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.

Keywords: SubPc, C₆₀, open circuit voltage (V_{OC}), molecular dipole, dipole orientation, organic photovoltaics (OPV)

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):

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

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 current reaching the heterojunction, and r_{PP} is

the polaron pair separation distance. The polaron pair binding energy can be calculated from the charge separation distance, as a coulombically bound pair,

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

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/C₆₀ junction is one of the first material sets to have its field-dependent recombination rate measured.⁷

SubPc-Cl coupled with C₆₀, shown in **Figure 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 coefficient¹² allows for thinner layers, which mitigates the short exciton diffusion length bottleneck. The high current density, 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 volts below ΔE_{HL} , presumably due to polaron pair binding and the strength of the interfacial dipole *viz. à vis* Eqs. (1,2). 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.

2. Experiments & 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/AgNO₃ 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 $15\ \Omega/\square$ 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 minutes. After cleaning, substrates were immediately dried in nitrogen and treated using UV-generated ozone for 10 minutes. 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-Cl and -F complex refractive indices fitted to measurements of 30 nm thick films on a silicon substrate. Photovoltaic cells were electrically characterized in an inert atmosphere under AM1.5D conditions for current density-voltage (JV) sweeps, and in air at 5 nm increments of monochromated light from a halogen lamp source for EQE measurements.

Electronic structure determination for SubPc-F and SubPc-Cl were carried out through density functional theory (DFT) calculations in Gaussian 09, using the B3LYP functional and 6-31G(d) basis set for all atoms.¹⁶ The molecular orbital basis set used was the 6-31G(d), as followed by Petersson *et al.*¹⁷ The structures have been optimized using the above-mentioned basis set without any symmetry (allowing for a maximum of degrees of freedom). The UV absorption

peaks were estimated considering the vertical excitations from the ground state applying time-dependent density functional linear response theory.¹⁸

Calculation of the polaron pair binding energy requires three contributions: the energy from Coulombic interaction, E_c , between the dimer electron (LUMO) and hole (HOMO), the interface polarization energy (E_p), and the Coulombic interaction between the induced charges at the interface and the polarons. Our calculations suggested that the latter contribution is negligible.

In order to calculate the E_c , molecules were first relaxed into their optimal isolated geometries, which were used to calculate the ionization energies of SubPc-Cl and SubPc-F, and electron affinity of C₆₀. Several configurations were calculated, notably a “bed” configuration, with the dipole facing SubPc, as seen in **Figure 1b**, and a ball-in-cup “umbrella” configuration, with a dipole facing C₆₀, as seen in **Figure 1c**. To compute the interaction, the empty HOMO was treated as a positively charged cloud, and, likewise, the LUMO was treated as a negatively charged cloud. This energy was computed from the wave function data projected onto a regular 3D grid as follows,

$$E_c = \frac{-q_e^2}{2\pi(\epsilon_{C60} + \epsilon_{SubPc})} \iint \frac{|\psi_H(\vec{r}_H)|^2 |\psi_L(\vec{r}_L)|^2}{|\vec{r}_H - \vec{r}_L|} d^3r_H d^3r_L, \quad (3)$$

where q_e is the charge of an electron, ϵ_{C60} is the dielectric constant of C₆₀, ϵ_{SubPc} is the dielectric constant of SubPc, ψ_H is the dimer HOMO, ψ_L is the dimer LUMO (See **Figure 1**), $\vec{r}_H$ is a position in the SubPc HOMO, and $\vec{r}_L$ is a position in the C₆₀ LUMO.

Areas of the heterojunction where SubPc is regularly aligned with C₆₀ have a net polarization at the interface. This system can be treated as a polarized monolayer at the interface of the two materials, similar to a polarizing interface texture effect. However, there is no

dependence on the distance to the interface, thus the energy for transfer of a charge carrier across the interface is,

$$E_p = \frac{q_e \sigma_{dp} \langle p_z \rangle}{2} \left[\frac{1}{\epsilon_{SubPC}} + \frac{1}{\epsilon_{C60}} \right]. \quad (4)$$

The interface polarization energy is $E_{\langle p_z \rangle}$, σ_{dp} is the dipole interface density, and $\langle p_z \rangle$ is the average individual dipole perpendicular to the interface. As mentioned above, we need to add E_c and $E_{\langle p_z \rangle}$ in order to calculate the binding energy. Therefore, the polaron pair binding energy is calculated through Eq. (3-5),

$$E_{PP} = E_c + E_p. \quad (5)$$

3. Results and Discussion

Fitted plots of the refractive index and extinction coefficient for solid films are shown in **Figure 2**. As a result of the absorption being largely due to resonance within the macrocycle, the optical constants remain mostly unchanged upon halogen substitution. The characteristic absorption spectrum of the subphthalocyanine molecule peaks near 580 nm, and two higher energy shoulders at 570 nm and 540 nm are present. The intense peak in the Q region is blue-shifted 3 nm upon halogen substitution, from 585 nm to 582 nm. In agreement with experimental results, the TDDFT calculated UV absorptions suggest a 5 nm blue-shift.

Following the work of Pettersson *et al.*, data are used in a Feng-Ghosh model¹⁹ to predict external quantum efficiency (EQE) and ensure that the exciton flux reaching the heterojunction is similar between the two donors, thus allowing for a direct comparison of the V_{OC} among otherwise identically performing devices. Though stacks optimized for maximum efficiency

upwards of 3% achieve this through increased absorption, thus increasing J_X , these changes have a minimal effect on the V_{OC} .

The experimentally measured EQE plotted in **Figure 3** shows that the absorption, exciton diffusion, exciton dissociation, and carrier collection at zero bias are largely the same between the two devices, resulting in similar EQE. It's understood from the complex refractive index shown in **Figure 2** that absorption efficiency in a PV cell incorporating either material should remain nearly identical. Assuming the post-dissociation carrier collection efficiency for thin bilayer OPVs to be unity, exciton diffusion lengths fitted to the EQE suggest exciton dissociation efficiency to be comparable between the devices ($L_D = 10.2$ nm for SubPc-Cl, and 10.3 nm for SubPc-F). The interface between MoO_3 and SubPc has been recognized as not fully quenching, as understood from previously reported EQE fits,²⁰ thus leading to overestimation of the exciton diffusion length in these samples.^{9,11,12}

The pointwise product of the EQE and AM1.5D spectra results in similar short-circuit current density (J_{SC}) between the two devices. Though this is somewhat lower than the J_{SC} measured at zero bias under AM1.5D illumination, the loss is most likely due to degradation in air. Indeed, we see in **Table 1** that the J_{SC} is statistically the same between the two device sets. The largest difference between the performance of SubPc-Cl and SubPc-F as OPV donors is clearly observed in the device current-voltage characteristics, as shown in **Figure 4**. The shaded translucent areas show a 95% confidence interval on the measurement, further illustrating that the difference in current measurements near J_{SC} is not statistically significant. In contrast, the difference between the V_{OC} values is indeed significant. Despite being lower in absolute value, the V_{OC} of SubPc-F is substantially closer to the thermodynamic limit than that of SubPc-Cl, as discussed below.

Table 1

		SubPc-Cl (Exp.)	SubPc-F (Exp.)	SubPc-F (Calc.)
J_{SC}	mA/cm ²	4.0 ± 0.26	3.9 ± 0.23	3.94
V_{OC}	V	1.06 ± 0.002	1.00 ± 0.019	0.97
FF	%	67.0 ± 1.0	62.8 ± 2.1	68.4
PCE	%	2.85 ± 0.16	2.44 ± 0.22	2.60

One source of the absolute V_{OC} difference between SubPc-Cl and SubPc-F can be attributed to the shift in the HOMO and LUMO levels upon halogen substitution. The inset of **Figure 4** shows the electronic levels of the active organic layers. The measured SubPc-F HOMO and LUMO energy levels are uniformly shifted 150 meV towards vacuum level relative to SubPc-Cl. This shift brings the HOMO of the donor closer to the LUMO of the acceptor, reducing ΔE_{HL} , the first term of Eq. (1). Namely, $\Delta E_{HL-SubPc-Cl/C60} = 1.84$ eV, while $V_{OC-SubPc-Cl/C60} = 1.06$ V, implying that the last two terms of Eq.(1) add up to 0.78 eV, a 42.4% loss due to polaron pair binding and Onsager-Braun dynamics. In comparison, $\Delta E_{HL-SubPc-F/C60} = 1.69$ eV, while $V_{OC-SubPc-F/C60}$ measures 1.00 V, implying that the last two terms of Eq.(1) add up to 0.69 eV, a 40.8% loss due to polaron pair binding and Onsager-Braun recombination dynamics.

Based on *ab initio* calculations, the electron affinity of the fluorine atom changes the partial charges on the two molecules of the polaron pair, as well as causing structural differences in the donor, relative to SubPc-Cl. Specifically, the axial bond length of SubPc-F (1.39 Å) is shorter than SubPc-Cl (1.88 Å). When calculating polaron pairs, the “umbrella” configuration was neglected, due to the much higher binding energy resulting in it being a site for recombination. The calculated r_{PP} for the “bed” configuration is 9.3 Å and 9.1 Å for SubPc-F and SubPc-Cl, respectively. In this case, the dipole of the donor results in an energetic hindrance to dissociation of the polaron pair into individual charge carriers, which has been calculated as an energy

penalty equal to 0.21 eV and 0.15 eV for SubPc-F and SubPc-Cl, respectively. Note that the larger separation distance for SubPc-F already provides a slightly lower binding energy, via Eq. (2). Subtraction of energetic assistance from the polaron pair binding energy has a direct influence on V_{OC} , as understood from Eq. (1).

JV curves calculated using the model proposed by Giebink *et al.* are shown as dotted lines in **Figure 4**. The curve for the device using SubPc-Cl was fit to experimental data and used to generate the curve overlaid on the SubPc-F data, with only the HOMO level, LUMO level, polaron pair separation distance, and binding energy used from DFT calculations. Note that the modeled J_{SC} values are nearly identical to those that were measured. The exciton flux from EQE modeling was fed into the model. The J_{SC} of SubPc-F is lower than that of SubPc-Cl, despite an overall lower binding energy, considering the dipole assistance; however, this region of the JV curve is likely dominated by photoconductivity in the organics, rather than the junction dissociation efficiency.²¹ As such, the lower J_{SC} for SubPc-F simply a result of lower exciton flux reaching the interface, however, a greater population of exciton quenching sites found in the (lower purity) SubPc-F may also lower J_{SC} . Additionally, the difference in fill factors is both an artifact of the lower V_{OC} , as well as potential trap states from impurities in SubPC-F, resulting in a higher ideality factor. This is especially prevalent in the comparison of modeled FF being so high, 68.4%. Importantly, much of the remaining difference between the modeled SubPc-F curve and measured SubPc-F curve is a result of the higher ideality factor. Most importantly, the V_{OC} is 0.97 V, which is particularly close to the measured value of 1.00 V, especially when considering the measurement is associated with a standard deviation of 19 mV. Creation of the SubPc molecule without a dipole will theoretically yield a device with a V_{OC} of approximately 0.90V.

Considering the possibility that the higher-than-expected V_{OC} is due to the polaron pair binding energy being lowered, we note the importance of dipole orientation. Brumbach *et al.* reported a V_{OC} for a titanyl phthalocyanine (TiOPc) donor achieving *less* of its potential maximum, as compared to copper phthalocyanine, which has no dipole. We attribute that result to TiOPc having a stronger dipole, but raising the binding energy, rather than lowering it. Additional examples can be found in literature, where the use of the oblong-shaped C_{70} in place of spherical C_{60} paired with SubPc-Cl affects the polaron pair orientations attainable, without modification of the dipole. This is likely a result of the separation distance alone, with a maximum V_{OC} attainable being 1.05 V for C_{70} ²² versus 1.10 V for C_{60} ⁹, further supporting the link between polaron pair orientation and V_{OC} .

4. Summary

In summary, a new small molecular donor material has been synthesized and applied in the study of fundamental processes governing the performance of OPV cells, isolating the role of permanent electric dipole with other structural features of the molecule remaining identical. While axial substitution of fluorine for chlorine resulted in a smaller HOMO-LUMO gap at the heterojunction, detailed modeling of the heterojunction permitted the comparison of observed V_{OC} to its thermodynamic maximum value. While the V_{OC} of SubPc-F devices fall short of its thermodynamic limit, it is 90 mV higher than what is attained by SubPc-Cl relative to *its* thermodynamic limit. We attribute this net effect to the larger dipole moment and the donor-acceptor interfacial structure that favor polaron pair dissociation. Furthermore, we have presented a framework for calculation of the JV curve for any polaron pair with a chemically modified dipole, assisted by *ab initio* calculations of the molecule structure and energetics.

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Figure 1: Energy levels are shifted by the dipole at the heterojunction, resulting in a decrease in ΔE_{HL} , as shown in (a). Potential orientations of SubPc include the (b) “bed” configuration and (c) “umbrella” configuration.

Figure 2: Imaginary (solid lines) and real (dotted lines) refractive indexes as function of wavelength for SubPc-Cl (black) and SubPc-F (red).

Figure 3: External quantum efficiency of devices made using SubPc-Cl (black) and SubPc-F (red) as the donor. Experimental measurements (X's) are overlaid on calculated EQE curves (solid lines).

Figure 4: JV curves for ITO \ 5 nm MoO₃ \ 13 nm SubPc \ 36 nm C₆₀ \ 10 nm BCP \ 100 nm Al, where SubPc refers to either SubPc-F (red) or SubPc-Cl (black). Dark lines represent the mean values averaged over 9 devices, whereas shaded regions represent a 95% confidence interval at that bias. Inset: energy level diagram and device stack. The dotted lines are calculated from the Giebink model using all the parameters from fitting SubPc-Cl, but with the HOMO level, LUMO level, polaron pair distance, and polaron pair binding energy of SubPc-F.

Figure 1

Figure 2

Figure 3

Figure 4