatially separated electron and hole transport layers were used for fabricating efficient organic light-emitting diodes.^[1] On the other hand in photovoltaic devices, owing to short exciton diffusion length in organic semiconductors, p- and n-conducting materials need to be in close contact which is usually realized by mixing them in one single layer yielding a so-called bulk-heterojunction structure.^[2–5] Recently, such donor-acceptor mixtures have been implemented also in organic field-effect transistors (OFETs). Ambipolar OFETs have been realized with a variety of material combinations, including polymer/fullerene blends,^[6] mixtures of soluble oligomers^[7] as

well as evaporated molecular hetero-layer structures and mixed layers.^[8]

Our recent studies in this field have focussed on the combination of hole conducting copper-phthalocyanine (CuPc) with the electron conducting fullerene C₆₀. We have investigated OFETs with various mixing ratios and film preparation conditions and have demonstrated ambipolar inverters with these blends.^[9] Using photoelectron spectroscopy, we have recently determined the occupied electronic levels and their changes upon mixing both materials.^[10] In this contribution we will summarize these results and discuss their implications in the context of photovoltaic cells based on a combination of CuPc as electron donor and C₆₀ as electron acceptor, respectively. In particular we will demonstrate that differences in the open-circuit voltages of heterolayer cells and bulk-heterojunction devices can be traced back to the electronic structure of the blends.

Film Morphology and Charge Carrier Mobility

For characterisation in OFETs, films of neat CuPc and C₆₀ and their mixtures have been prepared by thermal evaporation on pre-structured Si wafers covered with thermally grown SiO₂. The organic films

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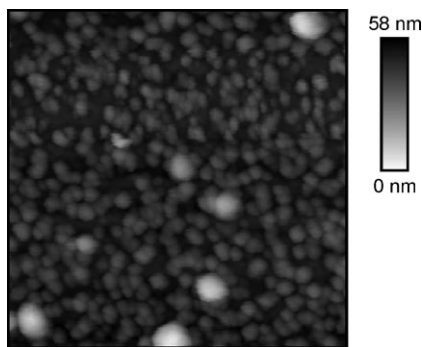


Figure 1.

Scanning force microscopy image taken in non-contact mode for a 1:1 mixed film grown at a substrate temperature of 375 K. The total image size is $2 \times 2 \mu\text{m}^2$. The film has an r.m.s. roughness of 6.5 nm.

were about 25 nm in thickness and the oxide about 300 nm. Details of the preparation can be found in Ref. [9]. Figure 1 shows as an example the morphology of a 1:1 mixture measured by non-contact scanning force microscopy (SFM). The image clearly demonstrates that one is not dealing with a molecular mixture of both materials but rather with a nano-phase separated structure. Note that the height scale is more than twice the nominal film thickness. Detailed studies^[9] show that the tendency for demixing is strongest for such a 1:1 mixture and decreases towards more asymmetric mixing ratios.

We have also determined the field-effect mobility from the saturation regime of OFETs for both electrons and holes as a function of the mixing ratio. For these studies we have varied the substrate treatment (oxygen plasma or silanization of the SiO_2 surface) and the substrate temperature during film growth. The resulting mobilities are displayed in Figure 2. Apparently, an exponential decrease of both μ_e and μ_h is observed upon dilution of the corresponding conducting material with the other species. A similar decrease has been reported in the literature for an ambipolar light-emitting system of co-evaporated molecular materials.^[11] Furthermore, we find that heating the substrate during evaporation in combination with silanization increases the mobilities of neat films

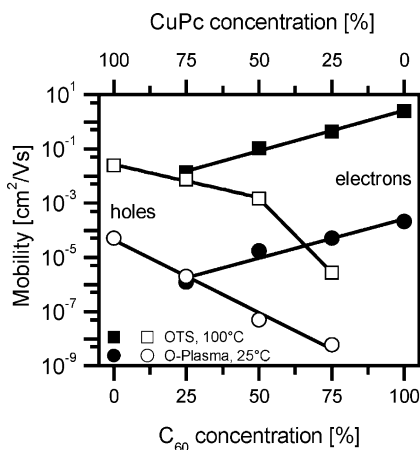


Figure 2.

Electron and hole mobilities determined from the saturation regime of OFETs as function of the mixing ratio. The filled symbols are related to the electron transport, the open symbols to the hole transport.

and mixed layers by up to four orders of magnitude. Remarkably, electron mobilities exceeding $1 \text{ cm}^2/\text{Vs}$ can be achieved in neat C_{60} films. We also note that independent of the film growth conditions balanced electron and hole mobilities are achieved at about 25% fullerene content in the mixture, which is an important prerequisite for inverters with symmetric switching behaviour.^[9]

The detailed mechanism behind the huge increase in mobility is still under investigation; however, our preliminary data acquired by SFM on films grown under different conditions indicate an increase of the grain size for OTS treatment in combination with elevated substrate temperature (100°C). Nevertheless, x-ray diffraction shows that the degree of crystallinity is affected only very weakly by the different growth conditions. The problem is that the field-effect mobility is very sensitive to the molecular arrangement of the first few monolayers at the surface of the gate dielectric which is hard to probe by measurements on 25 nm thick films.[#]

[#]Changes of the gate oxide capacitance can be ruled out as a source for different charge carrier mobilities because the OTS layer alters the insulator capacitance by less than 1%.

Electronic Structure

Using photoelectron spectroscopy the occupied electronic levels of neat films and mixtures of both materials have been determined with respect to the Fermi energy of an underlying gold substrate (for details see Ref. [10]). It was found that the energies of the highest molecular orbitals (HOMO), the core levels and the vacuum level vary linearly with the mixing ratio. Figure 3 shows the synopsis of these studies, viz. the dependence of the HOMO and lowest unoccupied molecular orbital (LUMO) levels of both materials as a function of the composition of the film. Thereby one should note that the LUMO level has not been measured so far in blends, but we have taken the data from inverse photoemission for neat films of CuPc and C₆₀ and extrapolated towards blends assuming the same shift of the LUMO levels that was observed for all other levels.^[10] In other words, we have assumed that the energy gaps of both materials stay constant in the mixture. This seems to be a reasonable assumption, as

there is no indication for charge transfer between both materials in the ground state that would lead to new features in the electronic structure.

Postulating that this model is correct, one can draw some interesting conclusions from Figure 3. First, it predicts that the injection barrier for holes into CuPc, i.e. the difference between the HOMO of CuPc and the Fermi level of Au (which is the reference level at binding energy zero in Figure 3) is larger than the barrier for electron injection into C₆₀, which is actually observed in OFETs.^[9] Further both injection barriers should decrease from neat films towards blends. However, if the contact resistance in OFETs is analyzed systematically (for details see Ref. [12]), one finds just the opposite behaviour: the contact resistance increases from neat films to blends. We have recently shown that this behaviour is indicative of diffusion limited injection where the decreasing mobility in blends (see Figure 2) is responsible for an increase of the contact resistance.^[12]

Photovoltaic Cells

Another consequence of the electronic level scheme shown in Figure 3 is related to photovoltaic cells based on CuPc and C₆₀ as a donor-acceptor system. Upon the absorption of light excitons generated in either of the two materials (within the reach of the respective exciton diffusion length) will be dissociated at the organic-organic interface leading to electrons in the LUMO of C₆₀ and holes in the HOMO of CuPc. This charge separation leads to a gradient of the chemical potential at the interface that drives the photocurrent through the cell.^[13] Thus the magnitude of the HOMO-LUMO offset between both materials will be related to the driving force, for which the open-circuit voltage can serve as an easily accessible experimental quantity.^[14] As already indicated by the arrows in Figure 3, the obtained electronic structure therefore allows the conclusion that the HOMO-LUMO offset in blends is significantly smaller than at the heterojunction between neat layers of CuPc and C₆₀.

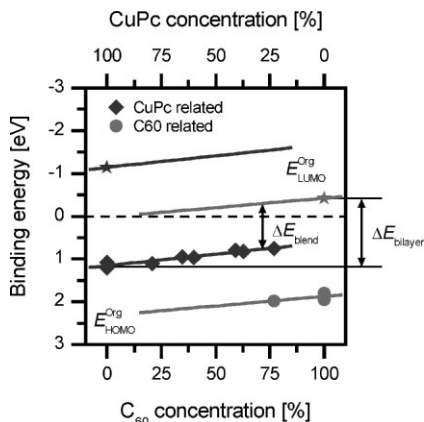


Figure 3.

Position of the HOMO and LUMO levels as determined from photoelectron spectroscopy as a function of the C₆₀/CuPc mixing ratio. The solid lines are linear fits of the measured values; the constant dashed line is the Fermi level of the Au substrate, for which we have determined a work function of 4.2 eV under the applied preparation conditions. The LUMO levels are calculated from the transport gap of the neat materials assuming a constant electron affinity.

To test this prediction we have measured the photovoltaic response of photodiodes with indium-tin oxide (ITO) anodes covered with 30 nm of the conducting polymer PEDOT:PSS (BAYTRON P), an 80 nm thick active organic layer and a LiF:Al cathode. Thereby we have compared a bilayer structure comprising 40 nm of CuPc and 40 nm of C₆₀ on the one hand and an 80 nm thick 1:1 mixture of both materials on the other hand. The obtained current-voltage characteristics in the fourth quadrant are shown in Figure 4 for different light intensities. It can be seen that the blend system has significantly higher short-circuit currents, but the built-in voltage where all curves cross each other is smaller by 0.25 V. For clarification we have plotted the open-circuit voltage in dependence of the light intensity in Figure 5. Evidently, the open-circuit voltage in the blend is by 0.15 V smaller and the difference is more or less independent of the light intensity. We note that the observed behaviour is in excellent agreement with recent numerical simulations by Marsh et al. [15].

Conclusion

We have investigated charge carrier mobility and electronic structure of neat films

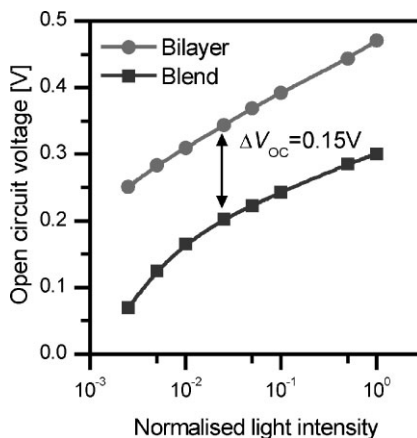


Figure 5.

The open circuit voltage of the cells shown in Figure 4 as a function of the light intensity. The maximum light intensity of the used Xe arc lamp equipped with AM1.5 filters was about 20 mW/cm².

and mixtures of CuPc and C₆₀ and have discussed the implications for photovoltaic cells based on these materials. We demonstrate that the bulk-heterojunction concept, though being very successful by providing a large active volume for exciton dissociation, has two weaknesses: (1) a reduction of charge carrier mobility and (2) a lower open-circuit voltage as compared to heterolayer structures. It will be a challenging task for future studies to control morphology and nano-phase separation on a length

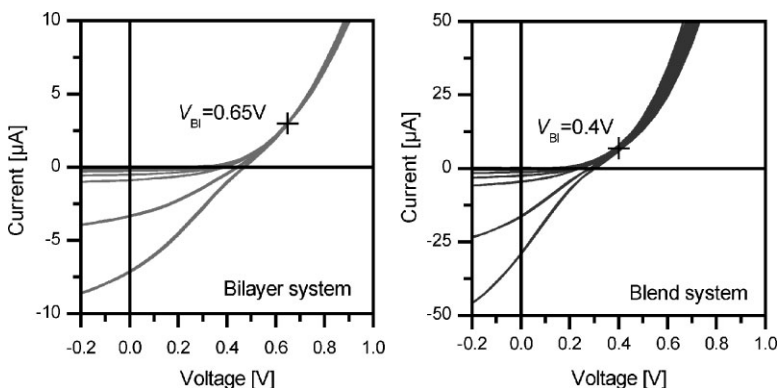


Figure 4.

Current-voltage characteristics for a bilayer (left) and a bulk heterojunction (right) solar cell with the device structure ITO/PEDOT:PSS/organic layer(s)/LiF:Al and an active area of about 4 mm². The curves are shown for different light intensities as indicated in Figure 5. The built-in voltage is marked as the crossing point of all curves.

scale suitable for both exciton diffusion and charge carrier transport to further improve molecular solar cells.

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