Cryscade Solar Ltd.

Efficiency Limit 49% for DBA Photovoltaic Cells

Cryscade Solar Whitepaper Version 2.0

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INTRODUCTION

The most efficient conventional solar cells are based on monocrystalline silicon pn-junction architectures. This technology, introduced in the middle of the past century, has proven to be a compact and sufficiently powerful source of energy for spacecrafts, remote locations, pocket electronic applications where cost is not considered as critical as function. However, even though semiconductor technology has progressed to a mature state, solar energy still remains not viable for most commercial applications such as residential power without substantial subsidies. To reach the full commercial potential of photovoltaics, the industry needs a means to reduce panel manufacturing costs while increasing efficiencies even beyond monocrystalline silicon performance to reach solar's full commercial potential.

To achieve higher efficiencies, solar cell designs must address two key aspects. The first is converting effective light absorption into independent, free charge carriers using a means that can separate these charges and avoid recombination. The second aspect is to provide an efficient transport of charges to respective electrodes.

All existing commercial solar energy harvesting technology today uses materials that absorb light and generate charges in the bulk of material that wander randomly through a 3D lattice until they hit electrode and contribute to the current that flows through the module. The problem is that when charges are wandering they can meet each other and recombine, annihilating each other into zero charge and creating heat. To achieve higher efficiency, this needs to be prevented.

The ideal solution would be to direct separated charges to different compartments that can prevent charge annihilation for a time period much longer then is required for charges to reach the appropriate electrodes and fully contribute to the generated current in the module.

Another problem is that charge transport to electrode is slow in 3D lattice because the stochastic wandering path takes more time, increasing the probability of recombination and disappearing. Charges travel faster if the path is well defined as 1D line with no wandering possible.

Cryscade proprietary Donor-Bridge-Acceptor (DBA) material self-assembles into monocrystalline homeotropic (vertical) alignment in such a way that allows control over recombination and creates 1D path to electrodes for charges. As this paper explains, such a novel structure provides a theoretical efficiency limit of 49%, which is significantly higher than the theoretical limits for monocrystalline traditional semiconductor cells like Si (31%), CdTl, etc.

MODEL DESCRIPTION

Cryscade Solar Ltd. is developing proprietary technology for *DBA molecular devices* which allows independent control of all key solar cells' parameters:.

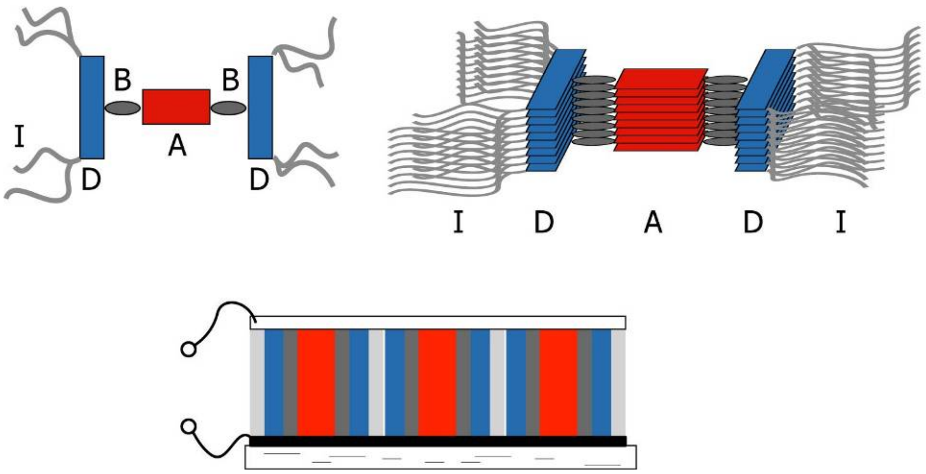


Fig. 1

In a single DBA molecule the electron donor (D) and electron acceptor (A) components are connected by a 'bridge' (B). This approach introduces greater flexibility into photovoltaic device architecture through molecular design and manufacturing of materials by methods of molecular engineering. We dubbed DBA molecule as n-peller.

The bridge B spatially separates D and A. This allows charge separation at the peak of energy level in the molecule immediately after light absorption and places charges in two different locations: A-acceptor holds electron and D-donor lacks electron so it holds a positive charge ("hole"). Charges that are held in these locations have difficulties to meet each other and annihilate. The time during which carriers stay separated before recombining is the separated carrier's lifetime. By structuring B-bridge properly, these carriers can be kept separated well beyond the time that is required for the charge to reach the intended electrode.

The bridge is an adjustable global variable in the molecular design since it controls the time during which photogenerated carriers stay separated. For different DBA molecular systems this time may vary from picoseconds to milliseconds.

The next important element of the DBA structure is ordering the DBA molecules in such a way that the Acceptors and Donors are connected with their respective electrodes. The DBA molecules are modified (see figure 1) so that they self-assemble in solution in corresponding stacks. When coated, these stacks form into crystalline structures that allow electrons to freely travel through the A-stack columns and "holes" through the D-stack columns safely, without danger of annihilation, traveling the shortest (1D) path to the electrodes. Selective electrodes are used so that each charge go to their appropriate electrode and do not recombine in the cell.

Cryscade's vertically structured solar cells are consistent with the concept of the 'ideal' photovoltaic structure. This structure is expected to ensure high conversion efficiency because:

1. Absorption of the material may be adjusted to fit sun spectrum by proper component selection for Donors and Acceptors
2. Charge separation takes place at every point of the material
3. Lifetime of separated carriers can be optimized
4. One-dimensional segregated charge transport reduces recombination

These points will be discussed further in the following sections.

EFFICIENCY DISCUSSION

A photovoltaic device converts the energy of incident light into electricity. The general working scenario is summarized as following:

> Light is absorbed by active material → Molecules of the material are excited → Molecular excitation results in a charge separation → Separated carriers travel through the substance → Carriers are collected at electrodes forming current

There are three stages of energy conversion in a solar cell that determine an efficiency of solar cell operation and corresponding parameters:

- ✓ light absorption: molecular extinction ε
- ✓ charge separation: probability of separation *p* (quantum efficiency) and lifetime τ
- ✓ charge transport: mobility μ

All existing solar cells architectures try to optimize these variables to achieve higher efficiency operation.

1.1. Absorption

The variable ε defines how many incident photons are absorbed in the bulk of material and may potentially be converted into charges. Proper selection of D and A components of the DBA molecule allows to create optimal absorption – the best possible absorption.

1.2. Charge separation

Probability of charge separation depends only on molecular structure and as reported in literature may achieve 100% [1–5]. For DBA it is an important fact that charge separation occurs at every molecule of the material. This means the probability of charge separation is a constant function of space coordinates, whereas in Si pn-junctions it exponentially decays with the distance from junction (Fig. 2).

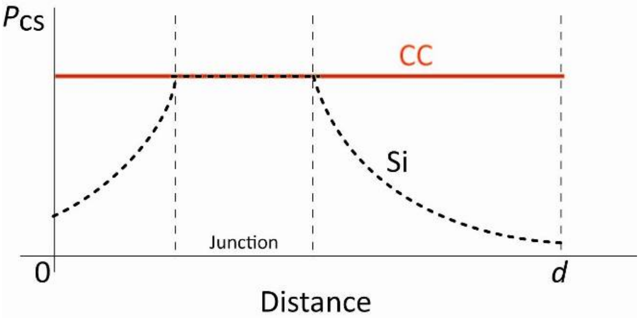


Fig. 2

Separated carriers lifetime is a function of molecular structure and may be tuned in a wide region: from picoseconds to micro- and even milliseconds [6].

1.3. Transport

To construct the described structure, flat polycyclic compounds for D and A moieties are used. They undergo ππ-stacking and self-assemble into electron and hole-conducting columns or 'wires' of A and D molecular parts. Molecular stacks with conjugated π system support effective charge transport demonstrating mobilities exceeding those of amorphous silicon and other thin film semiconductors. Separated charges are free to travel along the molecular stacks with mobilities of up to 1 cm^2/Vs [7–9,10]. Efficient transport takes place during the lifetime of separated carriers, τ. The speed of the carrier's movement is defined by mobility μ and thickness of the active layer, which means the path length to the electrode also defines the total absorption. Lifetime should be long enough to allow the charge with given speed to reach electrode across given path length. Design of molecule allows this to be made as long as it is required.

1.4. Recombination rate or lifetime

With proper molecule design charge lifetime can be controlled so that all charges will reach electrode in their lifetime. This means that potentially all absorbed light can go into charges and all charges go into electrical current.

For photovoltaics, this is referred to as an ideal “fill-factor is equal to 1.0”. Because nothing is perfect and fill-factor would not be 1.0 but if it is close enough then we can tolerate.

Controlling recombination rates shifts the importance of parameters in cell design to focusing on light absorption. If all charges that are created in the bulk of material are kept in existence until they reach electrode, then the only thing that matters is how much light can be captured and converted into charge. For DBA systems, dye materials are ideal for this function. Since there are many existing industrial (stable) dyes available, selecting those that provide broad spectrum coverage can be used to optimize absorbtion and maximize efficiency.

THEORETICAL LIMIT OF EFFICIENCY

1.5. Absorption

In contrast to photovoltaic counterparts, DBA molecular system may incorporate multiple dyes in order to optimally address the sun spectrum.

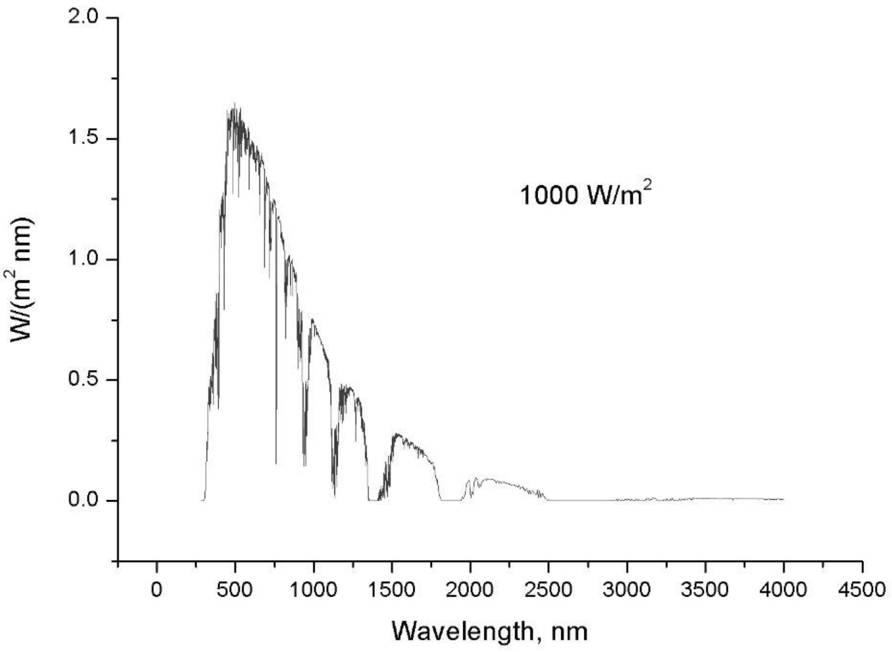


Fig. 3

Using sun spectrum $f(\lambda)$ presented in Fig. 3, we can numerically estimate the maximum electric power that can be produced by the device. Assuming that dyes can be selected that absorb all the photons having wavelengths between λ_0 and λ_g and all photons/light is converted into electric current with 100% quantum efficiency, then the current density at 100% quantum efficiency is

$$j(\lambda_0,\lambda_\mathrm{g}) = \frac{e}{hc}\int_{\lambda_0}^{\lambda_\mathrm{g}} f(\lambda)\lambda\, d\lambda$$

where *h* is Planck's constant, *c* is speed of light.

Open circuit voltage is connected with a given bandgap as

$$V_\mathrm{oc} = E(\lambda_\mathrm{g}) = \frac{hc}{e\lambda_\mathrm{g}}$$

Then for the electric power we derive the following expression

$$W(\lambda_g) = jV_{oc} = \frac{1}{\lambda_g}\int_{\lambda_0}^{\lambda_g} f(\lambda)\lambda\, d\lambda$$

The graph of the function $W(\lambda_g)$ in the full range of wavelengths is presented in Fig. 4. There is a maximum as high as 490 W/m^2 occurring at 1108 nm (or 1.12 eV). This is known as Shockley and Queisser optimum. The overall incident optical power is 1000 W/m^2, so we obtain the estimation of maximal conversion efficiency as 49%.

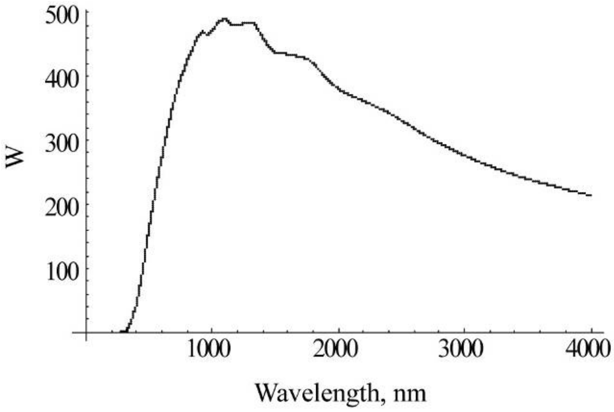


Fig. 4

The more realistic case is when the harvesting of short wavelengths is affected by absorption of glass substrates or packaging material. This leads to red shifting of λ_0. Figures in the table below show the potential efficiency in this case:

Blue edge of absorption (λ_0), nm	Optimal bandgap, eV	Red edge of absorption (λ_g), nm	Max efficiency, %
300	1.12	1100	49
400	1.12	1100	48
500	0.95	1300	42
600	0.93	1333	36
700	0.93	1333	29
800	0.92	1350	23

The table shows that proper adjustment of absorption spectrum of the material by choosing appropriate dyes for the roles of donors and acceptors expands the limits of conversion efficiency of DBA solar cells up to 49%.

1.6. Stack's work

How many charges can travel along one molecular stack simultaneously? The best case is when average raw power of sunshine per SQM of flat ground is 1000 W/m^2. Having *f*(λ), we know the energy in a spectral unit is $f(\lambda)d\lambda$ (Fig. 3). Integrating over the sun's spectrum we obtain flux of $4 \cdot 10^{17}$ photons/cm^2 s.

The consequence of this is that in case of a solar cell harvesting all the incident photons with 100% quantum efficiency (one electron per one photon), the electric current would be $4 \cdot 10^{17} \cdot 1.6 \cdot 10^{-19} =$ 64 mA/cm^2.

Assuming that the molecules have dimensions of 4 x 4 nm^2 and interplanar separation within a stack is 0.35 nm one may find how many molecules the photovoltaic film of, say 300 nm thickness consists of:

$$1 \times 1 \times 300\ 10^{-7}\ \text{cm}^3 / 4\ 10^{-7} \times 4\ 10^{-7} \times 0.35\ 10^{-7}\ \text{cm}^3 = 5.4 \cdot 10^{15}\ \text{molecules/cm}^2.$$

It makes about 100 photons/molecule per second. If the film's thickness is 500 nm there is approximately 1500 molecules in a stack. So we have 10^5 photon/stack per second or 1 photon/stack per 10 mks. This means that an electron-hole pair appears in a given stack every 10 mks. The separation carriers lifetime and therefore the carriers transport time is considered acceptable if in 100's of ns, which is much less than their born rate. Based on this analysis, we may conclude that most of the time the charge transporting stacks are empty and every light absorption event is separated from another which makes modeling simpler.

1.7. Transport

Compared to doped inorganic semiconductors, DBA semiconductors have very few mobile charges available. Extra mobile charges appear due to illumination only. As it follows from solar cell design, the charge separation process takes place in the direction perpendicular to the direction of charge transport.

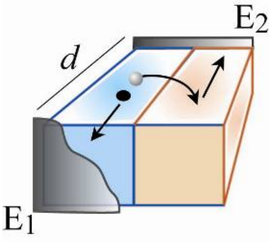


Fig. 5

Being separated, charges then travel in uniform crystalline periodic material. The material may be described as photo-conducting insulator having IV-curve in accordance with Ohm's law:

$$j = en\mu E = en\mu \frac{V - V_{\text{bi}}}{d}$$

where μ is the carriers' mobility, n is the carriers' generation rate, d is the film's thickness, V is the applied voltage, V_{bi} is the built-in field.

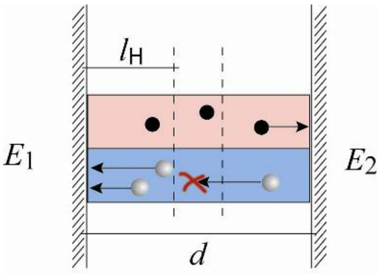


Fig. 6

Harvesting length is the maximal distance at which an electron has a chance to reach an electrode. While lower than d, it linearly depends on potential difference between electrodes:

$$l_{\mathrm{H}} = v\tau = \mu\tau \frac{V - V_{\mathrm{oc}}}{d}$$

Hence the characteristic voltage after which the current becomes constant may be expressed from the following relationship:

$$\mu\tau \frac{V - V_{\mathrm{oc}}}{d} = d$$

and

$$\delta = V - V_{\mathrm{oc}} = \frac{d^2}{\mu\tau}$$

IV curve of a solar cell with ideal structure under illumination is presented in Fig. 7.

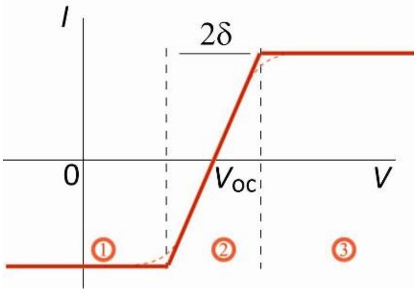


Fig. 7

Here are three regions discussed above: 1 and 3 are high voltage regions where all generated carriers are collected; 2 is a low voltage region where a portion of carriers dies on the route to electrodes.

Putting here the following assumptions: μ = 0.1 cm^2/Vs, τ = 500 ns, d = 500 nm to δ = 5then δ = 2 · 10^{-2} V. Recalling that V_{oc} is about 1 V we conclude that IV curve is square-like.

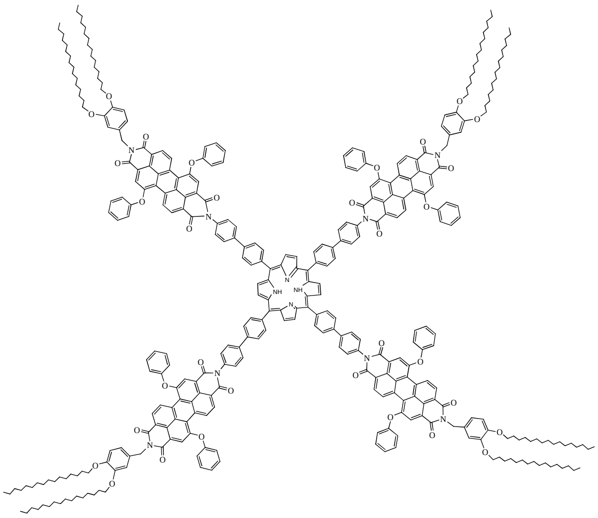
Simple calculations show that in this case the fill factor may be estimated as

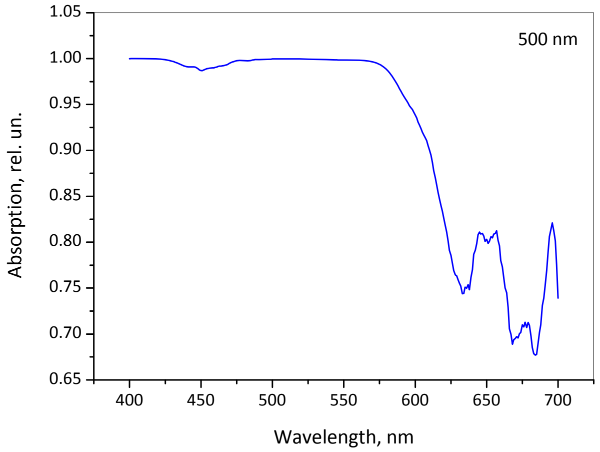
$$FF = \frac{V_{\mathrm{oc}} - \delta}{V_{\mathrm{oc}} + \delta} \approx 1$$

Is diffusion valuable in the geometry? Field drift must dominate diffusion, in other words drift length $l_{\mathrm{dr}} = \mu\tau \frac{V}{d}$ must be longer than diffusion one, $l_{\mathrm{df}} = \sqrt{\mu\tau \frac{kT}{e}}$. In our numbers $\frac{V}{d}$ is 2 · 10^4 V/cm, but $\sqrt{\frac{kT}{e}}$ at room temperature is about $\sqrt{\frac{kT}{e}} \approx 0.17$ $\mathrm{V}^{1/2}$. Comparing l_{dr} and l_{df} we come to the limitation of $\mu\tau > 10^{-10}$. Having μ = 0.1 cm^2/Vs the lifetime τ must be no less than 1 ns, which is easily achievable. The advantage here is that we can trade between τ and μ in order to improve the performance of a solar cell: lack of mobility may be compensated by longer lifetime and vice versa.

EXAMPLE

Let’s take for example the following n-peller:





Polyaromatic core here consists of porphyrin (acting as Donor) connected with four perylene petals (acting as Acceptors) through biphenyl bridge. Similar molecules were reported to provide 100% charge separation upon photoexcitation [1] and aggregate into columnar structures. In case these molecules are crystallized in a perfect homeotropic structure, the 500 nm thick film would provide conversion efficiency about 30%.

This example demonstrates that even this DBA material with not well adjusted absorption and too wide bandgap (2 eV) promises the same efficiency limit as Si ones do.

CONCLUSION

We assumed here that lifetime is under full control and is sufficient for our purposes. We assume that crystal stack is of good quality or good enough for this lifetime to be satisfactory long.

Under these assumptions DBA solar cell and ordinary solar cells are about 18% different in their upper efficiency limits. Best crystalline Si solar cells have 31% efficiency limit and best crystalline DBA cells have 49% efficiency limit.

DBA material is inexpensive and manufacturing process uses low cost coating.

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