

Origin of the open circuit voltage of donor-acceptor solar cells: Do polaronic energy levels play a role?

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This letter analyzes the influence of the energy of the highest-energy occupied molecular orbital (HOMO) and the single occupied molecular orbital (SOMO) (i.e., the low-energy polaronic level) of different electron donors (D) on the open circuit voltage (V_{OC}) value delivered by bilayer and bulk-heterojunction solar cells containing fullerenes as acceptor (A). The analysis further confirms that the V_{OC} of these devices scales with the energy difference between the HOMO of the D and the lowest-energy unoccupied molecular orbital of the A. As observed, a better relationship is obtained if the SOMO energy of the D—extracted from photoinduced absorption spectra—is considered.

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By virtue of their “soft” nature, solar cells exploiting a photoinduced charge transfer between organic donor (D) and acceptor (A) molecules with extended π -electron systems are promising to cost-effectively replace inorganic devices and/or to develop new applications in the general context of organic (opto)electronics. Commonly, organic solar cells are D/A bilayer or D:A bulk-heterojunction (BH) devices, but hybrid-mixed structures have also been designed.^{1,2} Moreover, devices containing dye-sensitized inorganic semiconductors (DSSCs) are D-A solar cells, too.³ In each case, absorption of photons primarily generates excitons (molecular “electron-hole” bound states) that undergo dissociation (photoinduced charge transfer) if proper energy offsets at the D-A interface—geometrically “flat” in bilayer devices and convoluted in BHs and DSSCs—are established.^{1–4} As such, in these devices the holes and electrons are directly formed within separated D and A phases, creating photoinduced chemical potential gradients that contribute to their further separation, promoting the photovoltaic effect.⁵ In other words, in D-A solar cells electrical field and diffusion can simultaneously contribute to charge carrier separation and migration.⁵ This characteristic also affects their open circuit voltage (V_{OC}). As discussed by Gregg and Hanna, the V_{OC} of a solar cell is, in principle, a function of both electrical and chemical potential gradients.⁵ However, when electrons and holes are photogenerated together in the same semiconducting phase, no photoinduced chemical potential gradients are established. For charge carrier separation, a classical built-in electrical potential (V_{bi}) difference is required. Thus, in this case, the upper limit to V_{OC} is settled by the difference between the electrode workfunctions. Conversely, in organic solar cells with separated D and A phases, photoinduced chemical potential gradients can also drive carrier separation; thus, V_{OC} can exceed the above V_{bi} .⁵ Indeed, the V_{OC} and polarity of organic solar cells mainly relate to the D-A interface energetic rather than that of the electrodes. This prerogative was already recognized for the D/A bilayer solar cells described in the seminal letter of Tang.⁶ On the other hand, due to their D:A interpenetrated structure, BH solar cells were firstly regarded as classical metal-insulator-metal

devices. In 2001 Brabec *et al.* pointed out that the V_{OC} of performing BH cells could exceed V_{bi} and suggested that it mainly relates to the energetic difference between the D’s highest-energy occupied molecular orbital (HOMO) and the A’s lowest-energy molecular orbital (LUMO), a quantity currently called effective energy gap, divided for the elementary charge q (V_{DA}) (Fig. 1, left).⁷

The establishment of an analytical relationship between V_{OC} and V_{DA} (or any other variable) is complicated by several factors. The dark current, photoconductivity, temperature, short circuits, carrier recombination, resistance related to thickness and geometry, and—in the case of BH cells—the degree of D-A phase-separation⁸ all affect in a convoluted way the experimental V_{OC} values. Nevertheless, a fast growing body of evidence is showing that in reasonably working D-A solar cells the higher the V_{DA} the higher is the V_{OC} . The data so far obtained suggest that a linear relationship holds between these two quantities.^{7,9–14} However, the experimental V_{OC} values are generally less than the currently supposed upper value, i.e., V_{DA} . Often the potential loss is about 0.3–0.4 V,¹⁴ but larger differences are also observed.¹² While this letter was in preparation, Rand *et al.* have explained this loss, taking into account the binding energy pay

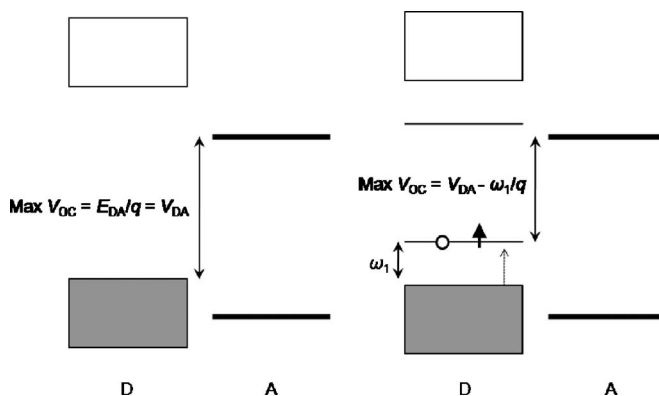


FIG. 1. Left: the current picture where the upper limit to V_{OC} is settled by the HOMO of the D and the LUMO of the A (V_{DA}). Right: the upper limit to V_{OC} is less by ω_1/q (polaronic potential loss) if the SOMO energy level of the charged D is considered. The low energy polaronic electronic transitions used to locate the SOMO’s energy is shown (dotted arrow and ω_1).

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TABLE I. HOMO, SOMO, and LUMO energy values refer to the normal hydrogen electrode electrochemical potential, the latter taken at -4.75 V vs vacuum. (BH: bulk-heterojunction, BL: bilayer.)

Entry	Donor	HOMO (eV)	ω_1 (eV)	SOMO (HOMO - ω_1) (eV)	Acceptor	LUMO ^a (eV)	V_{DA} (V)	$V_{DA} - \omega_1/q$ (V)	V_{OC} (V)	$V_{DA} - V_{OC}$ (V)	$(V_{DA} - \omega_1/q) - V_{OC}$ (V)
1 BH	PEDOTEHITN	4.50 ^b	0.25 ^c	4.25	PCBM	4.06	0.44	0.21	0.11 ^d	0.33	0.10
2 BH	P3HT	5.10	0.35 ^e	4.75	PCBM	4.06	1.04	0.69	0.63	0.41	0.06
3 BH	PTPTB	5.30 ^b	0.44 ^f	4.86	PCBM	4.06	1.24	0.80	0.67 ^f	0.57	0.13
4 BL	nd2	5.70	0.68 ^h	5.02	C ₆₀	4.1	1.60	0.92	0.72	0.88	0.20
5 BH	MDMOPPV	5.36	0.45 ^e	4.91	PCBM	4.06	1.30	0.85	0.83	0.45	0.02
6 BL	nda2	5.80	0.76 ^h	5.04	C ₆₀	4.1	1.70	0.94	0.89	0.76	0.05
7 BH ⁱ	PBEHTB	5.16	≤ 0.30	≥ 4.86	PCBM	4.06	1.10	≤ 0.80	0.77	≤ 0.33	≤ 0.03

^aReference 7.

^bReference 17.

^cReference 18.

^dReference 19.

^eReference 16.

^fReference 20.

^gReference 12.

^hReference 21.

ⁱReference 22.

to further separate the already dissociated but still coulombically bounded electron and hole.¹⁵ This letter is aimed to explore the possible role of the energetic of the initially formed carriers: a hole formed upon photoinduced charge transfer should be described by a single occupied molecular orbital (SOMO) (i.e., the low-energy polaronic level in systems with nondegenerate ground-state canonical forms)¹⁶ rather than by the HOMO of the neutral material. Due to the electron-phonon coupling typical of low-dimensional systems with delocalized π electrons, structural relaxations (mainly involving bond-length alternation) upward shift the SOMO into the energy gap of the neutral D.¹⁶ This shift, whose size ω_1 depends on the extent of the above relaxation, should be a mechanism of loss of V_{OC} as compared with the currently supposed upper limit V_{DA} (Fig. 1). This being the case, then the observed difference $V_{DA} - V_{OC}$ should equate (or at least relate) to ω_1 , a quantity that can be extracted from photoinduced absorption (PIA) spectroscopy data.

To explore this scenario, this letter analyzes the low-energy polaronic electronic transition (dotted arrow and ω_1 in Fig. 1)¹⁶ of seven Ds together with the V_{OC} values delivered by the corresponding bilayer or BH solar cells. Materials and devices for which electrochemical, PIA Vis-IR spectroscopy, and photovoltaic data are available are collated in Table I. All devices had the same electrodes and were reasonably functioning (let us say, delivering a short circuit current density of at least 1 mA cm^{-2}) under 0.8-1 sun illumination. Table I does not provide a very large set of data but encompasses different materials (polymers—including low energy-gap ones—and small molecules) as well as both bilayer and BH devices. It should be noted that the cells contain different fullerenes as A, namely C₆₀ or (6,6)-phenyl C61 butyric acid methylester (PCBM).⁷ Since their LUMO energies differ by only 0.04 eV,⁷ in a first approximation the V_{OC} values of the cells were plotted versus the energy of the D's HOMO and SOMO. The latter is calculated as the energy of the HOMO plus that of the polaronic transition ω_1 , a quantity estimated from photoinduced absorption spectra taking the maximum of the corresponding band.¹⁶ Both plots (not shown) suggest linear relationships, with higher V_{OC} corresponding to lower HOMO and SOMO energies, respec-

tively. However, when the SOMO energy is taken as variable, a better relationship with linear coefficient near unity is observed. To take into account the different electron affinity of the two As, the V_{OC} values are plotted versus V_{DA} and $V_{DA} - \omega_1/q$ in Fig. 2. As the data were taken in different laboratories using different materials and devices, the distribution of the data points is rather satisfactory.

Clearly, in agreement with the references cited above, the rising of V_{DA} leads to solar cells delivering higher V_{OC} values. However, considering the D's SOMO levels leads to a better linear relationship. The smaller dispersion seen in Fig. 2 right might not have a very important significance (subtracting ω_1/q , or “any” other amount, from V_{DA} obviously reduces discrepancies). Of major interest is that, again, the slope of the linear fit is about unity when the D's SOMO energy is taken into account, using $V_{DA} - \omega_1/q$ as variable. This suggests that $V_{DA} - \omega_1/q$ might indeed set the upper V_{OC} value of D-A solar cells. Interestingly, for well known Ds used in state-of-the-art devices, i.e., those with probably maximized V_{OC} values (entries 2 and 5)^{23–25} the difference between $V_{DA} - \omega_1/q$ and V_{OC} is limited to 20–60 mV.

The hypothesis that the SOMO of the D, rather than the HOMO, sets the limit to V_{OC} is further corroborated by the fact that the experimentally observed $V_{DA} - V_{OC}$ values depend linearly on ω_1/q , and again a slope nearing unity is observed (Fig. 3).

These results suggest that the V_{OC} of organic D/A solar cells containing fullerenes is rather well described by

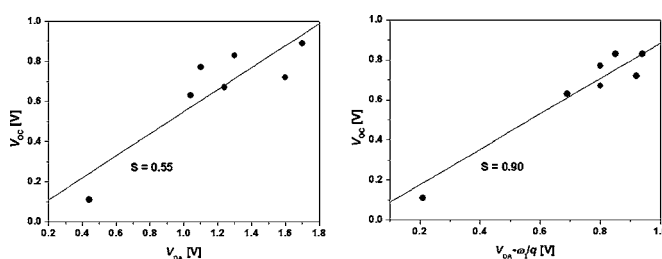


FIG. 2. V_{OC} values plotted vs V_{DA} (left) and V_{DA} minus the proposed “polaronic potential loss” ω_1/q (right). Please note the different x axes. The lines are linear fits (through origin) with slope S .

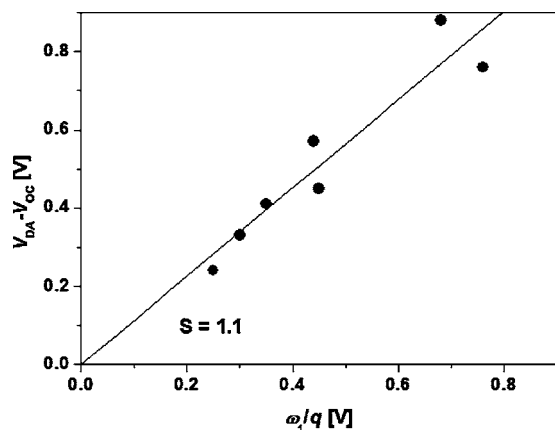


FIG. 3. The difference between the currently supposed *upper* open circuit voltage value (V_{DA}) and the experimental one (V_{OC}) as function of the proposed polaronic potential loss ω_1/q . The line is a linear fit (through origin) with slope S .

$$V_{OC} \approx (1/q)(|E_{SOMO^D}| - |E_{LUMO^A}|). \quad (1)$$

In (1) it is implicit that the $SOMO^A$ energy level does not strongly shift (as compared to that of the $LUMO^A$). Indeed, highly symmetric fullerenes are well-known for their small reorganization energy and structural relaxation upon electron uptake. However, effects due to structural relaxations should be more important in other classes of As, e.g., *n*-type conjugated polymers. Thus, a more general relation can be proposed:

$$V_{OC} \approx (1/q)(|E_{SOMO^D}| - |E_{SOMO^A}|). \quad (2)$$

Using (1), the difference between the predicted and the measured values is limited to 0.20 V, and can be as little as 0.02 V. These values are considerably smaller than the (apparent?) losses, up to ~ 0.9 V, observed taking V_{DA} as the upper limit for V_{OC} and certainly fall within the experimental errors. As such, (1) seems well suited to predict the maximum V_{OC} of organic solar cells containing fullerenes. The losses due to different mechanisms and phenomena, such as dark current, electron-hole binding energy, an overly homogeneous D-A mixing, or geometry related resistance, cannot be excluded.^{8,14,15} The impact of these factors is obviously different in different materials and devices.

To confirm these results and validate the proposed relationships, further data collection and analysis are required. Especially, the study of conjugated polymers as As (systems in which polaronic relaxation is expected to be important as in the Ds hereby considered) and that of the corresponding devices seem of interest. This letter should stimulate further

research on the topic and might contribute to a better understanding of D-A photovoltaic materials and device's physics.

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