Supporting Information for "Design Principles for Block Polymer Organic Double Heterojunction Solar Cells"

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Detailed description of calculation: ideal double heterojunction solar cells

Solar cell current-voltage characteristics were calculated numerically with the aid of Matlab software. Three main components to the current are as follows: current from charge photogeneration, $J_G(V)$, the dark current of the solar cell, $J_d(V)$, and the tunnelling current across the bridge, $J_t(V)$.

(1s) $$J(V) = -J_G(V) + J_d(V) + J_t(V)$$

In the calculation of DBA solar cell characteristics, the tunneling current across the bridge layer from the acceptor to the donor was calculated as a combination of tunneling through a trapezoidal barrier $J_{tb}^{A}(V)$ and Fowler-Nordheim tunneling, $J_{FN}^{A}(V)$.[1] The symmetric processes, which can be thought of a hole transfer from the donor to the acceptor, was also calculated ($J_{tb}^{D}(V)$, $J_{tb}^{D}(V)$).

(2s) $$J_t(V) = J_{tb}^{A}(V) + J_{tb}^{D}(V) + J_{FN}^{A}(V) + J_{FN}^{D}(V)$$

The tunneling process $J_{tb}^{A}(V)$ describes an electron in the LUMO level of the acceptor, $EA_{S0}(A)$, that tunnels across a bridge of thickness l_B into the HOMO level of the donor, $IP_{S0}(D)$. Because the process is inelastic and thus quite complicated, it was modeled as occurring in two simplified steps. First, the electron loses the necessary energy with unit probability and is assumed to tunnel elastically through the bridge using the following expression for the barrier height: $\phi_A = EA_{S0}(B) - IP_{S0}(D)$. The magnitude of the tunneling current was estimated by scaling the conductance to the conductance quantum $\left(\frac{2e^2}{h}\right)$ multiplied by the population of excess electrons in state $EA_{S0}(A)$. The latter was calculated by a voltage dependent Fermi factor $f(V,T)$ multiplied by an estimate of the areal density of interfacial states ($N = 10^{19}\ m^{-2}$).

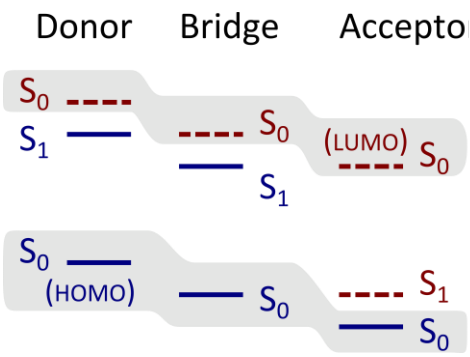

Figure S1. Energy levels of DBA solar cell. Electron affinities are given in red, ionization energies given in blue. States which do not actively participate in the charge generation process have been omitted for clarity.

(3s) $$J_{tb}^{A}(V) = \frac{2\,e^2}{h} N f_A(V,T)\, V\, \exp\left(-\frac{4\pi\, l_B \sqrt{2\,m\,\phi_A}}{h}\right)$$

The appropriate expression for Folwer-Nordheim tunneling uses identical parameters and is given below.[2] It is important to note that for the bridge length used in the calculations ($l_B = 10^{-8}\ m$) both tunneling contributions to the cell current were negligible.

(4s) $$J_{FN}^{A}(V) = \frac{e^2}{4h^2 \phi_A {l_B}^2} V^2\, N f_A(V,T)\, \exp\left(-\frac{8\pi\, l_B \sqrt{2\,m\,{\phi_A}^3}}{3ehV}\right)$$

Calculations for the complimentary tunneling processes which move holes from $IP_{S0}(D)$ to $EA_{S0}(A)$ used analogous expressions to Eq. 3s and Eq. 4s, with $\phi_D = EA_{S0}(A) - IP_{S0}(B)$.

The statistical population of excess carriers, $f(V,T)$, was determined by the energetic difference between the transport level and the quasi Fermi level.

$$(5s) \qquad f_A(V,T) = \left(1 + \exp\left[\frac{E_F - EA_{S0}^{A} - eV}{k_B T}\right]\right)^{-1}$$

The Fermi level without incident light or applied voltage was taken to be the mid-gap of the bridge molecule, specifically the transport gap, $EA_{S0}(B) - IP_{S0}(B)$. The optical gap is smaller than the transport gap by the exciton binding energy, E_B.

$$(6s) \qquad E_F = IP_{S0}(B) + \tfrac{1}{2}\big(EA_{S0}(B) - IP_{S0}(B)\big) = IP_{S0}(B) + \tfrac{1}{2}(E_G(B) + E_B)$$

As stated in the text, the energetic alignment at the bridge was taken to make electron and transfer a resonant process. In symbols $IP_{S1}(D) = EA_{S0}(B)$ and $IP_{S0}(B) = EA_{S1}(A)$. Eq. 6s can be used to fix the position of every energy level given an exciton binding energy (E_B) and the optical gap of each material. The exciton binding energy was identical for every material in any particular calculation, but was allowed to vary from calculation to calculation as noted.

The diode current across the bridge $J_{diode}(V)$ was calculated using the equation given below:

$$(7s) \qquad J_d(V) = e\,(1-R) J_0 \left(\exp\left[\frac{eV}{k_B T}\right] - 1\right)$$

With $R = 0.05$ being the reflectivity of the cell and J_0 is related to the blackbody radiation spectrum of the material responsible for the diode characteristics of the cell[3] which is the bridge in this case.

$$(8s) \qquad J_0 = \int_{E_G(B)}^{\infty} b_{ambient}(E)\, dE$$

With $E_G(B)$ being the optical gap of the bridge and $b_{ambient}(E)$ blackbody radiation spectrum at the cell temperature.

The current generation by the cell under illumination $J_G(V)$ was calculated as the fraction of the solar spectrum absorbed by the donor subtracted by its blackbody emission spectrum. The bridge material is assumed to be of negligible thickness to contribute meaningfully to light absorption of the cell. The cell is assumed to absorb all light with energy greater than or equal to the optical gap of the component with the narrowest optical gap. As will be discussed later, this model for the optical properties of the system has important consequences on the optimal donor and acceptor energy gap. Calculations for light absorption contain a small amount of reflection ($R = 0.05$), and it is assumed that every absorbed photon produces separated charges with unit efficiency. If the donor is the material with the lowest optical gap, the generation current in the cell is written as follows:

$$(9s) \quad J_G(V) = e(1-R)\, f_D(V/2,T) \int_{E_G(D)}^{\infty} b_{sun}(E) - b_{ambient}(E)\, dE$$

As stated in the main text, the donor material is unable to absorb light when it is charged. As such, current generation drops precipitously as $f(V,T)$ increases as a result of applied voltage. The cell voltage is assumed to influence the donor and the acceptor equally, thus the quasi Fermi level shift in any one of the materials will be half of the total, requiring that the voltage is divided by two in eq. 9s.

The efficiency of the solar cell was calculated directly from the cell current at the maximum power point, V_{max}, and divided by integrated solar power.

$$(10s) \qquad \eta = \frac{J(V_{max})\, V_{max}}{P_{sun}}$$

Discussion: V_{OC} in idealized double heterojunction cells

The open circuit voltage (V_{OC}) of a solar cell occurs when recombination currents exactly balance the charge generation current. In the idealized double heterojunction solar cells describe here, the recombination currents arise from ideal diode behaviour and tunnelling currents through the bridge.

(11s) $$J_G(V_{OC}) = J_d(V_{OC}) + J_t(V_{OC})$$

In the main text, it was shown that tunnelling currents for bridge materials greater than 5 nm are negligible. If we ignore tunneling currents and consider the case where the absorption of the cell is governed by the optical gap of the donor, we can write an expression for V_{OC}.

(12s) $$\left(1 + \exp\left[\frac{-E_G(B)+2\Delta E+eV_{OC}}{2k_BT}\right]\right)\left(\exp\left[\frac{eV_{OC}}{k_BT}\right] - 1\right) = \frac{\int_{E_G(D)}^{\infty} b_{sun}(E) - b_{ambient}(E)\, dE}{\int_{E_G(B)}^{\infty} b_{ambient}(E)\, dE}$$

Where $\Delta E = IP_{SO}(D) - IP_{SO}(B)$ is the energy offset between the HOMO of the donor and the bridge. Eq. 12s can be used to discuss some of the trade-offs which affect V_{OC}. Increasing the magnitude of the right hand side of eq. 12s increases V_{OC}. This favours bridge materials with a large optical gap, and donor materials with a small optical gap. The left hand side of eq. 12 cannot be simply factored, but inspection demonstrates that larger V_{OC} is obtained for bridge materials with a large optical gap and a small energy offset between the bridge and the donor. The conflict which prevents arbitrarily large V_{OC} from being obtained with low donor optical gap is that the optical gap of the donor cannot be made small and the optical gap of the bridge be made large without introducing a large energy offset at the donor-bridge interface. Physically, this consideration is the result of the decreased photocurrent at large applied voltages; a large energy offset at the donor-bridge interface and a donor with a small gap will quickly become saturated with charge as the applied potential pushes the quasi-Fermi level into the HOMO of the donor.

Fig. S2 shows the V_{OC} for ideal double heterojunction solar cells with differing exciton binding energies. The important aspect to note is the robustness of the double heterojunction cells to maintain a high voltage in the presence of large exciton binding energy, a factor which strongly contrasts with standard DA bulk heterojunction cells.

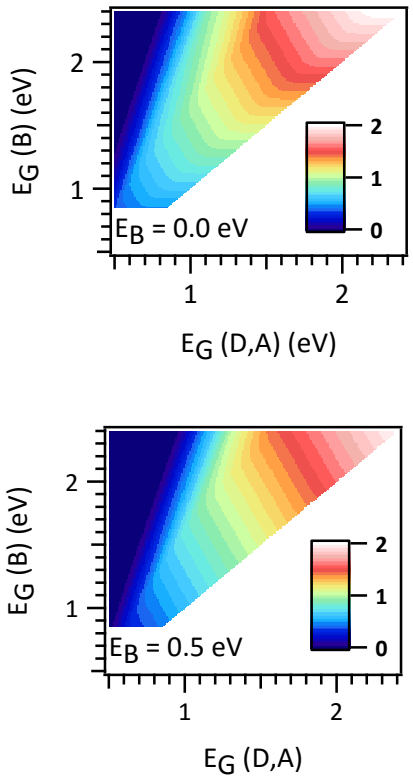

Fig. S2 V_{OC} for ideal double heterojunction solar cells for two values of exciton binding energy

Detailed description of calculation: DA solar cells

The performance characteristics of donor-acceptor (DA) solar cells were calculated using the same equations described above with several caveats. First, tunneling contributions to the current were not included. Second, the magnitude of the diode current is governed by the optical gap of the charge transfer exciton $E_G(CT)$.

$$\text{(10s)} \quad J_0 = \int_{E_G(CT)}^{\infty} b_{ambient}(E)\, dE$$

The Fermi level was set with reference to the donor and acceptor as in Eq. 6s. The relative positions of the energy levels was set using the following relationships:

$$\text{(11s)}\ IP_{S0}(D) = EA_{S1}(CT) - E_B$$

$$\text{(12s)}\ EA_{S0}(A) = IP_{S1}(CT) + E_B$$

The structure of the energy levels used in the calculation is shown in the Fig S2, which has been reproduced from the main text for the sake of clarity.

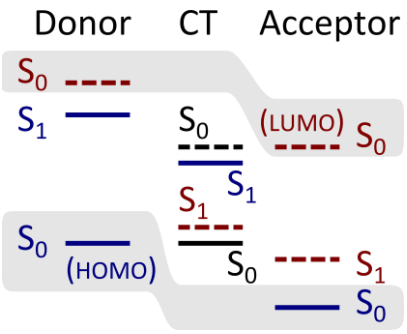

Figure S3. Energy level positions used in the calculation of DA solar cells. Electron affinities are given in red, ionization energies given in blue. Please note that the S_0 states of the CT exciton are theoretical constructs used to aid in the absolute placement of the S_1 levels.

Discussion: V_{OC} in idealized DA solar cells

We calculated the V_{OC} for DA solar cells using the formalism described above, and the results are presented in fig. 4s for two different values of the exciton binding energy. As in the main body of the text, the meaning of the "bridge optical gap" describes the energy offset at the DA interface, with the energy offset being given as $\Delta E = E_G(B) - E_G(D,A)$, where the optical gap of the donor and acceptor are assumed to be identical. The most important observation of fig. 4s is the senstivity of V_{OC} to exciton binding energy. The lack of this sensitivity is the primary benefit to the double heterojunction structure.

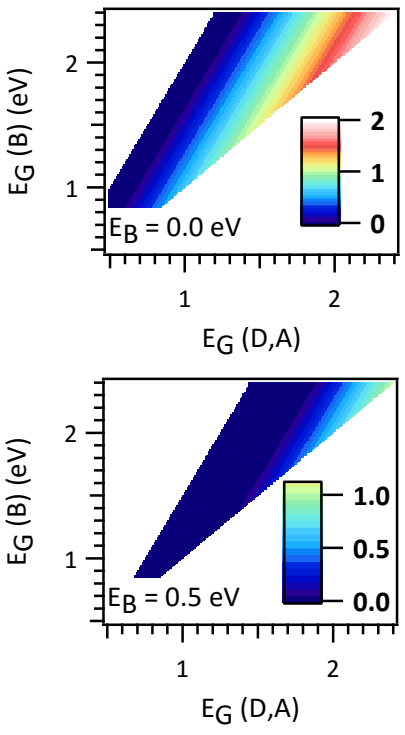

Fig. S4 V_{OC} for standard organic DA solar cells for different values of exciton binding energy.

References

(1) Ho Choi, S.; Kim, B.; Frisbie, C. D. Electrical Resistance of Long Conjugated Molecular Wires. *Science* **2008**, *320*, 1482-1486.

(2) Sze, S. M.; Ng, K. K. *Physics of Semiconductor Devices*; Wiley, 2006.

(3) Nelson, J. *The Physics of Solar Cells*; Imperial College Press, 2003.