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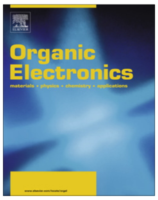

Letter

Effect of axial halogen substitution on the performance of subphthalocyanine based organic photovoltaic cells

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ABSTRACT

To probe the influence of molecular dipole on the open circuit voltage (V_{OC}) of molecular heterojunction organic solar cells, we study axially fluorinated boron subphthalocyanine/fullerene (SubPc-F/C_{60}) junctions. These exhibit an open-circuit voltage V_{OC} = 1.00 V, a value closer to the HOMO–LUMO offset at the donor–acceptor interface = 1.69 eV than the V_{OC} = 1.06 V measured for junctions between the archetypal chlorinated SubPc and C_{60}, with corresponding HOMO–LUMO offset = 1.84 eV. Aside from the axial halogen substitution, the two compounds exhibit similar molecular structure and optical absorption. The energy levels and structure of the heteromolecular polaron pair are calculated, and the ideal organic diode model for SubPc-Cl is modified accordingly, successfully reproducing the experimental SubPc-F device characteristics. The reproducible difference in V_{OC} is attributed to the different electric dipole strength between SubPc-F and SubPc-Cl and its influence on polaron pair dynamics at the heterojunction.

1. Introduction

The open circuit voltage (V_{OC}) in organic photovoltaic (OPV) cells is considerably lower than the minimum absorbed photon energy, reducing the practical efficiency of OPV cells relative to their thermodynamic limit [1]. While losses due to exciton binding energy are understood, other factors are currently debated. Previously demonstrated links between dark current and V_{OC} have suggested that charge recombination at the donor–acceptor (DA) interface is partially responsible [2], influenced by molecular structure and order at the DA junction [3]. This work examines the influence of the permanent electric dipole moment of the donor molecule on V_{OC}.

Giebink et al. introduced an Onsager–Braun kinetics-based model for ideal organic photovoltaic heterojunctions, successfully fitting current–voltage characteristics of OPV devices across a wide range of conditions [4]. In the Onsager–Braun model, the probability of dissociating a coulombically bound polaron pair at the DA junction depends on the charge separation distance and the local electric field. This probability is less than unity, and has the effect of reducing the achieved V_{OC} relative to the maximum allowed by the energy level difference, ΔE_{HL}, minus the polaron pair binding energy, E_{PP}, according to Eq. (1):

$$qV_{OC} = \Delta E_{HL} - E_{PP} - kTln\left(\frac{k_r N_H N_L}{\frac{\varsigma J_X}{r_{PP}}}\right), \qquad (1)$$

where k_r is the polaron pair recombination rate, N_H and N_L are the highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO) tail densities, respectively, ς is the maximum polaron pair density, J_X is the exciton flux reaching the heterojunction, and r_{PP} is the polaron pair separation distance. The polaron pair binding

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energy can be calculated from the charge separation distance, as a coulombically bound pair,

$$E_{PP} = \frac{1}{4\pi\epsilon}\frac{q^2}{r_{PP}}. \tag{2}$$

Clearly, intermolecular distance and the spatial distribution of occupied and unoccupied molecular orbitals affect r_{PP}, which in turn affects E_{PP} and V_{OC}. Additionally, the polaron pair dissociation rate, k_{PPd}, has a dependence on the local dipoles' strength and orientation, as they contribute to electric field at the interface, although their significance is not fully understood [5,6].

Some previous work used a contact transfer technique to study how the strength and orientation of an interfacial dipole affects V_{OC} [6]. The dipole shifts the ionization potential at the interface, thus increasing or decreasing ΔE_{HL} and the V_{OC}. Similarly, there is also a shift in the LUMO–LUMO and HOMO–HOMO offset, which may weaken the driving force for charge transfer, resulting in a lower dissociation efficiency.

One widely used donor of interest is boron subphthalocyanine chloride (SubPc-Cl). Its permanent molecular dipole and asymmetry suggests that polaron pair recombination could be orientation dependent, as molecular orientation with respect to the acceptor will affect both r_{PP} and the local electric field during charge transfer and separation. In addition to becoming one of the archetypal materials used in small molecular OPVs, the SubPc-Cl/C_{60} junction is one of the first material sets to have its field-dependent recombination rate measured [7].

SubPc-Cl coupled with C_{60}, shown in Fig. 1a, produces a large ΔE_{HL}, resulting in one of the highest reported V_{OC}'s for bilayer OPVs [8,9]. Its short exciton lifetime limits exciton diffusion [10,11], but at 585 nm the solid state absorption of SubPc-Cl exhibits a strong Q-band typical of porphyrins [12], arising from π–π^* transitions in the conjugated macrocyclic ring [13]. This strong absorption is in the yellow-orange range of the visible spectrum, where both solar photon flux and energy flux are relatively high. The high extinction coefficient [12] allows for thinner layers, which mitigates the short exciton diffusion length bottleneck. The high current density seen in this junction, when coupled with a high V_{OC}, enables efficiencies for single planar heterojunction devices upwards of 3% [9,14]. Nevertheless, the observed V_{OC} for SubPc-Cl/C_{60} junctions is 0.8 V below ΔE_{HL}, presumably due to polaron pair binding and the strength of the interfacial dipole *viz. à vis* Eqs. (1) and (2). Substituting the axial chlorine atom for fluorine (creating SubPc-F) is expected to shorten then boron–halogen bond length, reducing the electric dipole of the donor molecule, thereby affecting the local polaron pair kinetics and presenting an opportunity to isolate the effects of molecular dipole strength. Below, we compare the performance characteristics of SubPc-Cl and SubPc-F donor layers in a heterojunction OPV cell with C_{60} as the acceptor material, highlighting important differences and interpreting them in terms of the molecular-scale mechanisms that may be responsible.

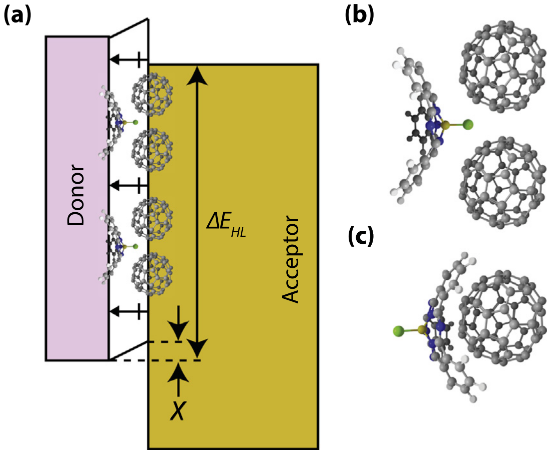

Fig. 1. Energy levels are shifted by the dipole at the heterojunction, resulting in an effective increase in ΔE_{HL}, as shown in (a). Potential orientations of SubPc include the (b) "bed" configuration and (c) "umbrella" configuration.

2. Experiments and simulations

Subphthalocyanine fluoride (SubPc-F) was synthesized from SubPc-Cl, using a previously reported method [15]. Following synthesis and evaporation of the solvent, products were rinsed with methanol and hexane (purchased from VWR and used as received) before subsequent purification by thermal gradient sublimation twice. The absence of SubPc-Cl and presence of SubPc-F was confirmed using atmospheric pressure chemical ionization mass spectroscopy, from which the purity was estimated to be greater than 92% SubPc-F by mass.

HOMO levels were measured by cyclic voltammetry on samples drop-cast onto a glassy carbon working electrode. Redox currents were recorded while ramping voltage at 0.1 V/s relative to an Ag/$AgNO_3$ reference electrode and Pt counter electrode in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Ferrocene was used to calibrate the oxidation potential. LUMO levels were inferred by adding the optical absorption "bandgap" to the HOMO levels determined by cyclic voltammetry.

Organic and inorganic thin films were thermally evaporated under a pressure of 10^{-7} Torr while thickness was monitored *in situ* by a calibrated quartz crystal microbalance. Substrates consisted of 15 Ω/□ ITO-coated glass slides purchased from Delta Technologies, LLC, and were cleaned in 250 mL each of dish soap in de-ionized water, pure de-ionized water, acetone, trichloroethylene twice, acetone twice, and 2-propanol twice before being boiled in a third beaker of 2-propanol for 10 min. After cleaning, substrates were immediately dried in nitrogen and treated using UV-generated ozone for 10 min. Film thicknesses used for devices were as follows: 5 nm MoO_3/13 nm SubPc-X/36 nm C_{60}/10 nm BCP/100 nm Al, with the top cathode defined by depositing through a shadow-mask having approximately 1 mm diameter circular apertures; X = Cl or F. Film thicknesses were calibrated with spectroscopic ellipsometry, with the SubPc-X complex refractive indices fitted to measurements of 30 nm thick films on a silicon substrate. Photovoltaic cells were electrically char-