#### PHYSICAL REVIEW B 83, 195326 (2011)

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# Thermodynamic efficiency limit of excitonic solar cells

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(Received 26 February 2011; revised manuscript received 27 April 2011; published 31 May 2011)

Excitonic solar cells, comprised of materials such as organic semiconductors, inorganic colloidal quantum dots, and carbon nanotubes, are fundamentally different than crystalline, inorganic solar cells in that photogeneration of free charge occurs through intermediate, bound exciton states. Here, we show that the Second Law of Thermodynamics limits the maximum efficiency of excitonic solar cells below the maximum of 31% established by Shockley and Queisser [J. Appl. Phys. **32**, 510 (1961)] for inorganic solar cells (whose exciton-binding energy is small). In the case of ideal heterojunction excitonic cells, the free energy for charge transfer at the interface,  $\Delta G$ , places an additional constraint on the limiting efficiency due to a fundamental increase in the recombination rate, with typical  $-\Delta G$  in the range 0.3 to 0.5 eV decreasing the maximum efficiency to 27% and 22%, respectively.

DOI: 10.1103/PhysRevB.83.195326

PACS number(s): 81.05.Fb, 88.40.jr, 88.40.hj

## I. INTRODUCTION

The Shockley-Queisser (SQ) limit<sup>1</sup> was derived in 1961 for inorganic solar cells using the principle of detailed balance,<sup>2</sup> which requires that the absorbed and emitted radiation fluxes be equal for a cell in thermal equilibrium. The SQ treatment is based on the premise that photon interactions with the cell occur via the generation and recombination of free electron-hole pairs. This is a good assumption for inorganic semiconductor solar cells because photon absorption leads to the direct generation of free carriers or to Wannier-Mott exciton (i.e., coulombically bound electron-hole) states with binding energy  $\langle k_b T$  that readily dissociate to form free carriers at room temperature.<sup>3</sup> (Here,  $k_b$  is Boltzmann's constant and T is the temperature.) As a result, the chemical potential of emitted photons<sup>4</sup> is the same as that of the electron and hole quasi-Fermi level splitting, which for an ideal cell is equal to the voltage difference between its contacts. $^{5-7}$ 

The situation is *fundamentally* different in excitonic (e.g., organic) semiconductors, where the primary excitations are tightly bound Frenkel and charge transfer excitons with binding energies typically ranging from 0.3 up to 1.2 eV, largely a result of the weak intermolecular electronic coupling and low dielectric constant characteristic of such materials.<sup>8–11</sup> In a defect-free material, dissociation of exitons into free carriers depends on factors such as the local electric field, the temperature, and, in the case of heterojunction devices, the free energy for charge transfer at the heterointerface.<sup>8,12–14</sup> Conversely, recombination ultimately proceeds from bound exciton or charge transfer states formed from the encounter of a free electron and hole.<sup>8</sup> Thus, in organic solar cells, photons interact only with the bound exciton population, and hence the luminescent photon chemical potential is that of the exciton gas, not that of the free electron and hole gas. The efficiency limit of an excitonic solar cell consequently depends on both the optical energy gap and the exciton binding energy, in contrast to the SQ limit for inorganic cells, which applies to the special case when exciton binding can be neglected. Here, we use the Second Law of Thermodynamics to calculate the fundamental efficiency limit of solar cells when exciton binding is non-negligible and find that it is in general lower than the SQ result.

In most practical organic solar cells, an exciton must encounter a heterojunction between donor and acceptor layers that provides a decrease in free energy to aid dissociation into free electrons and holes. Unfortunately, the presence of the heterojunction produces an unavoidable energy loss in the system and leads to increased recombination with a consequent decrease in efficiency. We have extended our thermodynamic framework to the case of heterojunction devices and find that the limit for current state-of-the-art organic solar cells lies in the range from 22% to 27%, dependent upon both exciton binding energy and the heterojunction free energy decrease.

#### **II. THEORY**

Excitons are charge neutral and thus must dissociate into free carriers to generate a photocurrent. As in all chemical reactions, the spontaneity of this process must be accompanied by a net decrease in Gibb's free energy, G, the change in which is given by  $^{15,16}$ 

$$dG = \mu dN = dE - TdS + PdV < 0.$$
(1)

Here  $\mu$  is the chemical potential, *N* is the particle number, *E* is the internal energy, *S* is the entropy, *P* is the pressure, and *V* is the volume. Figure 1(a) shows the reaction scheme and relevant energetics for the dissociation/recombination reaction between excitons and free carriers in a generalized excitonic solar cell; the specific case of a heterojunction cell Fig. 1(b) is treated subsequently. Since no mechanical work is done<sup>6</sup> and the net particle flux is equal to the cell current, *I*, we write the Gibb's free energy flux for this reaction as:

$$\Delta \dot{G}_{\rm diss} = (\mu_{\rm eh} - \mu_x)I/q = (E_{\rm eh} - E_x)I/q - T_a\Delta \dot{S}_{\rm diss},$$
(2)

where  $T_a$  is the ambient cell temperature, and the subscripts x and eh refer to excitons and free electron/hole pairs,



FIG. 1. (Color online) (a) Schematic diagrams showing the photovoltaic process for a generalized excitonic solar cell in the radiative limit. The incident solar photon flux  $(\dot{N}_s)$  is fully absorbed by the cell, forming bound exciton states with binding energy  $E_B$ . Radiative exciton recombination produces the luminescent photon flux  $(\dot{N}_r)$  emitted from the cell. Alternatively, excitons may dissociate to form free carriers in a reaction that requires heat input  $(\dot{Q}_{diss})$ to overcome the binding-energy barrier, detracting from the heat produced in the photovoltaic process,  $\dot{Q}_{pv}$ . The current from the liberated electrons ( $e^-$ ) and holes ( $h^+$ ) is given by *I*. (b) The donor-acceptor heterojunction cell operates similarly, except that the free energy change,  $\Delta G_{\rm CT}$ , at the interface induces charge transfer to form lower energy bound polaron pair states that have a binding energy,  $E_{\rm B,CT}$ . Radiative recombination only occurs from polaron pair states since all excitons reach the heterojunction in this ideal cell.

respectively. Since the entropy change is equal to the heat supplied to the reaction, viz.:  $T_a \Delta \dot{S}_{diss} = \dot{Q}_{diss}$ , and since  $E_{eh} - E_x$  is equal to the exciton binding energy,  $E_B$ , we have:

$$\mu_x - \mu_{\rm eh} = -E_B + q \dot{Q}_{\rm diss} / I > 0.$$
 (3)

According to Eq. (3), the reaction will not proceed and the cell will not generate photocurrent if the entropy increase upon dissociation (i.e., heat input to the reaction) does not fully compensate for the exciton binding energy. Whenever this is the case, the exciton chemical potential must increase with respect to that of the free electron/hole pairs to restore photovoltaic operation. In the limit of infinite-charge mobility,  $\mu_{eh}$  is constant throughout the cell and equal to the voltage, *V*, at its terminals. Hence, when  $\dot{Q}_{diss} > (I/q)E_B$ , heat input to the reaction is sufficient to drive exciton dissociation, and the exciton chemical potential can in principle equal the cell voltage, which simply recovers the SQ result.<sup>1,6</sup> However, when  $\dot{Q}_{\rm diss} < (I/q)E_B$ , the heat input is insufficient, and  $\mu_x$ must exceed V by the amount required to compensate for this deficiency.

The luminescent photon flux radiated from the cell is given by:<sup>6</sup>

$$\dot{N}(\mu, E_{\min}, T, f_{\omega}) = \frac{2f_{\omega}}{h^3 c^2} \int_{E_{\min}}^{\infty} \frac{E^2}{e^{(E-\mu)/k_b T} - 1} dE$$
$$= \frac{2f_{\omega}}{h^3 c^2} \int_{E_{\min}}^{\infty} \dot{n} dE, \qquad (4)$$

where *h* is Planck's constant, *c* is the speed of light, and  $f_{\omega}$  is the étendue. The lower integration limit,  $E_{\min}$ , is the minimum exciton absorption energy (corresponding to the optical energy gap) of the cell, and *n* is the spectral photon flux between *E* and *E* + *dE*. The possible increase of  $\mu_x$  relative to *V*, as discussed above, thus increases the radiative recombination rate as compared to a nonexcitonic solar cell and leads to a maximum efficiency that is *lower* than that given by the SQ limit. Physically, the increase in exciton chemical potential reflects a situation in which the exciton density must increase relative to that of free electrons and holes to compensate for unfavorable dissociation conditions (e.g., a large exciton-binding energy and/or small internal electric field) and thereby maintain a total dissociation flux that is capable of supplying the cell photocurrent.

The pivotal question now concerns the amount of heat supplied to the dissociation reaction, namely, does  $\dot{Q}_{diss} < (I/q)E_B$  ever occur? Intuitively, one expects an entropy increase upon dissociation from a bound exciton into more disordered free-carrier states,<sup>17</sup> but whether this is sufficient to sustain the accompanying increase,  $E_B$ , in internal energy is not readily apparent. Nevertheless, this process is ultimately limited by the Second Law of Thermodynamics,<sup>15</sup> which states that the total irreversible change in entropy of system and surroundings for any process must be  $\Delta S_{irr} > 0$ . This is clear upon considering that the supply of heat to dissociate excitons produces free carriers capable of doing work, thus leading to a net reduction in entropy.

The entropy generated in the photovoltaic process has been considered previously<sup>6,7,18</sup> and is given by

$$T_{a}\dot{S}_{pv} = \dot{Q}_{pv} = -IV + (\dot{E}_{s} - T_{a}\dot{S}_{s}) - (\dot{E}_{r} - T_{a}\dot{S}_{r})$$
  
=  $\int_{E_{\min}}^{\infty} [(\mu_{s} - qV)\dot{n}_{s} - (\mu_{x} - QV)\dot{n}_{r} + (\dot{\omega}_{s} - \dot{\omega}_{r})]dE,$   
(5)

where the subscripts *s* and *r* correspond to thermodynamic fluxes of radiation from the sun and cell, respectively. Here we have made use of the room-temperature equivalent chemical potential,<sup>18</sup>  $\mu_s = E(1 - T_a/T_s)$ , for the sun, which is taken to be a blackbody with temperature  $T_s$ . In Eq. (5),  $\dot{\omega}$  is the spectral energy flux of the grand canonical potential, which is

given by<sup>6</sup>

$$\dot{\Omega}(\mu, E_{\min}, T, f_{\omega}) = k_b T \frac{2f_{\omega}}{h^3 c^2} \int_{E_{\min}}^{\infty} (1 - e^{(\mu - E)/k_b T}) E^2 dE$$
$$= k_b T \frac{2f_{\omega}}{h^3 c^2} \int_{E_{\min}}^{\infty} \dot{\omega} dE.$$
(6)

The first line of Eq. (5) shows that the irreversible entropy generation of the cell is equal to the difference between the Helmholtz free-energy flux of incoming solar radiation and that of the outgoing luminescent radiation, less the work done by the cell.<sup>18</sup>

The total entropy production of the cell and its surroundings,  $\dot{S}_{irr}$ , is equal to the entropy generated by the photovoltaic process  $(\dot{S}_{pv})$  less that consumed to dissociate excitons  $(\Delta \dot{S}_{diss})$ . Since this total must be non-negative according to the Second Law of Thermodynamics, we require  $T_a \dot{S}_{irr} = \dot{Q}_{pv} - \dot{Q}_{diss} \ge 0$ . Thus, the *upper* bound for the heat input to dissociation is  $\dot{Q}_{diss} = \dot{Q}_{pv}$ . Since only radiative recombination is allowed,  $I = q(\dot{N}_s - \dot{N}_r)$ , and we use Eqs. (3)–(6) to write

$$E_B \int_{E_{\min}}^{\infty} (\dot{n}_s - \dot{n}_r) dE = \int_{E_{\min}}^{\infty} (\mu_s - qV) \dot{n}_s dE$$
$$- \int_{E_{\min}}^{\infty} (\mu_x - qV) \dot{n}_r dE$$
$$+ \int_{E_{\min}}^{\infty} (\dot{\omega}_s - \dot{\omega}_r) dE \qquad (7)$$

where  $\dot{n}_s$  and  $\dot{\omega}_s$  are evaluated using  $\mu_s$ , and  $\dot{n}_r$  and  $\dot{\omega}_r$  are evaluated using  $\mu_x$ . Equation (7) thus allows for an implicit solution of  $\mu_x$ . Figure 2 shows the calculation for an organic solar cell of exciton energy gap  $E_{\min} = 2$  eV and a binding energy  $E_B = 1.2$  eV. Here, we have taken the étendue as  $f_{\omega} = \pi \sin^2(\theta_s)$  per unit of cell area, where  $\theta_s = 0.267^{\circ}$  is the angle subtended by the solar disk, and a sun and ambient temperature of  $T_s = 5778$  K and  $T_a = 300$  K, respectively.<sup>6</sup>

#### **III. DISCUSSION**

Figure 2(a) shows the two sides of Eq. (7),  $(I/q)E_B$ and  $\dot{Q}_{\rm diss}$ , where the solid line is calculated using the SQ model for a conventional inorganic solar cell, neglecting the exciton dissociation requirement. Between approximately V = 1.4 and 1.6 V, we find  $\dot{Q}_{\text{diss}} < (I/q)E_B$ , and hence no photocurrent could be generated for an excitonic cell in this region. Enforcing thermodynamic consistency via Eq. (7), we obtain the red line, which causes the exciton chemical potential to increase over the cell voltage upper portion of Fig. 2(a) in the "problem" region of 1.4 < V < 1.6 V, such that the total heat generated by the cell just offsets that consumed in the dissociation reaction-hence, the cell is operating reversibly in this region. Solar-cell efficiency is given by  $\eta_P = J_{sc}V_{oc}FF/P_{inc}$ , where FF is the fill factor,  $V_{oc}$  the open circuit voltage,  $I_{sc}$  is the short-circuit current, and  $P_{inc}$  is the incident solar power. As shown in Fig. 2(b), the increase in exciton chemical potential significantly reduces the fill factor of the excitonic current density-voltage characteristic and the efficiency is consequently reduced to  $\eta_P = 19.9\%$  from the SQ limit of 23.1%.



FIG. 2. (Color online) (a) Entropy generation calculated for an excitonic solar cell with optical energy gap  $E_x = 2 \text{ eV}$  and binding energy  $E_B = 1.2 \text{ eV}$ . The black (*V*-shaped) curve represents the heat generated in the photovoltaic process ( $\dot{Q}_{pv} = T_a \dot{S}_{pv}$ ), and the solid blue curve is the heat input required for dissociation  $[(I/q)E_B]$  as calculated from the Shockley-Queisser theory, which neglects the thermodynamics of dissociation and leads to a region of negative total entropy generation for 1.4 < V < 1.6 V, in violation of the Second Law of Thermodynamics. In contrast, the excitonic theory maintains thermodynamic consistency by increasing the exciton chemical potential in this region (upper portion of the plot), which leads to a reduced fill-factor in the current-voltage characteristics shown in (b), and hence to a lower maximum power conversion efficiency ( $\eta_{EX}$ ) than that calculated from the SQ approach ( $\eta_{SQ}$ ).

Figure 3 shows the efficiency of an excitonic solar cell as a function of the optical energy gap for several different excitonbinding energies, which depend strongly on the dielectric constant of the medium and hence is inherently materialsdependent.<sup>11,14</sup> Below a binding energy of approximately 1 eV, there is always sufficient heat generated by the cell to drive exciton dissociation; however, for binding energies >1 eV, the maximum excitonic cell efficiency is decreased from that of



FIG. 3. (Color online) Maximum efficiencies predicted for excitonic solar cells as a function of optical energy gap for several different binding energies ( $E_B$ ) under 1 sun, assuming the sun is a black body with surface temperature  $T_s = 5778$  K. The excitonic limit falls below the SQ limit for  $E_B > 1$  eV.

the SQ cell and the efficiency peak moves toward a smaller energy gap.

According to Fig. 3, many organic semiconductors with  $E_B$  typically <1 eV,<sup>8–11 8–11</sup> could, in principle, reach the SQ limit if the entropy increase,  $T_a \Delta \dot{S}_{pv}$ , is entirely a result of the exciton dissociation process. This ultimately is not realistic since heat disperses randomly among all the atomic or molecular degrees of freedom within the material layer, and not just those local to the exciton. The entropy increase includes these processes, and hence the heat input to the dissociation reaction in bulk material that we have treated so far represents an upper limit.

Although the magnitude of the entropic contribution,  $T_a \Delta S_{\rm diss}$ , for a given dissociation event remains imprecise, it should be significantly less than the exciton-binding energy. This follows from the equilibrium constant between free carriers and excitons, given by  $K_{\text{diss}} = \exp(-\Delta G_{\text{diss}}/k_b T_a)$ , where, according to Eq. (2),  $\Delta G_{\text{diss}} = E_B - T_a \Delta S_{\text{diss}}$ . As photogenerated carrier yields are known to be very low  $(<10^{-3})$  at thermal equilibrium (i.e., under zero applied electric field) for excitonic materials such as, e.g., pristine organic semiconductors,<sup>8</sup> this implies that the entropic component is at least  $\sim 0.15$  eV lower than the exciton-binding energy. The consequence of this is a dramatic reduction in the maximum achievable efficiency that extends to exciton-binding energies much lower than 1 eV. Hence, it is apparent that if the actual entropy contribution to exciton dissociation is isolated from the total photovoltaic entropy that we have employed here, the thermodynamic efficiency limit for an excitonic solar cell will be lower than shown in Fig. 3.

It is precisely because exciton-dissociation yields are low in bulk material that all practical organic solar cells employ a heterojunction (HJ) with an energy offset between the energy levels of the electron donor and acceptor layers that provides the free energy required to obtain efficient dissociation.<sup>13,14,19,20</sup> The situation for an ideal heterojunction organic solar cell is shown in Fig. 1(b), where the incident photon flux is completely absorbed in the bulk layers to form excitons. Ideally, every exciton diffuses to reach the heterojunction, where the available free-energy decrease,  $\Delta G_{\rm CT}$ , induces charge transfer across the interface to form a bound polaron pair (BP) with energy  $E_{\rm BP} = E_x + \Delta G_{\rm CT}$  (note  $\Delta G_{\rm CT} < 0$ ), and a binding energy  $E_{\rm B,CT}$  that is significantly smaller than that of the bulk exciton. These bound pairs must then dissociate to form free carriers. The same thermodynamic arguments used to explain the dissociation reaction above apply here as well, except that  $E_{\rm B,CT}$  is now the relevant binding energy. It is evident from Fig. 3 that BP dissociation will not be thermodynamically limited, at least in the rigorous limit of Eq. (3), since the binding energy of bound pairs is typically <0.5 eV.

In principle, the BP state can also absorb photons, as required by detailed balance and as observed experimentally.<sup>21,22</sup> However, since the BP is an interface state, both its oscillator strength and density (2 dimensions at the interface vs. 3 dimensions in the bulk) are necessarily smaller than that of the bulk materials. As a result, the BP absorption coefficient is typically two to three orders of magnitude lower than that of the bulk exciton transitions.<sup>21,22</sup> Thus, whereas, in the ideal case, the bulk absorbance of the cell,  $\alpha(E)$ , is unity above the exciton energy gap, it is significantly lower in the region between  $E_{BP}$  and  $E_x$ . This is not a physically rigorous limit since, in principle, the cell could be made arbitrarily thick to ensure complete BP absorption. Rather, this is a practical assumption since the absorbance of bound pairs remains negligible in a realistic cell in which the bulk absorbance is large.

From these assumptions, we rewrite the current-voltage characteristic for the HJ cell as

$$I/q = \int_{E_{\rm BP}}^{\infty} \alpha(E) \left[ \dot{n}_s - \dot{n}_r \right] dE$$
  
$$\alpha(E) = \begin{cases} 0 \quad \text{for} \quad E < E_{\rm BP} \\ \alpha_0 \quad \text{for} \quad E_{\rm BP} < E < E_x, \\ 1 \quad \text{for} \quad E_x < E \end{cases}$$
(8)

where we take  $\alpha_0 = 10^{-3}$  as typical of the ratio between bound pair and bulk exciton absorption.<sup>21, 22</sup> Equation (8) differs from the bulk cell through the dependence of  $\alpha(E)$  on energy, which implies that the larger band gap of bulk materials dominates in absorption (at  $E > E_x$ ), whereas the smaller energy gap bound pairs dominate the emission (at  $E > E_{BP}$ ). Consequently, the radiative recombination rate is increased since it occurs via the low-energy bound-pair states. This situation is analogous to an inorganic quantum well solar cell in which the quantum well absorption is negligible, but the presence of the wells leads to increased recombination. We note that the essence of Eq. (8) has been considered previously to account for band gap fluctuations in inorganic cells<sup>23</sup> as well as in the use of a Gaussian distribution for  $\alpha(E)$  to model the absorption of polymer solar cells.<sup>24</sup>

Figure 4 shows the cell efficiency calculated using Eq. (8) at 1 sun with  $T_s = 5778$  K as a function of the exciton opticalenergy gap for several values of the driving force for charge transfer,  $-\Delta G_{\rm CT}$ . The SQ limit is shown for reference in the limit that  $-\Delta G_{\rm CT} \rightarrow 0$ , although this comes at the expense of producing negligible power since there is no driving force for excitons to form bound pairs (and subsequently free carriers) in the first place. As  $-\Delta G_{\rm CT}$  increases, the efficiency peak



FIG. 4. (Color online) Maximum efficiency predicted for an ideal donor-acceptor solar cell as a function of exciton optical energy gap and several values of the free energy for charge transfer at the heterojunction,  $-\Delta G_{CT}$ . Increased recombination from the lower energy bound-pair states leads to reduced efficiency due to the decrease in open-circuit voltage, as shown in the inset for a cell with  $E_x = 1.8$  eV.

decreases monotonically and shifts toward higher exciton band gap. The peak efficiency also depends on BP absorbance,  $\alpha_0$ . Equation (8) shows that the SQ limit is recovered in the limit of either  $\alpha_0 \rightarrow 0$  or  $\alpha_0 \rightarrow 1$ . However,  $\alpha_0$  must be greater than zero due to the existence of the BP state, and its maximum is limited by the low oscillator strength and dimensionality of this state. In the physically relevant range  $10^{-4} < \alpha_0 < 10^{-2}$ , as discussed above, the efficiency decreases for increasing  $\alpha_0$ and ultimately varies by less than 2% from the values shown in Fig. 4. Although the efficiency limits in Fig. 4 are based on values of  $\alpha_0$  obtained from experiment, the conclusion is general: *any* heterojunction organic solar cell in which exciton dissociation results in a lower energy state with incomplete coupling to the radiation field necessarily operates with an efficiency below the SQ limit.

Previous work has empirically established a lower limit of  $-\Delta G_{\rm CT} \sim 0.1$  eV required to obtain efficient charge transfer, however,  $-\Delta G_{\rm CT}$  is nearer to 0.5 eV in current state-of-the-art polymer and small molecule cells as a result of additional requirements such as the need to avoid recombination into low-lying triplet states.<sup>12,19,25,26</sup> Taking  $-\Delta G_{\rm CT}$  typical of most devices in the range 0.3 to 0.5 eV<sup>14,19</sup> thus leads to a maximum efficiency ranging from approximately 27% to 22%, corresponding to energy gaps of 1.35 eV and 1.5 eV, respectively. Note that this result does not limit the efficiency of tandem (or multijunction) cells, but only the separate elements that comprise such a device.

The inset of Fig. 4 shows that the efficiency drop is entirely due to a decrease in cell open-circuit voltage. Since the small BP binding energy does not limit dissociation,  $V = \mu_{\rm BP}$ , and hence when  $qV \rightarrow E_{\rm BP}$ , the recombination term diverges. In this case, the maximum possible open-circuit voltage is  $qV_{\rm oc}^{\rm max} = E_{\rm BP}$ , which occurs in the limit of high-incident intensity (e.g., optical concentration) or as  $T_a \rightarrow 0.^{14,21,27}$  This limit was previously derived for HJ cells from considerations of device physics.<sup>27</sup>

Including the effects of nonradiative processes, which often dominate recombination in practical organic solar cells, further suppresses the open-circuit voltage from the limiting case treated here. It is worth noting, however, that decreasing the electronic interaction between the HJ constituent materials reduces both the oscillator strength of the bound pair (e.g., its coupling to the radiation field via  $\alpha_0$ ) and the orbital overlap that facilitates nonradiative decay, thus increasing  $V_{oc}$ . This has recently been observed in experiments where the degree of  $\pi$ - $\pi$  intermolecular orbital overlap between donor and acceptor molecules was varied,<sup>28</sup> in support of this approach as a useful design strategy for increasing the efficiency of HJ organic solar cells.

#### **IV. CONCLUSIONS**

In summary, we have shown that the solar power conversion efficiencies of excitonic solar cells with binding energy >1 eV are fundamentally lower than that established by Shockley and Queisser for inorganic solar cells. In particular, a large exciton binding energy requires the exciton chemical potential to exceed that of the free carrier pairs, leading to increased radiative recombination and reduced efficiency. We have presented a rigorous approach for evaluating the efficiency limit of excitonic solar cells based on the Second Law of Thermodynamics that recovers the result of Shockley and Queisser in the limit of zero exciton-binding energy.

We have also investigated the case of donor-acceptor heterojunction excitonic solar cells, where all excitons undergo charge transfer at the interface and radiative recombination is from bound pair states at the HJ. By virtue of their lower energy, BPs increase the recombination rate and hence lower the maximum attainable efficiency. For a minimum driving force  $-\Delta G_{\rm CT} \sim 0.1$  eV necessary to obtain efficient charge transfer in organic heterojunction solar cells, the SQ limit is theoretically attainable, whereas for current state-of-the-art donoracceptor material combinations with  $-\Delta G_C T \sim 0.5$  eV, the limit is only 22%. These results generalize the long-standing Shockley-Queisser limit to include solar cells in which exciton binding is non-negligible, and thus provide a firm theoretical framework to evaluate a rapidly growing class of photovoltaics made of materials such as organic semiconductors, carbon nanotubes, inorganic colloidal quantum dots, and hybrid composites.

### ACKNOWLEDGMENTS

This work was supported by Department of Energy, Office of Basic Energy Sciences, Energy Frontier Research Centers: The Center for Solar and Thermal Energy Conversion at the University of Michigan (Award DE-SC0000957, which supported the analysis work of S.R.F.) and the Argonne-Northwestern Solar Energy Research (ANSER) Center (Award No. DE-SC0001059, M.R.W., G.P.W., N.C.G.). The Center for Nanoscale Materials is funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-06CH11357 (N.C.G.). S.R.F. also thanks the Air Force Office of Scientific Research and the collaborative R&D program with technology advanced country [2009-advanced-B-015] by the Ministry of Knowledge and Economy of Korea for support of experimental efforts that supported the analysis of these molecular systems.

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