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Microstructure and charge carrier transport in phthalocyanine based semiconductor blends

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ABSTRACT

The continuously growing and wide-spread utilization of blends of organic electron and hole conducting materials comprises ambipolar field-effect transistors as well as organic photovoltaic cells. Structural, optical and electrical properties are investigated in blends and neat films of the electron donor material Cu-phthalocyanine (CuPc) together with fullerene C₆₀ and Cu-hexadecafluorophthalocyanine (F₁₆CuPc) as electron acceptor materials, respectively. The difference in molecular structure of the spherical C₆₀ and the planar molecule CuPc leads to nanophase separation in the blend, causing charge carrier transport which is limited by the successful formation of percolation paths. In contrast, blends of the similar shaped CuPc and F₁₆CuPc molecules entail mixed crystals, as can be clearly seen by X-ray diffraction measurements. We discuss differences of both systems with respect to their microstructure as well as their electrical transport properties.

INTRODUCTION

From the mid 1990s the concept of “bulk-heterojunction solar cells” revolutionized the field of organic photovoltaics: Yu *et al.* reported a polymeric solar cell with an interpenetrating donor/acceptor material system which enables a spatially distributed interface accounting for the small exciton diffusion lengths in organic semiconducting materials [1]. Since that time, blends of organic electron and hole conductive materials are widely used for ambipolar charge carrier transport and photovoltaic cells. The application of distributed interfaces in organic solar cells has the advantage that excitons can efficiently dissociate throughout the whole volume of the organic layer yielding higher amounts of free charge carriers as compared to a bilayer system. Nevertheless, for an efficient transport, each material must provide continuous paths to the contacts. Both aspects entail a competition between efficient charge carrier dissociation and preferably undisturbed transport properties inside the blend.

In this study we present the analysis of two model systems for donor-acceptor blends. These are (i) Cu-phthalocyanine (CuPc) combined with the Buckminster fullerene C₆₀ and (ii) CuPc in combination with its fluorinated counterpart F₁₆CuPc. While CuPc acts as the donor or p-conductor, C₆₀ and F₁₆CuPc are the n-conducting acceptor materials. In addition to studying the fundamental structural and optical properties, centering on the question of phase separation or formation of mixed crystals, we extend our analysis to electrical charge carrier transport properties. The materials used have been previously investigated in similar configurations partially with different donor or acceptor materials [2,3], however, no systematic comparison with respect to the influence of the mixing behavior on the transport properties was reported.

EXPERIMENT

Diodes for ambipolar charge carrier transport and unipolar hole-only devices were fabricated on commercially available indium-tin-oxide (ITO)-coated glass substrates (Merck) which were cleaned with different solvents in an ultrasonic bath followed by an oxygen plasma treatment in order to enhance the work function of ITO and to improve wettability for the aqueous suspension of the intrinsically conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, purchased from H.C. Starck as BAYTRON P). The organic layers were grown by vacuum deposition from low-temperature effusion cells with a base pressure of about 10^{-7} mbar and deposition rates between 0.35 Å/s for neat films and up to 1.4 Å/s for the material with the higher volume fraction in the mixtures.

For the ambipolar setup, a thin (5 Å) layer of LiF was deposited prior to deposition of the Al cathode which was evaporated through a shadow mask to a thickness of 1000 Å, giving an active area of 2×2 mm². For hole-only devices, the organic semiconductor is sandwiched between a PEDOT:PSS coated ITO substrate and a Au counterelectrode combined with an electron blocking layer consisting of a 40 nm thick layer of N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) or alternatively a thin layer of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F₄TCNQ). For pure electron transport the organic layer is framed between an Al electrode at the bottom and a LiF/Al counterelectrode on top, restricting the injection to electrons. The overall thickness of the organic layer amounts to 200 nm for the CuPc/C₆₀ system and 80 nm for the CuPc/F₁₆CuPc system. The structural formulas of the materials used are depicted in figure 1.

CuPc and F₁₆CuPc were purchased from Sigma Aldrich as sublimed grade and additionally purified by thermal gradient sublimation prior to deposition. C₆₀ was purchased from Sigma Aldrich as sublimed grade and used as received. The mixed layers were grown by codeposition from independent evaporation sources, with the deposition rates monitored by two quartz-crystal microbalances.

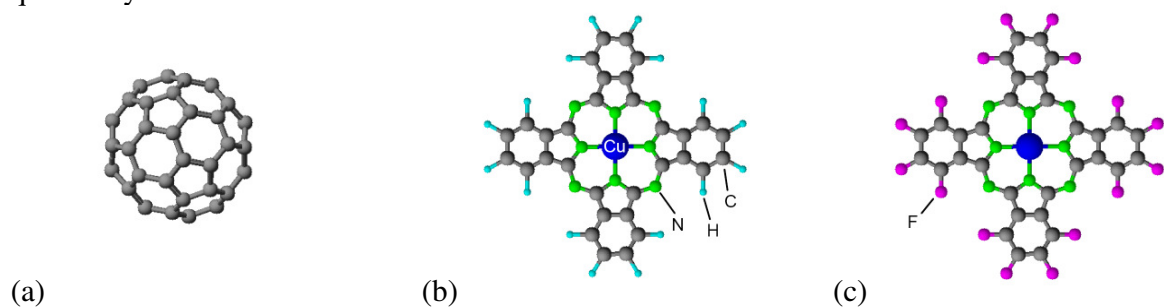


Figure 1. Chemical structure of (a) buckminsterfullerene C₆₀, (b) Cu-phthalocyanine (CuPc) and (c) fluorinated Cu-phthalocyanine (F₁₆CuPc).

Assuming insulating organic films without intrinsic charge carriers and traps, the quantitative analysis of the current-voltage characteristics was realized using the model of trap-free space charge limited currents [4] extended by the Pool-Frenkel like field-dependence of the mobility [5], resulting in a current density given by

$$j_{SCLC} = \frac{9}{8} \epsilon \mu_0 \frac{V_{eff}^2}{d^3} \exp \left(0.89 \beta \sqrt{\frac{V_{eff}}{d}} \right),$$

with the zero-field mobility μ_0 , the field activation parameter β and the layer thickness d . In order to account for a built-in potential V_{bi} caused by electrodes with different work-functions, an effective voltage V_{eff} is considered which equals the externally applied voltage reduced by V_{bi} . The parameters μ_0 , V_{bi} and β are determined by fitting the measured current-voltage characteristics in the higher voltage range.

Optical absorption spectra were measured on neat and blended films deposited on ITO-coated glass substrates covered with PEDOT:PSS using a Varian Cary 50 UV/Vis-spectrophotometer. The X-ray scattering measurements were conducted on a GE/Seifert X-ray diffractometer (Cu K α 1 radiation, multilayer mirror, and double bounce compressor monochromator). While electrical characterization could be realized without exposure to air, X-ray scattering as well as absorption measurements have been performed under ambient atmosphere.

RESULTS and DISCUSSION

Structural properties X-ray scattering measurements, performed in θ - 2θ geometry, for neat, mixed and bilayered films are depicted in figure 2 for the material combination CuPc/C₆₀ (a,b) and for CuPc/F₁₆CuPc (c). Both types of phthalocyanines show well pronounced diffraction peaks. In addition to previous measurements [6,7], the parallelized and monochromated incident beam enables the detection of the C₆₀ diffraction peak.

The diffraction pattern of the CuPc/C₆₀ blend displays the same peak positions as detected for the respective neat films and was in the literature assigned to the (200)-reflection of the α -phase of CuPc [8] and the (111)-peak of the fcc structure of C₆₀. This observation rules out the formation of a solid solution but is a clear indicator of phase separation with coexisting crystallites of both materials. This can be ascribed to the different molecular structures of the flat CuPc molecule and the spherical C₆₀. By contrast, the similar molecular structure of CuPc and F₁₆CuPc leads to the formation of a mixed crystal in the blend clearly visible by a diffraction peak which is positioned between the Bragg-reflections of the neat films (see figure 2(c)). This mixed crystal may exhibit a similar structure like the neat phthalocyanines [9,10].

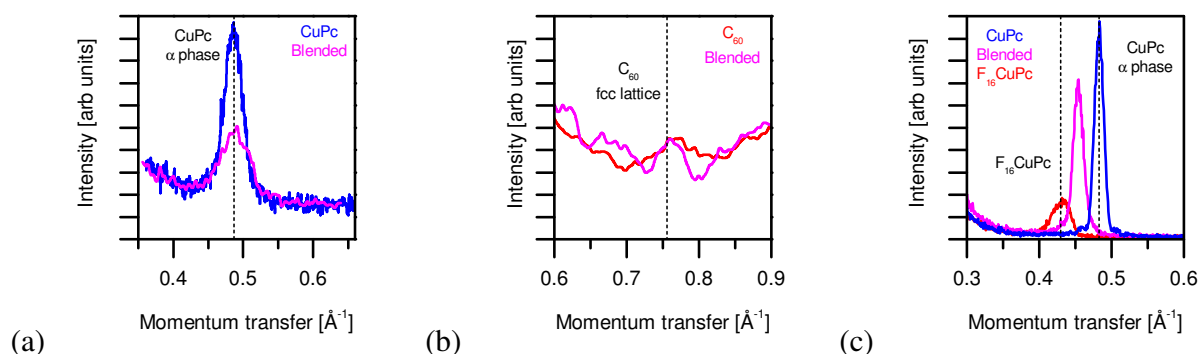


Figure 2. X-ray diffraction spectra for neat, bilayered and blended films of the material system (a,b) CuPc/C₆₀ and the (c) CuPc/F₁₆CuPc.

The structural size of the crystallites can be estimated from the width of the diffraction peaks, which is of particular interest in case of phase separated crystals appearing in the CuPc/C₆₀ blend. Using the relation $\Delta q_z \sim 2\pi/L$ with Δq_z being the width of the diffraction peak, the coherence volume L corresponding to the size of the crystallites can be evaluated to about

10 nm for both CuPc and C₆₀. Thus, phase separation in this material system can be ascribed to a relatively small length scale in comparison to the large scale phase separation detected in the system pentacene/fullerene [11].

The film morphology of 1:1 blended films of both material combinations are depicted in figure 3, as investigated by non-contact scanning force microscopy (SFM). The materials have been deposited onto SiO₂/Si or PEDOT:PSS/ITO/glass at a substrate temperature of 100 °C. Even at a nominal thickness of 25 nm, maximum heights of up to 58 nm are observed in the blend of C₆₀ and CuPc, which approves the model of demixing and phase separation proposed by X-ray scattering. By contrast, the blended CuPc/F₁₆CuPc films show a needle-like structure with similar morphologies as the neat films [7]. This observation confirms the structural result of mixed crystals.

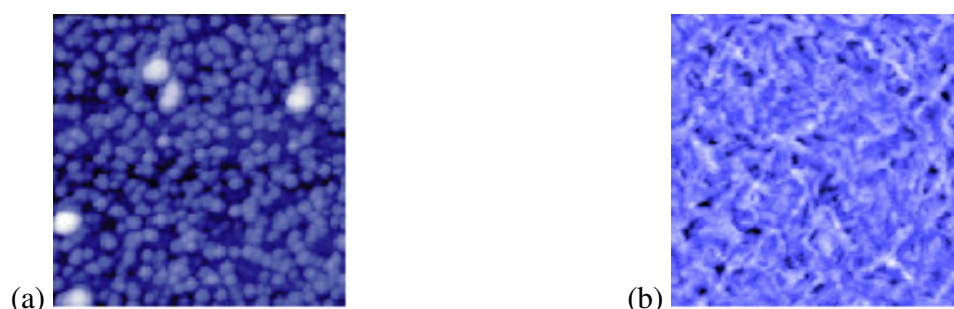


Figure 3. Scanning force microscopy images taken in non-contact mode of 1:1 blended films (nominal thickness of 25 nm) of (a) C₆₀ and CuPc deposited on a SiO₂/Si substrate (Max. height: 58 nm, RMS roughness: 6.5 nm) (b) CuPc and F₁₆CuPc deposited on a PEDOT:PSS coated ITO substrate (Max. height: 15 nm, RMS roughness: 2.0 nm) with a total image size of 2×2 μm².

Optical absorption spectra Regarding the suitability of the blends for solar cell applications, we analyzed the absorption spectra of neat films as well as blends with a mixing ratio of 1:1 of both material systems, depicted in figure 4. Neat films of CuPc and C₆₀ show complementary absorption behavior in the visible spectral range, which qualifies this material combination for application over the whole visible spectrum including the near IR. The spectrum of the blend displays a shape corresponding to a linear combination of both neat spectra, which confirms the model of phase separation [12].

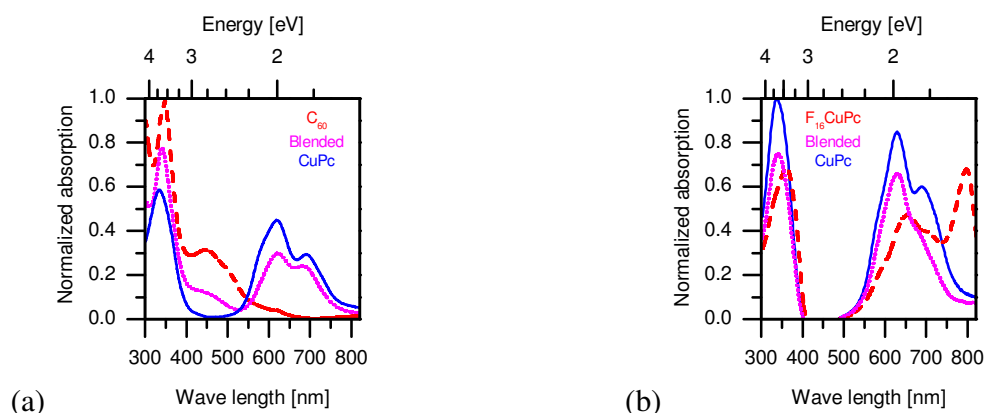


Figure 4. Absorption spectra in the UV-Vis range of neat films and 1:1 blends: (a) CuPc/C₆₀; (b) CuPc/F₁₆CuPc.

In contrast, both CuPc and F₁₆CuPc show hardly any absorption in the blue-green wavelength range of the visible spectrum between the two absorption edges at $\lambda = 400$ nm and 550 nm, making this material combination not very favorable for sunlight application. The slightly differing curves in the higher wavelength range can be assigned to the difference in the interaction of the molecules in the unit cell [13,3]. When mixing both molecules the intensity of the peak at 793 nm, which may be attributed to a non-herringbone structure [10], is reduced drastically.

Electrical properties Investigations of electrical transport properties of neat and blended films have been realized by fabricating hole-only, electron-only and ambipolar diodes [14]. The corresponding *I-V* characteristics are analyzed using a fit based on the trap-free SCLC model described above. The zero-field mobilities of the CuPc/C₆₀ material system in dependence on the concentration are extracted from the fit results and summarized in figure 5(a). It can be seen that both charge carrier types are transported in CuPc as well as in C₆₀, even though the unipolar mobilities depend strongly on the mixing ratio. Starting from neat C₆₀ the electron mobility decreases exponentially with increasing CuPc addition and shows a further reduction when switching over to neat CuPc. These aspects allow for the conclusion that the electron transport in the blend is predominantly carried by C₆₀ molecules and decreases in the blend where the hopping distance between the molecules is increased. The unipolar hole mobility changes uniformly over the whole concentration range. As a consequence of the ambipolar nature of both CuPc and C₆₀, the ambipolar mobility in the blends is higher than the sum of unipolar hole and electron mobility. A consolidated view of these factors indicates that the charge carrier transport in blended films is mainly based on the excellent electron transport properties inside conductive paths of C₆₀.

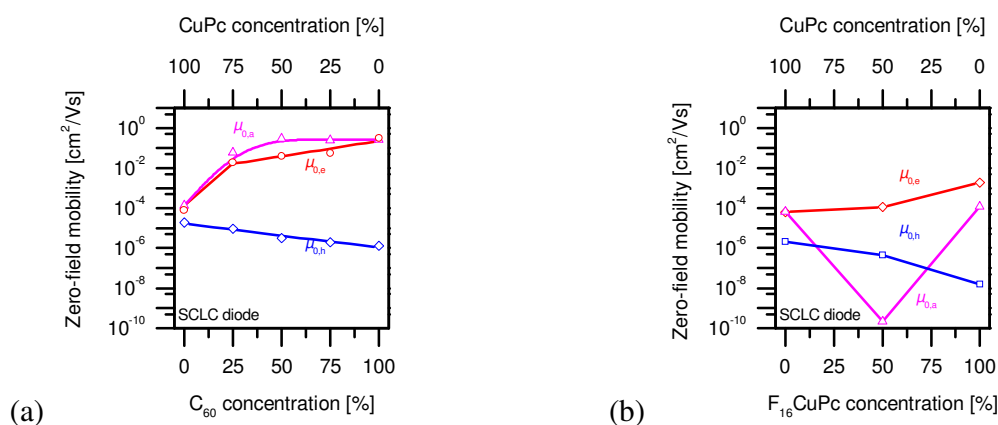


Figure 5. Zero-field mobilities for electron-only, hole-only, and ambipolar transport determined from the SCLC model for neat and blended films of CuPc/C₆₀ (a) and CuPc/F₁₆CuPc (b).

The zero-field mobilities of the CuPc/F₁₆CuPc material system are depicted in figure 5(b). The unipolar mobilities in the blended films are in-between the ones of the neat films, indicating that the blend contains mixed crystals with similar π - π overlaps as compared to the neat films. In contrast to the CuPc/C₆₀ material system, the ambipolar mobility inside the CuPc/F₁₆CuPc blend is several orders of magnitude lower than both unipolar mobilities as well as the ambipolar mobilities of the neat films. Since the unipolar mobilities are high, it is hardly

probable that the extremely low ambipolar transport in the blend is due to an absence of percolation paths. Instead, the reduced ambipolar mobility is probably related to the simultaneous presence of both charge carrier types. A tentative explanation may be found in the generation of charge transfer (CT) excitons which might be created by the injection of both charge carrier types [15]. As a result, these CT excitons would limit the transport by blocking the occupied molecules for further injected charge carriers. The generation of CT excitons can be facilitated by the high electron affinity of the F₁₆CuPc which is located close to the ionization potential of CuPc [16]. For proving this phenomenon further work is in progress.

SUMMARY

It has been demonstrated that blends of CuPc and C₆₀ as compared to mixed films of CuPc and F₁₆CuPc display different types of film growth, namely phase separation and mixed crystal formation. The transport properties of the phase separated blend of CuPc/C₆₀ are based on percolation paths of the different phases and dominated by the electron transport in C₆₀. By contrast, blends of the phthalocyanines CuPc and F₁₆CuPc demonstrate the formation of mixed crystals. A drastically reduced ambipolar mobility was found in the blend and might be assigned to the generation of charge transfer excitons in neighboring CuPc and F₁₆CuPc molecules created by the simultaneous injection or photogeneration of both charge carrier types.

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