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Low dark leakage current in organic planar heterojunction photodiodes

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It is often suggested that the dark leakage current of organic photodiodes is due to extrinsic leakage paths that do not involve the electronic junction. By studying a series of devices, where the acceptor is kept constant (C70) and the donor material is varied, we find a direct correlation between the strength of the sub-gap signature of the charge-transfer states and the leakage current. Attributing the differences in the sub-gap absorption to the donor’s sub-gap states suggests that the donor’s side of the junction should be made longer, to push the Fermi level at V = 0 towards the acceptor’s LUMO, and thus, an optimized value of 800 Pdcm\(^{-2}\) at V = −1 V is reported. Published by AIP Publishing. https://doi.org/10.1063/1.4996826

Organic photodiodes (OPDs)\(^1\)–\(^4\) are being presented as a promising complementary or an alternative to inorganic based photodetectors for detection/imaging applications.\(^5\)–\(^8\) A major challenge preventing polymer or small molecule based OPDs from producing a high-quality photodetector is their dark current level under reverse bias, which is usually several orders of magnitude higher than the required value. Low reverse bias dark current, often referred to as leakage current, is essential for higher specific detectivity \(D^*\) and large dynamic ranges which are the key figure of merits of any photodetector. We note that we are interested in the actual reverse bias dark current and are not to be confused with the ideal-diode’s reverse dark saturation current density, \(J_0\), which is the preexponent factor of the forward current. It has been shown in some works that by employing thick active layers,\(^9\) electron/hole blocking layers,\(^10\)–\(^12\) and different donor active materials,\(^13\) the leakage current to some extent can be suppressed. Despite these successes, it remains a challenge because the physical processes which govern the losses and determine the dark leakage current are relatively unclear, and hence, it is still an active area of research. Also, not always care is taken that while minimizing the reverse (leakage) current the forward diode current will not be compromised.

Here, we report the dependence of the reverse bias dark current of an acceptor C70 based planar heterojunction (PHJ) diode on different donor molecules [copper phthalocyanine (CuPc), boron subphthalocyanine chloride (SubPc), 1,1-bis [(di-4-tolylamino) phenyl] cyclohexane (TAPC), tetraphenyl-dibenzoperiflanthene (DBP), and chloroaluminum phthalocyanine (ClAlPc)]. Similar comparisons were studied before but in the context of solar cells’ open circuit voltage\(^14\),\(^15\) and less in the context of the reverse bias dark current. It is common (to many technologies) that reverse leakage current has a low dependence on both voltage and temperature.\(^16\),\(^17\) This has led to a range of explanations and models some of which are concerned with the junction itself\(^18\)–\(^20\) while others deal with extrinsic factors and thus often lump it under the notion of parallel or shunt resistance.\(^15\),\(^16\),\(^21\) To decide whether our diodes belong to the former or latter group, we study identical device structures and use the dark current at −1 V as an indication for the level of leakage current. We found that the leakage current reduced from CuPc/C70 to TAPC/C70 and to SubPc/C70 with an overall reduction of 2 orders of magnitude. To study the physical mechanism behind this result, we performed both temperature dependent J-V and subgap external quantum efficiency (EQE) analyses. Finally, as TAPC lends itself easier (compared to SubPc) for device optimization, we report a value of 800 Pdcm\(^{-2}\) at −1 V for PHJ TAPC/C70 devices.

All devices were fabricated on top of an indium tin oxide (ITO) coated glass substrate. The ITO substrates were cleaned & dried as described elsewhere.\(^22\) Ultra-high purity (UHP) grade organic materials CuPc, C70 (CreaPhys), SubPc, TAPC, DBP, and ClAlPc (Lumtec) were used as received. The first device structure used consists of a patterned ITO anode, a 70 nm solution deposited thick film of copper thiocyanate (CuSCN, Sigma 99%) as the hole transport layer (HTL), a 20 nm thick film of donor, a 40 nm thick film of C70 as an acceptor, a 8 nm thick film of bathocuproine (BCP, Lumtec 99.99%) as the hole/exciton blocking layer, and 30 nm thick Mg covered by a 60 nm thick Ag as the cathode. To avoid perimeter leakage, the edges of the patterned ITO were covered by a 100 nm polyimide layer, and the device area was 18.4 mm\(^2\) (variation of leakage current between 1, 4, and 18 mm\(^2\) devices was less than a factor of 2). The dark current-voltage of all the devices was characterized using a semiconductor parameter analyzer (B1500 A, Agilent Technologies) inside a nitrogen filled glovebox. Temperature dependent dark J-V characteristics were analyzed using a K-20 temperature controller (MMR Technologies), and the signal was read using a Keithley 2612 source meter. Spectrally resolved external quantum efficiency (EQE) was obtained outside the glove box with measured samples kept in the nitrogen atmosphere inside a holder. Light from the monochromator (Oriel, CS130) was chopped at 80 Hz, and the signal was amplified (Low-Noise Current Preamplifier SR570) and finally read using a lock-in amplifier (EG&G 7265). The samples for cyclic voltammetry (CV) measurements were prepared as evaporated films on...
ITO substrates with ITO acting as the working electrode. All measurements were made inside a glove box in an inert atmosphere of N2.

Figure 1(a) shows the molecular structural formula of the active materials used in this study, and the energy level diagram of all the materials is shown in Fig. 1(b). Figure 1(c) shows the schematic of the investigated PHJ device in a stack ITO/CuSCN (70 nm)/Donor (20 nm)/C70 (40 nm)/BCP (8 nm)/Mg (30 nm)/Ag (60 nm), using the donor materials CuPc, TAPC, SubPc, DBP, and CIAIPc. Because of the higher and extended absorption spectrum in the visible range, C70 was used in place of the commonly used C60 acceptor. To place the HOMO/LUMO values in the proper context, Fig. 1(d) shows the cyclic voltammogram of two of the active materials. It shows that when using the tangential to estimate the onset, the two materials are assigned the same energy level. However, as was shown for fullerene, it is also clear that this simple procedure does not capture the entire picture or it may explain the range of values reported in the literature.

The measured dark and light performance characteristics of the devices are shown in Fig. 2. Organic photovoltaics (OPVs) with the structure similar to those studied here, using SubPc/C70 and CuPc/C70, have been reported before. The solar cell characteristic parameters such as open circuit voltage (Voc), short circuit current (Jsc), and power conversion efficiency (PCE) of these devices are consistent (listed in Table I) with the literature values. The dark J-V characteristics (see Fig. 2) show typical diode behavior, with the leakage current part at low forward voltage being clearly visible for TAPC & SubPc donor devices. The ideal-diode’s reverse dark saturation current density, J0, of the devices was obtained by extrapolating the exponential part, which is linear on the semi-log scale, and finding the intercept on the y-axis (see the inset in Fig. 2). The actual slope defines the ideality factor, n.

In this paper, the term leakage current is used for currents that are not part of the main (“ideal”) diode characteristics. As discussed in the introduction, such leakage currents could be due to shunt paths, thermal activation of carriers at the D/A interface, or thermally and/or electrically activated injection of carriers at the contacts. To quantify the leakage, we defined the actual dark leakage currents as the value measured under a reverse bias of −1 V. The extracted currents’ values are also collected in Table I. Since, in the ideal case, there is a direct relationship between kT log(J0) and the open circuit voltage (Voc), we added the Voc values to Table I too.

Examining the obtained values in Table I, we note that there is a rough correlation between kT log(J0) and the change in the energy difference between acceptor LUMO and the donor’s HOMO. Namely, J0 is relatively well behaved and can be safely associated with excitation across the junction. The actual leakage current (Jleak) is however 2–8 orders of magnitudes higher. Specifically, the change from CuPc to TAPC reduced Jleak only by a factor of ~15, compared to 107 in J0. Namely, while by going from CuPc to TAPC and SubPc, there was a significant improvement in the leakage current, there is still significant room for improvement. This is especially true for the TAPC based device which happens to also have the lowest ideality factor.
In an attempt to better identify the physical origin of the currents at low bias, we obtained the temperature dependence of the dark J-V between 200 K and 300 K. The ideal-diode’s reverse dark saturation current density, \(J_0\), is thermally activated and can be expressed as\(^{17}\)

\[
J_0 = J_{00} \exp \left( - \frac{\phi_B}{KT} \right),
\]

where \(\phi_B\) is the activation energy, \(J_{00}\) is the prefactor, and \(KT\) is the thermal energy. It is also accepted that for a diode with an ideality factor \(n\), the actual energy barrier \(\Delta E\) is \(\Delta E = \phi_B / n\).\(^{11}\) We found that close to room temperature, the activation energies of \(J_0\) for (CuPc, TAPC, and SubPc) devices are \(\phi_B = (0.45 \text{ eV}, 0.5 \text{ eV}, \text{ and } 0.65 \text{ eV})\), and using the \(n\) values and Eq. (1), we get for the energy barrier \(\Delta E = (0.75 \text{ eV}, 0.65 \text{ eV}, \text{ and } 1.0 \text{ eV})\). Namely, there is relative correlation between the activation energies and \(V_{OC}\), suggesting that both are determined by the same processes at the junction.

Turning the focus to our main interest, dark current responses observed in the lower energy part is often referred to as charge transfer (CT) excitation and serves as a measure for the absorption of these states.\(^{32,33}\) The primary interest from this measurement was the estimation of the sub-gap density of states in different donor’s based devices and to reach energies below those of the CT state associated with \(J_0\) (note the new feature that is revealed beyond 1200 nm or below 1 eV). The results in Fig. 3(a) can be divided into three groups. In the first, there is the CuPc/C\(_{70}\) device showing a very broad response. In the second are grouped the TAPC, DBP, and ClAlPc which show a second feature beyond 1200 nm. The SubPc donor devices have the lowest absorption tail, and beyond 1000 nm, it is below our detection limit. Since C\(_{70}\) is the common acceptor in all the devices, we attribute the pronounced sub-gap absorption to the donor material in all devices. We note that the relative strength of the sub-gap states [Fig. 3(a)] and of the leakage currents [Fig. 3(b)] are correlated and are grouped according to the low energy sub-gap states. This suggests that the leakage current is associated with excitations across the D/A interface through sub-gap or CT states. To test this hypothesis, we inserted a thin (7 nm) layer of TAPC between CuPc and C\(_{70}\). The EQE of this triple active layer is shown as the dashed black line in Fig. 3(a), and its J-V curve is shown (symbols) in Fig. 3(b). We note that both the sub-gap EQE and the reverse leakage current changed to match those of the TAPC/C\(_{70}\) bi-layer device. Careful examination of the sub-gap EQE of the triple active layer (dashed line) shows some remains of CuPc at \(\sim 1100 \text{ nm}\) and close to our set-up noise margin, indicating the quality of the surface coverage of CuPc by TAPC.

![FIG. 3. (a) External quantum efficiency (EQE), extended to the sub gap range, for devices of different donors. (b) J-V curves PHJ based on different donors. Both (a) and (b) also show a CuPc/C\(_{70}\) device where a thin (7 nm) TAPC layer was inserted between (black, dashed line). (c) Sketch of physical mechanisms at play at the donor-acceptor interface in the measured devices.](image-url)
Figure 3(c) shows schematically the physical picture we suggest for the source of the leakage current in the above diodes. Moving from CuPc to TAPC and to SubPc, the density of the donor’s tail states reduces and consequently the probability for low energy CT states that could promote excitation across the D/A interface reduces. Namely, we claim that the increased leakage current is due to a higher generation-recombination at the junction and that the latter is enhanced by the donor’s sub-gap states tailing from the HOMO level.

If the main issues are the tail states of the donor’s HOMO level, then it would be beneficial to position the Fermi level at $V = 0$ between those states and the acceptors LUMO. This can be achieved by lengthening the hole’s side of the junction. Attempting to optimize the SubPc/C70 cell was not successful due to the SubPc properties being highly dependent on the film thickness. The optimized TAPC/C70 device structure was ITO/CuSCN (150 nm)/TAPC (60 nm)/C70 (40 nm)/BCP (8 nm)/Mg (30 nm)/Ag (60 nm) which consisted primarily of enhancing the thickness of a high mobility hole transporting layer. The J-V characteristics of this device are shown in Fig. 4 along with those of a device having about half the CuSCN film thickness. Also compared to the previous figures, we note that $J_{\text{leak}}$, at $-1$ V, has reduced to 800 pA cm$^{-2}$, while the exponential part of J-V in the forward direction is not affected. Statistic across 3 substrates or 6 devices showed the ranges to be 3–8 nA cm$^{-2}$ and 800–1100 pA cm$^{-2}$.

In conclusion, different donor based planar heterojunction devices are studied for their reverse bias leakage current. We find that temperature dependent dark J-V exhibits activation energies that are too low to be correlated with common energetics of the materials used to construct the devices (i.e., HOMO-LUMO differences or reverse injection barriers). We show that the deep tail states at the donor/acceptor junction are efficient generation-recombination centers and are one of the main sources of the leakage current. Also, as our study indicated that most of the subgap tail states are due to the donor material, we found that positioning the Fermi level (at $V = 0$) through device design can farther suppress the leakage current. From the practical point of view, we show that by minimizing the tail state density, i.e., by using a less electronically disordered material, leakage current can be greatly reduced. Also, by designing the device such that most of the built-in voltage drops across the donor side, an ultralow leakage current of 800 pA cm$^{-2}$ at $-1$ V for TAPC/C70 is obtained. Deciphering the details of the leakage mechanism at the junction requires further studies and will be reported at a later stage.

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