

Factors Limiting Device Efficiency in Organic Photovoltaics

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The power conversion efficiency of the most efficient organic photovoltaic (OPV) cells has recently increased to over 10%. To enable further increases, the factors limiting the device efficiency in OPV must be identified. In this review, the operational mechanism of OPV cells is explained and the detailed balance limit to photovoltaic energy conversion, as developed by Shockley and Queisser, is outlined. The various approaches that have been developed to estimate the maximum practically achievable efficiency in OPV are then discussed, based on empirical knowledge of organic semiconductor materials. Subsequently, approaches made to adapt the detailed balance theory to incorporate some of the fundamentally different processes in organic solar cells that originate from using a combination of two complementary, donor and acceptor, organic semiconductors using thermodynamic and kinetic approaches are described. The more empirical formulations to the efficiency limits provide estimates of 10–12%, but the more fundamental descriptions suggest limits of 20–24% to be reachable in single junctions, similar to the highest efficiencies obtained for crystalline silicon p-n junction solar cells. Closing this gap sets the stage for future materials research and development of OPV.

are well established and known as the Shockley–Queisser limit.^[2] The starting point for the present discussion is to recognize the fundamentally different mechanism of photocurrent generation in OPV devices as compared to inorganic solar cells (Figure 1). In classical, inorganic p-n junction solar cells, charge pairs are generated spontaneously upon photon absorption and photocurrent generation is facilitated by differential doping on either side of a planar junction, creating highly selective pathways for opposite charges to travel to opposite contacts. In organic semiconductors the same approach cannot be used, because the localized nature of the electronic states and the low dielectric permittivity, cause photoexcited states to be confined to a small volume (few nm³) in space and create a large (0.1–1 eV) Coulombic barrier to dissociation into separate electrons and holes. In most OPV devices, this is addressed using a heterojunction of two different organic semiconductors with

offset energy levels, the donor (D) and acceptor (A), that make that the D⁺/A[−] charge-transfer (CT) state is more energetically favorable than the exciton state of either D or A. Furthermore, low charge mobilities – due to the localization of charged states – mean that charge recombination is more likely, while the difficulty in doping organic semiconductors without causing strong exciton quenching places high demands on the selectivity of contacts to direct the photocurrent.

All of these factors influence OPV device efficiency. Low mobility leads to poor collection efficiency but can be addressed using thin layers with high absorbance or through improved materials. Limited contact selectivity facilitates charge recombination at the electrodes but can be managed using interlayers. The heterojunction reduces the available electrochemical potential energy beyond the losses due to thermalization and recombination, but this effect can be addressed using material combinations with a minimal energy offset that still allows charge pair separation.

The key factor that distinguishes OPV from single-junction conventional photovoltaic (PV) devices in a theoretical sense is the heterojunction. Whilst research efforts are likely to deliver organic semiconductors with high enough mobility to enable collection across optically thick device layers and highly selective organic semiconductor-electrode contacts, they are unlikely to eliminate the need for a heterojunction. To incorporate the effect of the heterojunction properly, it is necessary to understand the mechanism of charge separation. This is now

1. Introduction

The advancement of the power conversion efficiency of organic solar cells, reaching over 10% recently,^[1] in single-junction and tandem cells has been achieved by the development of new materials and device architectures, directed by an enhanced understanding of the operational mechanisms. The real limit to organic photovoltaic (OPV) cell power conversion efficiency may seem a simple question, yet it is complex enough to create an interesting discussion in recent years.

For solar cells based on inorganic semiconductor p-n junction cells the limits to solar energy conversion efficiency

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commonly believed to involve: i) the transport of a photoexcited singlet state to a region containing donor and acceptor type species; ii) the spontaneous transfer of energy from the singlet exciton (D^* or A^*) to an excited charge-transfer (CT) state based on donor (D^+) and acceptor (A^-) molecules, possibly in competition with energy transfer to a lower lying neutral (singlet or triplet) excited state of the system; iii) thermal and possible electronic relaxation of the excited CT state; and iv) evolution of the excited CT state to a separated charge pair, with electron located in the acceptor material and hole in the donor. Stages (iii) and (iv) may happen on similar time scales. Moreover, stage (iv) may involve a variety of species of different degree of attachment, such as geminate bound pairs. For the present purpose we will consider all bound pairs as charge-transfer (CT) states and all separated pairs as charge separated (CS) states. This desired series of events requires some gradient in free energy to drive it. This energy step is the main additional feature that must be included in models of limiting power conversion efficiency. We note that relaxation of the singlet to the triplet state may occur during stage (i). In some materials this process is very efficient. Like singlet excitons, also triplet excitons in D or A can provide the D^+/A^- CT and CS states at the interface. However, the exchange energy lowers the energy of triplet compared to excitons, and limits the energy of the CT and CS states that can be formed.

In this paper, we will first describe the approaches to determination of the practical and limiting efficiencies of solar cells, then review the empirical approaches that have been used to estimate the maximum practically achievable efficiency in OPV, and subsequently discuss the approaches made to adapt the detailed balance theory of limiting efficiency to incorporate the charge-transfer stage.

In the discussion that follows, we define the optical gap of the device E_g as the minimum of the optical gaps of the donor and acceptor material, and we assume the light is absorbed in the material with the lower gap. We distinguish the optical gap from the electrical gap, which is the difference in energies of the states that are occupied by free electrons and free holes. To a first approximation the electrical gap E_{CS} is given by $E_{LUMO}^A - E_{HOMO}^D$, the difference between the energies

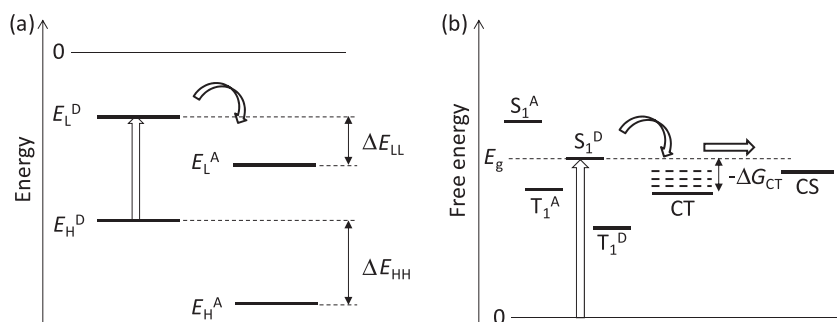


Figure 1. a) Energy levels involved in charge separation in a single-particle picture. b) Energy levels involved in charge separation in a state-diagram picture. In this diagram we assume excitation of the donor to the singlet state. Excitation of the acceptor or excitation to a triplet state would lead to equivalent processes, producing the same D^+/A^- CT and CS states, although possibly with different kinetics. Triplet states T_1^D and T_1^A can only generate D^+/A^- CT and CS states when these are sufficiently close in energy.



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of the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor.

2. Approaches to Efficiency in Solar Cells

2.1. Diode Equation

In the simplest, empirical approach, the solar cell is modelled as a current generator in parallel with a diode, generating two opposing currents when illuminated. These are added to deliver a net current density J at a given potential difference between the terminals, V :

$$J = J_0 (\exp(qV/nkT) - 1) - J_{sc} \quad (1)$$

where J_{sc} represents the short-circuit current density delivered by the light, J_0 the saturation dark current of the diode, q is the

elementary charge, k the Boltzmann constant, T the temperature, and n the diode ideality factor. In conventional devices, J_0 relates to the ease of charge transport and injection over the p-n junction and mainly influences the open-circuit voltage V_{oc} , while n relates to the mechanism of charge recombination and affects the fill factor, FF .

The power conversion efficiency is quite generally defined as the maximum of the extracted power density JV relative to the incident solar power, P_{sun} :

$$\eta = \frac{\max(JV)}{P_{sun}} \quad (2a)$$

and is equivalently written as:

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{sun}} \quad (2b)$$

V_{oc} is related to the diode parameters through:

$$V_{oc} = \frac{nkT}{q} \ln \left(\frac{J_{sc}}{J_0} + 1 \right) \quad (3)$$

This general framework is used to describe the performance of OPV devices as well as conventional solar cells. In good OPV devices where there is little charge recombination at short-circuit, J_{sc} is approximately determined by the charge photogeneration rate in the device, and thus by the device optical absorbance weighted by the exciton dissociation efficiency (which is near unity in the best devices). qV_{oc} has been found to be linked to $E_{LUMO}^A - E_{HOMO}^D$, provided that contacts are not limiting. This is in contrast to p-n junctions where V_{oc} is determined by the optical gap and the doping levels. The factors determining FF in OPV devices are not completely clear. FF essentially describes how well charge collection competes with charge recombination for a device in forward bias, but does not distinguish between different causes of poor collection, such as poor charge transport, strong dependence of recombination on charge density, or the influence of electrical bias on charge pair separation. The diode equation is commonly used to describe OPV J - V curves but the light J - V is seldom equal to the sum of dark current and photocurrent, as assumed in Equation 1. In practical devices, current and voltage outputs are modified through a variety of processes, whose effects can phenomenologically modelled as being due to parasitic series and parallel resistances. If those are known and are voltage and light independent, then they can be readily subtracted to deliver the underlying electrical response.

2.2. Detailed Balance Limit

Shockley and Queisser (SQ) made the first calculation of the limiting power conversion efficiency of a photovoltaic device in the case that all avoidable losses could be switched off.^[2] The resulting detailed balance formulation is based on the following assumptions:

- All photons with energy $E > E_g$ are absorbed.
- All non-radiative recombination pathways are switched off, while the device radiates like a black body with chemical potential $\mu > 0$.

- Each net absorbed photon leads to one electron in external circuit, hence the internal quantum efficiency (IQE) is unity.
- The extracted electrons have an electrochemical potential $\mu = qV$, where μ is the difference in the quasi Fermi levels of the separately thermalized electron and hole populations.

The radiative loss results from the fact that a system that has a non-zero probability for absorption of light of a given wavelength must necessarily have a finite probability of emitting light, as demonstrated through Einstein's detailed balance treatment of the absorption and emission of light. In the dark, with no applied bias, the cell absorbs radiation from the ambient and emits an equal amount of radiation, where cell and ambient are both assumed to radiate like black bodies at the ambient temperature, T . When the system is biased, such that the charge-carriers population are each in quasi thermal equilibrium but with quasi Fermi levels separated by μ , then the emission of light is found to be amplified by a factor of approximately $\exp(\mu/kT)$ relative to the equilibrium, black-body case.^[3,4] These assumptions lead to the following expression for the extracted current density J (defined in the same sense as the diode current):

$$\begin{aligned} -\frac{1}{q}J &= \beta \int_0^\infty b_{sun}(E)a(E)dE \\ &+ (1 - \beta) \int_0^\infty b_{ambient}(E)a(E)dE \\ &- \exp(qV/kT) \int_0^\infty b_{ambient}(E)a(E)dE \end{aligned} \quad (4)$$

where $b_{sun}(E)$ is the spectral photon flux density incident on a flat surface from the Sun, $b_{ambient}(E, T)$ is the spectral photon flux density emitted by a black body at temperature T , $a(E)$ is the device absorbance of photons of energy E , β expresses the concentration (intensity) of solar irradiation, and we have used $\mu = qV$. We have used the result from generalized detailed balance that the emissivity of the device is equal to its absorbance at any photon energy.

Equation 4 applies for a general absorbance spectrum. Maximum power conversion efficiency is obtained for a step-like absorbance of the form:

$$a(E) = \begin{cases} 0 & E < E_g \\ 1 & E \geq E_g \end{cases} \quad (5)$$

whence:

$$\begin{aligned} -\frac{1}{q}J &= \beta \int_{E_g}^\infty b_{sun}(E)dE \\ &+ (1 - \beta) \int_{E_g}^\infty b_{ambient}(E)dE \\ &- \exp(qV/kT) \int_{E_g}^\infty b_{ambient}(E)dE \end{aligned} \quad (6)$$

Separating the light-intensity-dependent and voltage-dependent terms, we have an expression of the same form as the ideal diode equation for which $n = 1$:

$$J = -J_{sc} + J_0 (\exp(qV/kT) - 1) \quad (7)$$

where:

$$J_{sc} = q\beta \int_{E_g}^{\infty} (b_{sun}(E) - b_{ambient}(E)) dE \quad (8a)$$

and:

$$J_0 = q \int_{E_g}^{\infty} b_{ambient}(E) dE \quad (8b)$$

In this picture, where the cell is in thermal equilibrium with the ambient and the intensity of solar radiation is fixed, the only parameter influencing the $J(V)$ relationship is the optical gap E_g . When η (from the maximum of JV/P_{sun}) is plotted as a function of E_g , the efficiency peaks at a value of around 33% at $E_g = 1.3$ – 1.4 eV (this will be seen in Section 4.1 below). This is the maximum fraction of incident solar power that can be converted into electrical work by a single-junction device. Of the remaining solar radiation, some 32% is lost due to photons of $E < E_g$ that are not absorbed, and some 23% is lost through thermalization of energetic charges generated by photons of $E > E_g$ to lower energies close to the band edge.

The detailed-balance relationship between absorption and emission has been extended to the case of practical solar cells by Rau who showed that a reciprocal relationship must exist between the quantum efficiency for current extraction (the energy dependent external quantum efficiency $EQE(E)$) and the quantum efficiency for electroluminescence φ_{EL} .^[5]

$$\varphi_{EL}(E) = EQE(E) b_{ambient}(E, T) \left[\exp\left(\frac{qV}{kT}\right) - 1 \right] \quad (9)$$

This essentially results from the efficiency of charge transport from point of charge generation to electrodes being equivalent to that from electrodes to point of charge pair recombination, and it allows for only a fraction of charge losses to occur via radiative recombination.^[5] The formulation allows the practical dark saturation current J_0 to be related to the EQE:

$$J_0 = \frac{q}{\varphi_{EL}} \int_0^{\infty} EQE(E) b_{ambient}(E, T) dE \quad (10)$$

In applying the detailed balance approach to organic solar cells, the main modification to the theory is in introducing the process of charge separation and in distinguishing the energies of excited states in components materials and at the interface. Approaches to such extension of the SQ theory will be reviewed in Section 4 below.

3. Empirical Approaches to Limiting Efficiency in OPV

3.1. Practical Efficiency Limits in Single-Junction Cells

Whilst the detailed balance approach could deliver a rigorous answer to the question of limiting efficiency in OPV, it would require highly ideal materials with properties that are hard to realize. To gain insight into the improvements that may be achievable in practice, several more empirical approaches have been taken that incorporate the properties of organic semiconductors as presently known. Such properties include the absorption spectrum, the exciton lifetime, the charge carrier mobility, or the required offset between energy levels to dissociate excitons into free charges. By establishing empirical limits to the efficiency, it is not so much the answer obtained that is relevant, but rather the question of which of the identified losses may be avoidable. Detailed insights into the avoidable losses will direct materials scientists to design and develop improved semiconductors and device structures.

With this objective, various empirical approaches to limiting efficiency have been developed in order to establish design rules for new materials and device configurations. Following the successful demonstration of η values of 2.5%^[6] and 3%^[7,8] for devices made from blue-green absorbing polymers combined with fullerene acceptors, the real prospect was opened up of reaching efficiencies over 5% by using polymers that span more of the solar spectrum. This led to development of new materials with small optical gaps, in order to increase photocurrent and possibly open-circuit voltage. In the effort to design such polymers, attention was paid to the frontier orbital energy levels of donor and acceptor (for open-circuit voltage), the number of photons absorbed, and the driving force for charge transfer.^[9] In 2006, Scharber et al.^[10] were first to publish quantitative design rules for donors in bulk-heterojunction solar cells using phenyl C₆₁ butyric acid methyl ester (PCBM) as common acceptor. These design rules are based on an empirical estimate of the open-circuit voltage (V_{oc}) in terms of the energies of the HOMO of the donor (E_{HOMO}^D) and the LUMO of the acceptor PCBM (E_{LUMO}^A), thus:

$$V_{oc} = (1/q) (-|E_{HOMO}^D| + |E_{LUMO}^A|) - 0.3V \quad (11)$$

where 0.3 V is an empirical value, representing losses in transport to the electrodes. This equation was found to describe the V_{oc} of 26 different bulk-heterojunction solar cells spanning a range from 0.1–1.0 V.^[10] The formula builds on previous studies which demonstrated that both E_{HOMO}^D and E_{LUMO}^A directly affect the V_{oc} ,^[11,12] and holds provided that ohmic contacts are realized with the active layer.^[13] Scharber et al.^[10] further considered that an energy difference $\Delta E_{LL} = 0.3$ eV (Figure 1) between the LUMO of the donor and the LUMO of the acceptor is sufficient for efficient charge separation. The energy difference between the two HOMO levels must fulfill the same criterion to prevent energy transfer rather than the desired electron transfer. By considering that photons are only absorbed by the polymer and not by the fullerene the limit to power conversion efficiency then only depends on the LUMO level of the donor. To obtain a practical limit to the efficiency Scharber

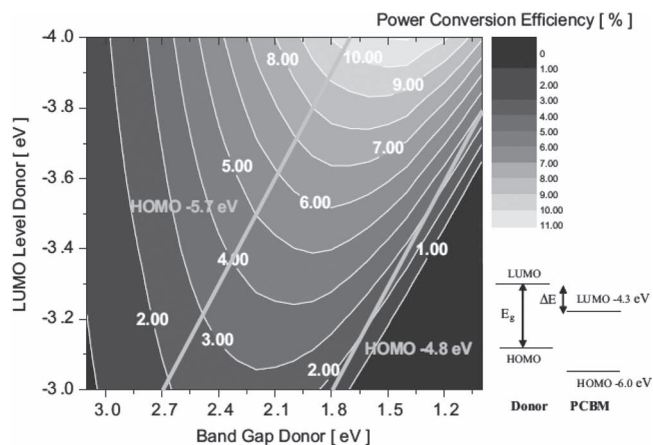


Figure 2. Contour plot showing the calculated energy-conversion efficiency (contour lines and colors) versus the bandgap and the LUMO level of the donor polymer according to the model described above. Straight lines starting at 2.7 eV and 1.8 eV indicate HOMO levels of -5.7 eV and -4.8 eV, respectively. A schematic energy diagram of a donor PCBM system with bandgap energy (E_g) and the energy difference (ΔE_{LL}) is also shown. (Note that this plot is based on the assumption that the LUMO of PCBM lies at -4.3 eV. The results would be modified if the PCBM LUMO lies at a higher level, as reported, but the qualitative features remain. Reproduced with permission.^[10] Copyright 2006, Wiley-VCH.

et al. assumed that the EQE of the solar cell for photon energies equal to or larger than the bandgap energy of the donor and the FF of the cell are both equal to 0.65. These numbers were chosen as representative of the best experimental system at the time. They do not represent fundamental limits, and have in fact been exceeded in several optimized cells already. **Figure 2** shows the “Scharber plot” of power conversion efficiencies in AM1.5 (air mass 1.5) solar irradiance that results from these assumptions, as function of the optical gap and LUMO level of the donor.

Figure 2 shows that efficiencies of over 10% should be achieved for $1.65 < E_g < 1.35$ eV and $E_{LUMO}^A < -3.9$ eV. It also demonstrates that the optimum optical gap is somewhat larger than the optimum in the SQ limit (of ≈ 1.3 eV), and shows that for any given optical gap, it is advantageous to push down the donor LUMO and HOMO energies.

Koster et al. took a rather different approach to estimate the ultimate efficiency of polymer:fullerene bulk-heterojunction solar cells.^[14] As a starting point they used 3.5% efficient P3HT:PCBM solar cells and combined charge-carrier mobility measurements with photocurrent-voltage measurements to quantitatively describe the J - V characteristics with a numerical model that includes drift and diffusion of charge carriers, the effect of space charge on the electrical field, and a field- and temperature-dependent charge-carrier generation rate. The model consistently describes the electrical characteristics of the P3HT:PCBM cell and was subsequently used to explore the effects of changing some of the critical energy levels.^[14] The rationale behind this idea is that whilst P3HT:PCBM solar cells represent efficient photon-to-electron conversion, they are limited by a LUMO-LUMO offset that is larger than needed to overcome the charge pair binding energy ($\Delta E_{LL} = 1.1$ eV) and by too large an optical gap ($E_g = 2.1$ eV).^[14] By raising the acceptor

LUMO level (i.e., lowering ΔE_{LL} from 1.1 to 0.5 eV and leaving the polymer levels unchanged), Koster et al. showed that the device efficiency could increase to more than 8%. By lowering the LUMO level of the donor (i.e., lowering E_g from 2.1 to 1.5 eV and leaving the fullerene levels unchanged) an efficiency increase to 6.6% is predicted. In calculating these efficiencies, the authors assumed a realistic absorption spectrum and did not insist that all photons of $E > E_g$ are absorbed. By changing the LUMO levels of both polymer and fullerene, an efficiency of 8.6% is predicted for $1.9 < E_g < 2.0$ eV. The fact that a fairly high value is predicted for the optimal E_g is partly a consequence of the absorption spectrum used. Finally, Koster considered the case of a prospective polymer with a hole mobility as high as the electron mobility of PCBM. In this case, when using $E_g = 1.9$ eV and $\Delta E_{LL} = 0.5$ eV, an efficiency of 10.8% was predicted for a 200 nm thick film.

Minnaert and Burgelman also described phenomenological estimates to the efficiency limits of OPV and consider ideal, optimistic and realistic scenarios.^[15] Of these the optimistic scenario is most relevant to discuss since the maximum efficiency in the ideal scenario (39.7%) exceeds the Shockley–Queisser limit and the efficiency realistic scenario (5.8%) has already been surpassed. In this optimistic scenario they consider that $\Delta E_{LL} = 0.2$ eV suffices to achieve $EQE = 0.90$ and further assume that $FF = 0.70$ and $V_{oc} = 0.7(E_g/q)$. Under these assumptions an efficiency of 15.2% can be expected for an absorber with $E_g = 1.6$ eV having an absorption band with a width of 400 nm. We note that when taking $EQE = 0.65$ and $FF = 0.65$ as used by Scharber,^[10] the estimate of Minnaert and Burgelman^[15] would change to 10.2%, close to the maximum predicted by Scharber et al.^[10]

Lunt et al. derived a semiempirical estimate for the practical upper limit to the power conversion efficiency for a single-junction nanostructured PV by considering that the maximum demonstrated V_{oc} for these devices reaches 80% of the SQ limit, due to recombination phenomena.^[16] In combination with practical upper limits for photocurrents and fill factors ($EQE = 0.75$ below the bandgap and $FF = 0.75$), the maximum efficiency for a single-junction cell derived by Lunt et al. is 17%.^[16]

Veldman et al. considered the state-diagram picture of OPV operation to find an empirical estimate to the maximum efficiency.^[17] They considered that the open-circuit voltage of a bulk heterojunction solar cell is limited by the energy of the charge-transfer (CT) state at the donor-acceptor interface. This choice is consistent with observations of photocurrent generation through direct excitation of the sub gap CT complex.^[18] By measuring E_{HOMO}^D and E_{LUMO}^A and the open-circuit voltage for solar cells for a series of six different donor materials and nine different acceptor materials, including polymer and non-fullerene small molecular acceptors, and correlating these to the CT energy (E_{CT}) obtained from electroluminescence experiments they found that:

$$qV_{oc} = E_{CT} - 0.47 (\pm 0.06) \text{ eV} \quad (12)$$

This estimate is consistent with the finding of Vandewal et al.^[19,20] Veldman et al.^[17] further showed experimentally that a relatively small free-energy difference for charge transfer ($-\Delta G_{CT} = E_g - E_{CT}$, with $(E_g = \min(E_g^D, E_g^A))$ of 0.1 eV suffices for charge transfer to occur from neutral exciton to CT state.

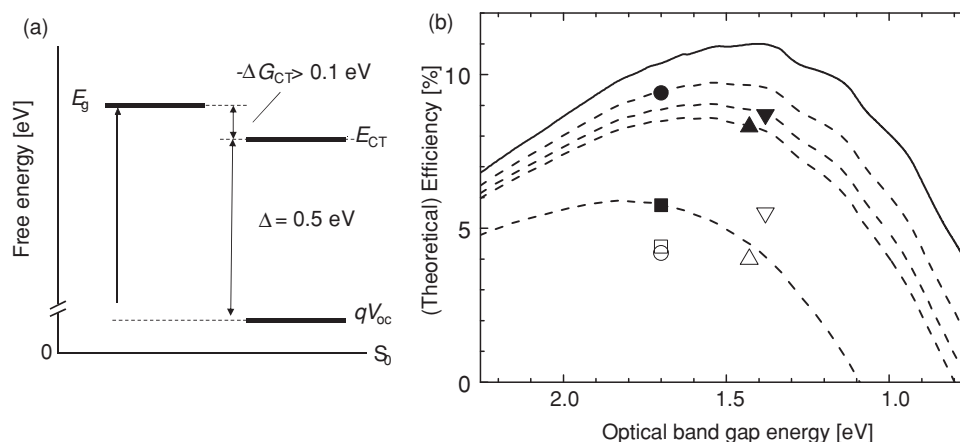


Figure 3. a) State energy diagram. b) Theoretical efficiency of bulk-heterojunction photovoltaic devices with $E_g - qV_{oc} = 0.60$ eV (solid line) versus the lowest optical bandgap of the two materials, calculated using the AM1.5 spectrum, $FF = 0.65$, and assuming constant $EQE = 0.65$ between 3.5 eV and E_g . The dashed lines show the theoretical efficiencies for devices using the larger $E_g - qV_{oc}$ offsets for (from top to bottom): PF10TBT:[60]PCBM (0.70 eV, circles), PCPDTBT:[70]PCBM (0.76 eV, down triangles), PBDTPP2:[70]PCBM (0.80 eV, up triangles), and P3HT:[60]PCBM (1.09 eV, squares). The closed markers represent the theoretical efficiency, the open markers the device efficiencies. Reproduced with permission.^[17] Copyright 2009, Wiley-VCH.

Together these estimates lead to a minimum energy loss from E_g to qV_{oc} of 0.6 eV (under the experimental conditions of room temperature and 1 sun illumination). Then, making the same assumptions as Scharber et al.^[10] (i.e., considering that $EQE = 0.65$ and $FF = 0.65$), Veldman^[17] arrived at a simple curve for the maximum power conversion efficiency as function of the optical bandgap. An efficiency of 11% is predicted for materials with $E_g = 1.37$ – 1.45 eV (Figure 3).

In their work on practical efficiency limits Servaites et al. took the EQE as being the product of an assumed internal quantum efficiency (IQE) of 0.9 and an experimental transmittance spectrum of indium tin oxide/glass, resulting in weighted averages $EQEs$ of 0.75–0.80.^[21] For the V_{oc} , they made the same assumption as Scharber et al.^[10] but expressed Equation 1 in terms of optical gap and LUMO-LUMO offset:

$$qV_{oc} = E_g - \Delta E_{LL} - 0.3 \text{ eV} \quad (13)$$

Their approach differed from prior approaches in treating FF as part of the optimization for each ΔE_{LL} . For this Servaites et al. assume that the J - V curve can be described by the classical diode equation which includes the series and parallel resistances and assume that the parallel resistance includes a contribution that quantifies the field dependence of charge separation at $V = 0$ and increases with increasing LUMO offset. In this way they treat the FF limit as a function of lowering ΔE_{LL} . For a given ΔE_{LL} they optimize the donor optical gap and show the efficiencies above 10% should be possible for systems that generate charge carriers efficiently at $\Delta E_{LL} = 0.3$ – 0.4 eV.

The studies described above yield a fairly consistent picture, namely, that the maximum power conversion efficiency η decreases and the optimum value for optical gap increases as the difference between the optical and electrical gaps (given either by $E_g - E_{HOMO}^D + E_{LUMO}^A$ or by $E_g - E_{CT}$) increases. Moreover, using similar assumptions about the fill factor and external quantum efficiency (i.e., about the transport and recombination processes), the models arrive at similar estimates for the

maximum realistically achievable power conversion efficiency (typically of 10–12%).

Regarding the identification of avoidable loss mechanisms, it is clear that the free-energy difference driving charge separation is an important factor; but it is also clear that the efficiency of charge collection and the mechanism of recombination (subsumed in the above into FF and EQE) are also very important. The values of these parameters used in above calculations have already been exceeded in some cases, indicating that the practical limit reached of 10–12% may be an underestimate. Meanwhile experimental studies continue to focus on the factors that determine the lower limit to ΔG_{CT} .^[22–27]

In the discussion above we have limited the examples to solid state OPV devices. We note, however, that dye-sensitized solar cells (DSSCs) are similar in many ways. In DSSCs, titania functions as electron acceptor for the photoexcited dyes, while an electrolyte is used to regenerate the dye in its initial state. The efficiency of dye-sensitized solar cells has long been in the 10–11% region,^[28] but was recently raised to 12.3%.^[29] Haman et al. have discussed the efficiency limits of DSSCs and concluded that simultaneous development of new dyes, electrolytes, and photoanodes can lead to DSSCs with efficiencies exceeding 16%.^[30]

3.2. Practical Efficiency Limits in Tandems

In single-junction solar cells, significant energy losses are unavoidable. Photons with energies smaller than the optical gap cannot be absorbed and photons with larger energies will lose their excess energy via thermal equilibration. Tandem solar cells can reduce these losses by using separate subcells, each converting a different part of the solar spectrum. Thermalization losses of high energy photons are lowered by conversion in the wide gap subcell, and transmission losses are reduced by absorption of the low energy photons in the small gap cell. The most practical way to split the spectrum is with a vertical stack

of cells into a two terminal device where the top cell peels off the higher energy photons and is electrically connected to the next cell through an ohmic contact (or recombination zone). This concept is readily applicable to thin, multilayer molecular devices. Semiconducting organic molecules and polymers are being explored for tandem solar cells, taking advantage of the strong and narrow absorption bands of the individual layers to increase the spectral coverage.^[31–35] In fact, the highest reported efficiencies for organic solar cells of 10.6% and 10.7% are based on tandem configurations of solution processed polymer solar cells and vacuum deposited small organic molecule cells, respectively.^[36,37] For comparison, the detailed balance limit for a classical, two junction series constrained tandem device is 45.3%.^[38]

A first quantitative attempt to address the efficiency potential of organic tandem solar cells was published by Minnaert and Burgelman,^[15] considering ideal, optimistic and realistic scenarios. Their assumptions for calculating maximum obtainable efficiencies are similar to these used for the single junctions described above. In the optimistic scenario, assuming an absorption window of 400 nm for each layer, and considering that both cells have $\Delta E_{LL} = 0.2$ eV, $EQE = 0.90$, $FF = 0.70$, and $V_{oc,i} = 0.7(E_{g,i}/q)$, a maximum efficiency of 23.2% is predicted for two complementary absorbers with $E_{g1} = 1.7$ eV and $E_{g2} = 1.1$ eV. A likewise empirical estimate of the maximum efficiency was presented by Lunt et al.^[16] Assuming a non-idealized PV performance ($EQE = 0.75$ below the bandgap, $V_{oc} = 0.8 \times V_{oc}(SQ)$, and $FF = 0.75$) as discussed in Section 3.1, Lunt et al. calculated a power conversion efficiency of 24% for a stacked, current-matched, two-cell nanostructured tandem structure.

Dennler et al. have developed design rules for donors in bulk heterojunction tandem solar cells, essentially following the Scharber model ($EQE = FF = 0.65$ and $\Delta E_{LL} > 0.2$ eV).^[39] Necessary refinements with respect to the single cell case differences are changes in absorption due to the different device layer structure. For the front subcell (high E_g), absorption is reduced because there is no adjacent reflective back contact and for the back subcell (lower E_g) some light filtered out by the top cell. Dennler et al. further assume that the V_{oc} of the tandem is the exact sum of the V_{oc} s of the two subcells and that the short-circuit current is equal to the smaller of the subcells' currents ($J_{sc}^{tandem} = \min(J_{sc,1}, J_{sc,2})$). Although these assumptions are not necessarily correct,^[40] they do represent a very valid first approximation. Figure 4^[39] quantifies the highest efficiencies realistically achievable with a tandem cell and the bandgaps of the two complementary donor materials needed for this goal. The calculations are based on optimal LUMO levels of the two polymers of -4.0 eV, implying $\Delta E_{LL} = 0.3$ eV with PCBM, similar to Scharber et al.^[10] Comparing Figure 2 and 4 shows that under the assumptions made, the tandem configuration can outperform the single cell efficiency in OPV. The optimum tandem behavior is expected from stacking of materials of similar E_g , as the optimum is found close to the diagonal. The calculations predict a maximum value of 15% to be achievable for a front cell with $E_g = 1.6$ eV and a back cell with $E_g = 1.3$ eV. Compared to the $\approx 11\%$ that can be reached for a single-junction cell with $E_g \approx 1.4$ eV,^[10] this implies an increase of efficiency of the tandem versus the best single-junction cell of $R \approx 40\%$. This

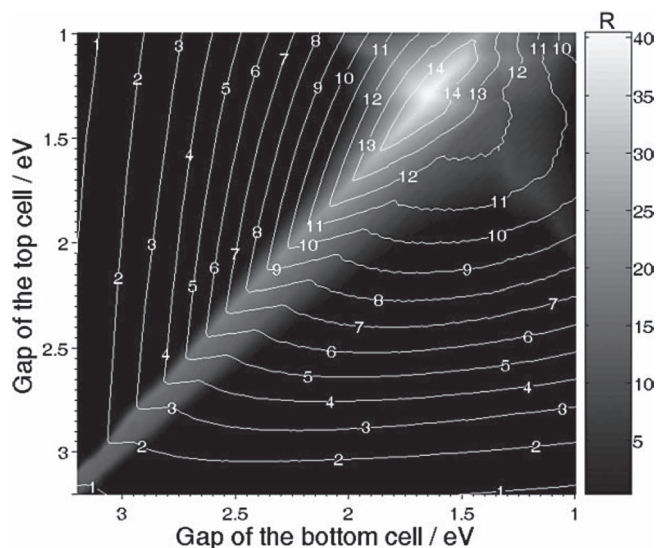


Figure 4. Percentage of efficiency increase of a tandem cell over the best single cell (R) for a device comprising a top subcell and a bottom subcell based on donors each having a LUMO level at -4 eV and each blended with a fullerene acceptor of LUMO = -4.3 eV. The variables are the bandgap of both donors. The lines indicate the efficiency of the tandem devices. Reproduced with permission.^[39] Copyright 2008, Wiley-VCH.

can be compared to the increase of some of the most efficient experimental tandem structures found to date of $R \approx 20\%$ ^[34] and $R \approx 25\%$.^[35]

4. Detailed Balance Limit to OPV Efficiency

In applying Shockley–Queisser theory to the organic solar cell we must recognize that the states that are filled following charge separation and are responsible for generating the electrochemical potential are, in general, different from the states that are occupied by the absorption of light in either of the component materials. This issue may be considered in two ways. Firstly, we may use a thermodynamic picture in which we consider the population in the electrical (or CT) states to be in quasi thermal equilibrium with directly excited charges and treat the system as a single gap system with a non trivial density of states. Alternatively, we may consider the problem within a kinetic picture where the populations of directly (above gap) excited charges are not in quasi thermal equilibrium with the charges in conduction states but are related through a charge-transfer reaction of finite rate.

4.1. Thermodynamic Approaches

The thermodynamic approach was justified by the observations that photons could be excited directly into sub gap states, assigned to CT states,^[41,42] that such sub gap absorption led directly to photocurrent generation^[18] and that electroluminescence from the same sub gap states could be correlated to photovoltage.^[20] This evidence that optical transitions bridging the so called electrical gap led to photovoltaic action allowed the system to be considered as a single gap photovoltaic system but

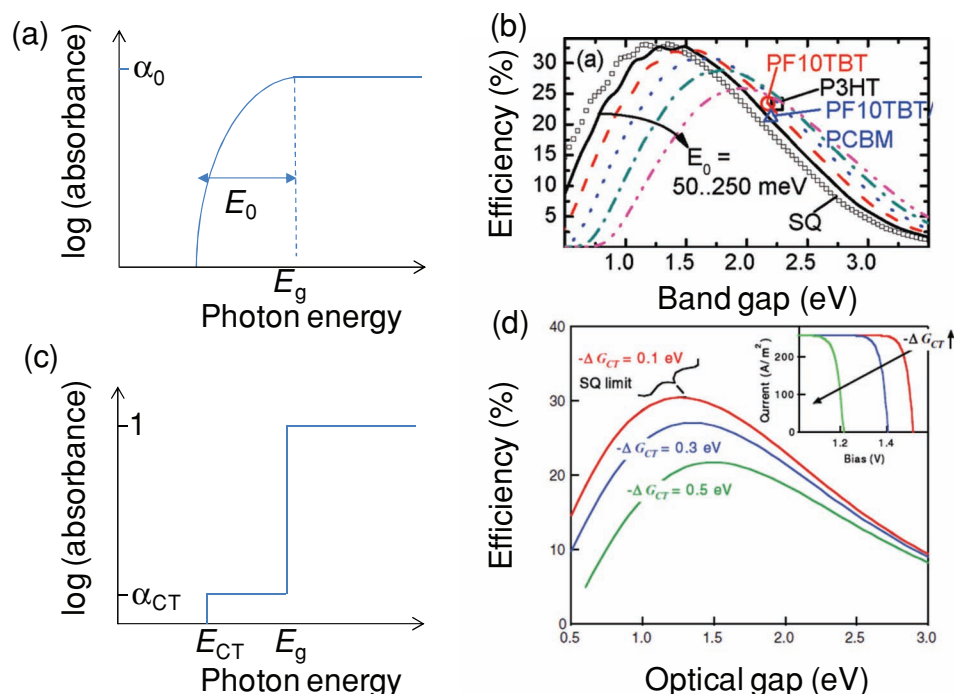


Figure 5. a) Absorbance spectrum with a Gaussian CT state spectrum. b) Calculated limiting efficiencies as a function of the Gaussian width, E_0 . c) Absorbance spectrum with a step-like CT state spectrum. d) Calculated limiting efficiencies as a function of the difference between optical gap and CT state energy, $-\Delta G_{CT}$. b) Reproduced with permission.^[43] Copyright 2009, American Chemical Society. d) Reproduced with permission.^[44] Copyright 2011, American Physical Society.

with the step like absorption profile assumed in SQ replaced by a more general form.

This approach was first implemented by Kirchartz et al.,^[43] using a density of states (DoS) function consisting of a half-Gaussian of varying width E_0 joined to a step-like absorbance of magnitude α_0 at the optical gap energy E_g :

$$a(E) = \begin{cases} \alpha_0 \exp\left(-\frac{(E-E_g)^2}{2E_0^2}\right) & E < E_g \\ \alpha_0 & E \geq E_g \end{cases} \quad (14)$$

The implicit assumption was that charges excited into this composite DoS through excitation above or below E_g form a single population in quasi thermal equilibrium. Kirchartz showed that as the half width of the Gaussian tail increases from 0 to 0.25 eV, the limiting power conversion efficiency, η_{\max} , decreases from the detailed balance limit of 33% to around 24% while the optimum value of E_g increases from 1.3 to 2 eV (Figure 5a).^[43] When compared to a step like, unit absorbance (Equation 5) any alternative absorbance spectrum generally results in a lower limiting efficiency in the detailed balance limit. The photocurrent is reduced relative to the step-like case with the same absorbance threshold, while voltage remains almost unaffected. It is also a general finding that the optimum E_g increases relative to the step-like absorbance case when sub gap absorption is introduced at energies $E < E_g$: the sub gap transitions reduce the effective absorbance threshold and increase emission losses, while raising E_g shifts all transitions to higher energy and partly compensates for the emissive losses.

Kirchartz used measured absorbance spectra to infer E_g and the width of the sub-gap absorbance spectrum for different practical polymer:fullerene combinations.^[43] The modified detailed balance methods predict a power conversion efficiency much higher than observed in practice (e.g., 23.4% for a poly-fluorene based blend device compared to an observed value of 4.2%). The difference can be rationalized in terms of imperfect exciton dissociation, imperfect charge separation, limited transport and, importantly, other recombination pathways than non-radiative.

A similar approach was taken by Giebkink et al.,^[44] Koster et al.,^[45] and by Gruber et al.^[46] but using a finite, step like spectrum for the CT absorbance rather than a Gaussian, and combining this weakly absorbing CT state spectrum with a unit absorbance for $E > E_g$:

$$a(E) = \begin{cases} 0 & E < E_{CT} \\ \alpha_{CT} & E_{CT} \leq E < E_g \\ 1 & E \geq E_g \end{cases} \quad (15)$$

In agreement with the earlier studies,^[43] all these authors found that η_{\max} reduces and the optimum optical gap increases as the difference between the CT state energy E_{CT} and the optical gap E_g , i.e., $-\Delta G_{CT}$, increases (Figure 5b,d). The effect of the magnitude of CT absorbance on the limiting efficiency versus E_g curve is relatively weak.^[44,46] Koster et al. have shown that η_{\max} has a minimum at a low (order 10^{-2}) value of α_{CT} .^[45] The achievable η_{\max} depends upon the value of $-\Delta G_{CT}$, reaching the SQ limit when $-\Delta G_{CT} = 0$. For the reasonable estimate of

$-\Delta G_{CT} = 0.5$ eV, all groups find a maximum efficiency in the range 20–22% at an E_g of around 1.5 eV. This is compatible with the slightly higher efficiency reached by Kirchartz^[43] for a Gaussian CT absorption of a slightly narrower energetic extent ($\eta_{max} = 24\%$ at $E_0 = 0.3$ eV).

The effect of finite absorbance at energies $E < E_g$ has been discussed in some detail previously in the context of inorganic solar cells of limited thickness^[3] and devices containing quantum wells,^[47] leading to similar conclusions. Those studies also explored how control of the angular range for absorption and emission influence efficiency.

The use of a Gaussian form for the CT absorbance can be justified within the terms of non-adiabatic Marcus theory. Here, the molecular species is assumed to perform vibrations around its equilibrium configuration with a total energy that depends quadratically on the displacement from equilibrium. In its photoexcited state it performs similar vibrations but with, in general, a different equilibrium configuration. This means that a range of photon energies are capable of exciting the system with some combination of initial and final vibrational states. After accounting for the density of vibrational modes and their occupation probability, the absorption spectrum $\alpha(E)$ is found to follow a Gaussian form:

$$\alpha(E)E \propto \frac{f}{\sqrt{\lambda kT}} \exp\left(-\frac{(E - E_{CT} - \lambda)^2}{4\lambda kT}\right) \quad (16)$$

where f is the oscillator strength for the optical transition. Here, the reorganization energy for the transition, λ , quantifies the energy required to rearrange the molecule from its ground state to its excited configuration. In this case the emission spectrum is also based on a Gaussian but centered around the lower energy, $E_{CT} - \lambda$, so that the peaks of the reduced absorption and emission spectra are thus shifted by a Stokes shift of 2λ . Vandewal et al. used this framework to model the absorbance of charge-transfer states and then applied Rau's modified detailed balance relation (Equation 10) along with Equation 3 to describe the dark current and V_{oc} in terms of λ , luminescent efficiency and other parameters.^[48] If applied to the calculation of limiting efficiency the approach would yield similar results to Kirchartz,^[43] however, the physical basis is slightly different. In the previous case the distribution of transition energies in the absorbance spectrum is assumed to result from disorder in the electronic energies of the molecular species in the sample while in this case there is a single electronic transition energy but the molecule occupies different vibrational states, i.e., it does not involve so-called energetic disorder. Depending on the origin of the energetic disorder in the first case, the two physical mechanisms could be distinguished through the temperature dependence of the absorbance spectrum. This may be relevant to design of materials: since different synthetic strategies would be taken to avoid vibrational and electronic disorder in order to reduce the CT absorption bandwidth and access higher efficiencies.

Giebink et al. also addressed the question of entropy change during photovoltaic energy conversion.^[44] This is relevant for organic photovoltaics because the relatively large binding energy of electron hole pairs means that the photovoltaic process must release sufficient heat to dissociate the bound electron hole

pairs. If the binding energy is too large, then entropy can be conserved only if the chemical potential of the exciton exceeds that of the electron hole pairs, and this leads to reduced current output and reduced efficiency. Such a phenomenon would only be expected in extreme cases where the electron-hole pair binding energy exceeds 1 eV. For a heterojunction device, the pair binding energy will normally be smaller than this and photogeneration therefore always consistent with entropy increase. This study suggests that entropy change will not limit performance.

These studies all lead to the shared finding that replacing the step-like, unit absorbance of the classical SQ case with an absorbance edge that varies over a range of energies leads to a lower value of the optimum efficiency relative to the SQ case and a higher value of the optimum gap for direct (non CT) photon absorption. They arrive at a consensus that $\eta_{max} \approx 20\%$ is reasonable at $E_g = 1.5$ eV and $-\Delta G_{CT} = 0.5$ eV. The doubling in $\eta_{max} \approx 20\%$ with respect to the value reached above from a range of empirical approaches can be largely explained by the larger value of $EQE \times FF$ for the detailed balance case (1×0.85) compared to the empirical case (0.65×0.65).

All of the above thermodynamic approaches are based on the assumption that charges in different energy states are in quasi-thermal equilibrium. This does not allow for the dissociation of excitons or charge pairs to be kinetically limited. Approaches that include kinetic effects are discussed next.

4.2. Kinetic Approaches

A first attempt to calculate the detailed-balance limiting efficiency of molecular solar cells allowing for limited charge-transfer rates was made by Nelson and co-workers.^[49,50] In this study, a charge-transfer stage is introduced between the photoexcited species (or chromophore) and different molecular species responsible for transporting the charge (Figure 6). Using Marcus theory the charge-transfer rate from chromophore to acceptor K_{ca} is given by:

$$K_{ca} = \frac{|J|^2}{\hbar} \sqrt{\frac{\pi}{\lambda kT}} \exp\left(-\frac{(\Delta E_{ca} - \lambda)^2}{4\lambda kT}\right) \quad (17)$$

where J is the electronic transfer integral for the transition, ΔE_{ca} the (positive) difference in LUMO energies and λ here the reorganization energy for the charge-transfer reaction. A twin heterojunction, one each for electron and hole transfer, is used to simplify analysis but the qualitative results apply equally well to a single heterojunction. Photon absorption and emission occur in the chromophore, giving rise to a local electrochemical potential obeying detailed balance. Charge is transferred to the transport materials at a rate described by Equation 17, and it is allowed for charge to transfer back to the chromophore not only to the excited state (as always required in thermodynamic equilibrium) but also to the ground state (effecting charge recombination). The rationale here is that the same parts of the molecules will, in general, be involved in the transfer of an electron, say, from electron acceptor to the LUMO of the chromophore and to the HOMO of a positively charged chromophore, and so the latter lossy process cannot, in general, be switched

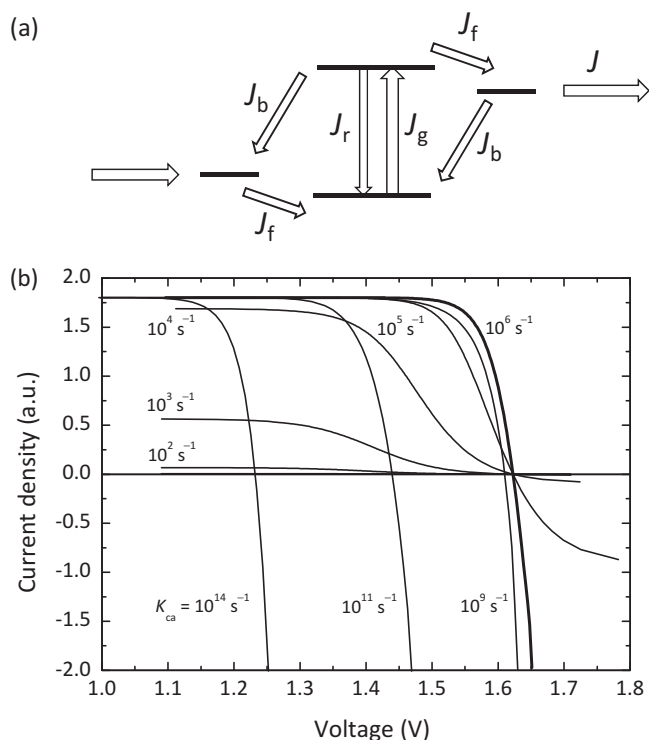


Figure 6. a) Schematic showing the electron fluxes involved in the kinetic model in Ref.[49]. Within the central chromophore, absorption (J_g) and radiative recombination (J_r) are related through detailed balance. The rates of charge transfer in the photocurrent direction (J_f) and against it (J_b) are both described by Marcus theory. The net photocurrent J is due to the sum of forward minus reverse fluxes. b) Calculated J - V curves under monochromatic illumination for different values of the forward charge-transfer rate, with the assumption that forward and backward rates depend on the same electronic coupling term. The J - V curve with the highest power density is obtained at some intermediate value of the charge-transfer rate, not at the fastest rate of charge transfer. b) Adapted with permission.[49] Copyright 2004, American Physical Society.

off. Introducing this interfacial recombination pathway requires that different quasi Fermi level difference apply in the chromophores and the transport materials, and that affects the photovoltage. The current is calculated as the net forward current due to photogenerated flux minus all radiative and non-radiative loss fluxes and output voltage as the difference in quasi Fermi levels in the acceptor and donor. Rates can be varied by varying the electronic coupling or the reorganization energy. The key finding is that when charge transfer away from the chromophore is too slow, the J - V curve develops a sigmoidal form typical of transport limited behavior, while when interfacial recombination is too fast, the photovoltage is reduced. In the case where the electronic coupling for the forward transfer and recombination are linked, then there is an optimum degree of electronic coupling where power conversion efficiency is maximized. This phenomenon of “kinetic redundancy” – that too close electronic contact between the species involved in photoinduced charge transfer is detrimental – has been observed in dye-sensitized systems and may well apply in organic systems.[51]

In this first study, a monochromatic system was studied containing a single type of chromophore, sensitive to a single

photon energy, representative of excitation by photons just at the optical gap. This was so that the effects of transfer rates could be studied independently of the effects of light harvesting. The methodology was later adopted and extended to model the observed photocurrent due to panchromatic illumination in small molecular heterojunctions by Rand et al.[52] Whilst not used to simulate limiting efficiencies in that work, those authors and others[53] could justify the use of Marcus theory to describe photocurrent generation with the observation of an optimum energy offset at the heterojunction, as predicted from Marcus formalism.

Kirchartz et al. extend on the studies reported in Section 4.1 by combining a detailed balance treatment of light absorption and emission with dynamics of exciton diffusion and a ΔG_{CT} dependent charge-separation probability.[54] They found that the limiting efficiency for the detailed balance case that incorporates a heterojunction (Section 4.1) is reduced by some 10–20% by the limited exciton and charge dynamics.

Godovsky took a purely kinetic approach, describing photocurrent as the result of a sequence of exciton dissociation and charge-separation steps, each described by Marcus theory.[55] He found that photocurrent and efficiency reduce as the energy difference between the donor LUMO and acceptor LUMO (which in his model is directly related to the reorganization energy for charge transfer) increases. The resulting efficiency values are rather larger than for the thermodynamic model for the same $-\Delta G_{CT}$, probably because of a very approximate estimate of V_{oc} and FF .

5. Conclusions

Compared to inorganic p-n junction solar cells the most important factor influencing limiting efficiency is the donor-acceptor heterojunction. To account for this difference both empirical and theoretical models have been developed that describe the limits to photovoltaic energy conversion in organic solar cells.

Empirical models based on the modification of J_{sc} and V_{oc} through the influence of variations in the HOMO and LUMO energies relative to practical devices deliver a maximum practical efficiency of 10–12%, for safe values of the interfacial energy offset of 0.3 to 0.5 eV. That reasoning applied to single-junction devices is compatible with the best devices demonstrated, and is sometimes exceeded, suggesting that some of the assumptions are too pessimistic. A similar reasoning applied to tandem devices leads to expected efficiencies of about 15%, which is still slightly higher than best experimental values to date, showing that tandems can still be improved.

Most theoretical models take the Shockley–Queisser detailed balance approach and apply it to a device characterized by an energy gap E_g but with a finite absorption probability for lower energy photons into interfacial or charge-transfer states. The introduction of such lower energy transitions at low strength tends to reduce the maximum efficiency and enlarge the optimum optical gap to a degree that depends on the energy offset. For a safe value of that offset of 0.3–0.5 eV, 20–24% power conversion efficiency could be expected. The difference of a factor of two compared to the empirical case can largely be explained by differences in ideal and actual internal quantum

efficiency (i.e., 1 vs. 0.65) and fill factor (i.e., 0.85 vs. 0.65). We note that these estimates are very close to the maximum efficiency (25%) of crystalline silicon p-n junction solar cells.

These modified detailed balance models do not, however, allow for the effect of the dynamics of charge removal from the donor:acceptor interface, and their effect on the voltage developed. Some models attempt to combine the kinetics of charge separation and transport with the detailed balance formalism, but none as yet have done that for an idealized molecular system in panchromatic light. Incorporating the kinetics of the interfacial charge-transfer processes will be important in establishing the limiting value of the interfacial energy offset and so pointing to the true limiting efficiency for organic bulk heterojunctions. Before this can be done a validated model for the charge-separation process is needed. Such a model should invoke the dynamics of charge relaxation through the manifold of electronic and vibrational excited states.^[56] High efficiencies are most likely to be available when that relaxation is exceptionally slow (see, for example, work by van Eersel et al.^[26]), or when the cost of charge separation can be reduced for example by increasing the local dielectric permittivity.^[45,57]

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