

# Novel Monocrystalline Photovoltaic Material with Controllable Carrier Lifetime

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## Abstract

We developed a new class of photovoltaic Donor-Bridge-Acceptor (DBA) materials for solar cells that enable molecular level charge separation and segregated transport of charges to appropriate electrodes. Our technology allows independent and precise control of the key solar cell parameters such as light absorption band, life time of separated carriers and mobility of charge carriers, as well as material processability. Due to special molecular structure, quantum efficiency of the charge separation approaches 100%. Along with the molecular design, we have developed a deposition technique which forms single-crystalline homeotropically-aligned photovoltaic DBA thin films. To the best of our knowledge, this represents the first design of electrode-to-electrode monocrystalline photovoltaic material with controllable lifetime of carriers. Homeotropic alignment of donors (p-type material pipe) and acceptors (n-type material pipe) provide potentially the most efficient structure for light harvesting.

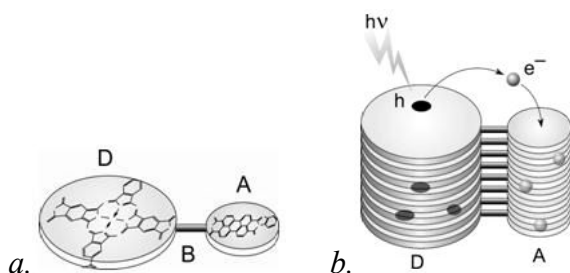
## 1. Introduction

Development of high performance solar cells forces a compromise between the requirements of high charge carriers' mobility and large surface contact area for p- and n-type semiconductors. On one hand it would be desirable to provide conditions favorable for splitting of excitons formed at any point of photovoltaic layer as a result of light absorption. But on the other hand, separated carriers need to have isolated and high-mobility pathways to electrodes. Various "ideal" bulk heterojunction solar cell structures have been proposed to further optimize these parameters where n- and p-type rods, which are connected to n- and p-type electrodes respectively, are interlocked in sub-nanometer proximity to each other.

We made this structure instead on the molecular level by stacking donor-bridge-acceptor (DBA) structures in congruent homeotropic (vertical stacks of donors and correspondingly of acceptors) fashion.

## 2. DBA molecular system

We recognized that monocrystalline DBA stacks of molecules are an ideal solution for photovoltaic systems efficiency. The DBAs consist of Donor (capable to donate an electron) and Acceptor (capable to receive an electron) moieties connected with a Bridge designed to promote a one-way electron transfer from D to A (Fig. 1a) or, in other words, control lifetime of separated charges.



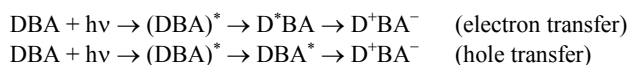
**Figure 1. DBA molecular design (a) and columnar supramolecules (b)**

The bridge spatially separates D from A and decreases the probability of recombination. Such a system interferes with the electronic coupling between D and A, controlling the way the electron transfer occurs either by tunneling or by hopping. This allows the system to essentially control the lifetime of carriers.

Donor and Acceptor components by themselves (as single molecules) have unique HOMO and LUMO (HOMO<sub>D</sub> and LUMO<sub>D</sub> for Donor and HOMO<sub>A</sub> and LUMO<sub>A</sub> for Acceptor). When molecular orbitals of Donor and Acceptor fuse it results in their mutual disturbance and the molecular system should be treated as a single molecule. This molecule has HOMO which is nearly equal to HOMO<sub>D</sub>, whereas LUMO is close to LUMO<sub>A</sub>. When we examined the electron density in HOMO/LUMO states of such a DBA system, we found that at HOMO most of electron density is localized on D, but at LUMO it is mostly localized on A. It appears that phonon-assisted "diagonal" transfer of electron density from Donor to Acceptor takes place upon excitation: DBA + hv → (DBA)\* → D<sup>+</sup>BA<sup>-</sup>. Charge separation occurs at the event of excitation, which is beneficial for capturing energy and separating charges for a usefully long time.

In addition, since DBA molecules are closely packed, into stacks with intermolecular separation of about 3.4 Å (Fig. 1b), than overlapping of π-electrons of adjacent π-conjugated molecular planes results in the formation of π-electron system distributed along stacks. This manifests itself as a tailing of HOMO and LUMO levels and changes them into hole and electron conducting bands correspondingly. After excitation and charge separation the electron and hole are free to travel along their respective stacks.

When the bridge orbitals are separated from those of D and A, the charge transfer may be achieved in one step by tunneling (or superexchange). In this case, the REDOX state of the bridge is not changed, and the bridge serves as an inert virtual medium [2]. The initial exciton dissociates by tunneling an electron or a hole through the bridge, forming the D<sup>+</sup>BA<sup>-</sup> radical ion pair:



Intramolecular transfer may be presented as a limiting case of tunneling where virtual exciton takes part.

The rate constants of coherent transport can be calculated by the well-known Marcus formalism [3]. Rate constants of charge separation and charge recombination depend on free energies of corresponding processes, which, in turn, depend on REDOX potentials of donor and acceptor and exhibit an exponential decay as a function of the distance between them [4]. Adjusting oxidation and reduction potentials of donor and acceptor recombination rate to be controlled and minimized. Experiments demonstrate that recombination time (or separated carriers' lifetime) may be controlled in the range from 10<sup>-12</sup> up to 10<sup>-1</sup> seconds.

Elongation of the bridge could potentially change the charge transfer mechanism. Superexchange exponentially decays and gives way to the sequential electron hopping. This is especially the case when the donor and bridge molecular orbitals are spaced closely together. Usually this incoherent regime proceeds in two steps; the initial exciton D\* dissociates by

transferring an electron to the conjugated bridge giving an intermediate radical pair  $D^+B^-A$ , then the bridge is oxidized and the charge goes to the acceptor moiety forming the  $D^+BA^-$  radical ion pair. The dependence of the electron transfer rate on the DA distance is rarely linear or renders only limited linear region. The incoherent transport is a highly diabatic process, which makes it sensitive to molecular vibrations and conformational flexibility.

The properties of bridge control lifetime of photogenerated carriers. For different DBA molecular systems this time may vary from picoseconds to milliseconds.

### 3. Charge transport

Other variable parts of material design involve Donor and Acceptor moieties which are flat polycyclic dye components.

Donor and Acceptor determine the absorption spectrum of the DBA molecule, which controls the harvesting efficiency. Polyaromatic components form into molecular stacks via  $\pi\pi$ -interaction. Molecular stacks with conjugated  $\pi$  system support effective charge transport [5]. Some of these ordered materials have actually exhibited mobilities for charge carriers higher than amorphous silicon. Stacking DBA together by  $\pi\pi$ -interaction – donor to donor and acceptor to acceptor – results in a formation of separate ‘pipes’ or ‘stacks’ for electrons and holes.

Donors and Acceptors should be stacked in separate pipes as depicted in Fig. 1b. Proper molecular geometry of the DBA system makes such precise stacking possible. Camomile-like system (aka ‘n-peller’) prevents other than target positioning of molecular parts: Donor and Acceptor stack to each other vertically forming Donor and Acceptor stacks.

### 4. Recombination

For highly efficient solar cells, the photovoltaic material should keep charges separated for the period of time necessary for charge transport to the corresponding electrode. Recombination needs to be kept to a minimum and carrier lifetimes at a maximum.

#### 4.1. Lowest limit of separated carriers lifetime

Typical distance between Donor and Acceptor moieties is about 2 nm. This is much smaller than effective Coulomb radius,  $r_c = q/4\pi\epsilon\epsilon_0kT$ , where the potential energy of an electron-hole pair becomes to be equal to  $kT$  (at  $T = 300K$   $r_c \approx 18.0$  nm). This radius is a characteristic separation between electron and hole, starting from which the probability of their recombination rapidly increases.

The life time of separated carriers must be enough to allow their transport at the distance of  $r_c$ . At larger distances the carriers are essentially free.

This critical time may be estimated from a simple model of continuous electric current. In accordance with the definition of carriers’ mobility  $\mu$  within a bulk material, their drift speed is  $\langle v \rangle = \mu E$ , where  $E$  is the average electric field in the sample.

Further  $E \approx \Delta U/H$ , where  $\Delta U$  is the potential difference applied,  $H$  is the thickness of the sample. The desired time period  $\tau$  will be the time required to travel through the ‘thickness’ of the molecule  $\delta$  with the average velocity:

$$\tau \approx \frac{r_c}{\langle v \rangle} = \frac{r_c H}{\mu \Delta U}.$$

As an example, for  $H = 500$  nm,  $\mu = 10^{-2}$  cm<sup>2</sup>/Vs,  $\Delta U = 1$  V results in a time period of  $\tau = 10$  ns. Hence, lifetime of separated charges should be greater than 10 ns.

### 4.2. Recombination suppression

Ordered DBA photovoltaic materials dimensionality results in very short distance for charge transfer; from 3D as in molecular blends to 1D for molecular stacks and from 3D stochastic wandering to 1D diffusion. This also results in further suppression of charge recombination.

Let  $\gamma$  be the average number of holes approaching in a time unit to the given electron at the distance  $r_c$  under assumption of 3D motion of electron in a disordered molecular blend. The corresponding average electron velocity is  $\bar{v}$ .

When electron-hole pair is created and then gets separated, the free electron and hole start to move in opposite directions. Their recombination may be caused only by alien carriers knocked out by the other photons. Furthermore, a molecule where the separation of the second pair took place must be located within the same molecular stack of diameter  $d$ . The probability of such an event is about  $(r_c/d)^2$  times less than in the 3D case.

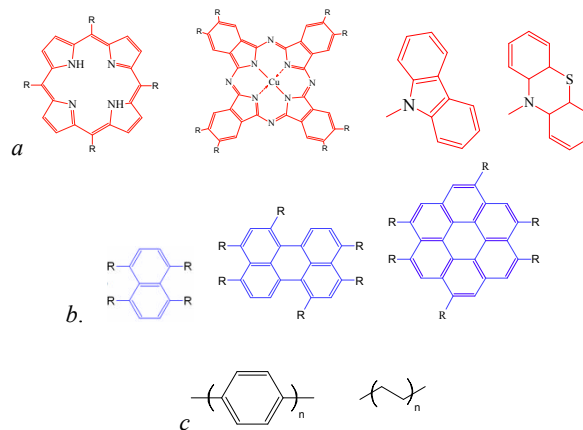
Moreover, the average velocity  $\bar{v}_1$  of 1D thermal motion of the electron is approximately 2 times more than that of 3D case,  $\bar{v}$ . That is why in 1D structure the value of  $\gamma$  is at least

$\left(\frac{r_c}{d}\right)^2 \frac{\bar{v}}{\bar{v}_1} \approx 100$  times reduced. In other words, electrons

traveling along the DBA molecular stack participate in recombination acts 100 times less than in disordered material.

### 4.3. Building blocks

The components of DBA molecule each have their distinct responsibilities. Donor and Acceptor determine the absorption spectrum of the whole molecule as well as the self-assembling properties; nature of Bridge governs the separated carriers’ lifetime; side-chains define solubility and thermal properties of the material. Hence, absorption, lifetime and solubility and stability are all controlled by molecular design. Typical elements or building blocks for DBA systems are presented in Fig. 3.



**Figure 3. DBA molecule building blocks: donors (a), acceptors (b), bridges (c)**

DBA molecules were first described by Prof. Wasielewski [6]. It was shown that these molecules absorb light, provide charge generation and separation with internal quantum efficiencies up to 100%, and keep charges separated for a certain time period.

We took this basic concept and introduced side substituents like alkyl chains, linear or branchy, into periphery of DBA molecules in order to control solubility and stability of the molecule. These side chains also play the valuable role of insulator between stacks of DBA molecules, preventing

crosstalk or recombination of carriers between donors of one DBA stack and neighboring Donor and Acceptors of another DBA stack.

#### 4.4. Efficiency

In practice, the photoexcited electron can decrease its potential energy in the process of thermalization until it reaches the lowest level in the conduction band. On our case, this is the LUMO band of the DBA system.

As a consequence of thermalization, the semiconductor bandgap is often regarded as a measure for the achievable voltage (the higher the bandgap, the higher the voltage).

However, a low bandgap material can absorb more photons and thus increase the number of photogenerated charge carriers (i.e. photocurrent). Therefore, the lower the bandgap, the higher the photocurrent becomes. Hence, there is an optimal bandgap for a given illumination spectrum. The maximum power conversion efficiency for a semiconductor with a given bandgap is defined by Shockley-Queisser limit under assumption of only radiative recombination and sun-like illumination. For a semiconductor bandgap between 1.3 and 1.5 eV this value is 30%.

Charge separation within DBA molecules (Section 2 above) shows that the theoretical limit of efficiency for DBA-based solar cells is also 30%.

Use of multiple active layers with different DBA structures absorbing mutually complementary wavelength ranges (also known as multi-junction or tandem) makes it possible to increase the maximum efficiency in accordance with the Table 1.

**Table 1. Solar Cell Efficiency versus Number of Layers**

Number of layers	Efficiency, %
1	30
2	44
3	50
6	58
$\infty$	68

Tandem architecture of solar cells with DBA materials can be implemented by low-cost large-area roll-to-roll deposition technique.

### 5. Molecular alignment

After establishing absorption and carrier lifetime properties of the material, the most important aspect is to form one-dimensional charge carrier pathways that control mobility of the carriers and path length between electrodes. The desired material structure is achieved by a combination of molecular design, deposition and the crystallization process.

#### 5.1. Self-assembly and crystallization.

DBA molecules have two distinct parts: aromatic conjugated aryl part and chain-like alkyl groups attached to the aryl part on its periphery. Aryl parts have strong self-assembly or stacking properties and Alkyl groups control solubility in alkyl solvents.

Aryl solvents are good for the aryl parts and alkyl solvents are good for the alkyl parts of the DBA molecule. The best solubility for the composite molecule would be with alkyl and aryl solvents mixed in a certain proportion that corresponds to the composition of parts in the molecule. If solvents have a different affinity to corresponding parts of the molecule, then the composition of the mix of solvents would be different and the difference in affinity should be taken into account.

As part of this research, we have explored the concept of partial solubility of molecular parts in corresponding solvents. Crystallization takes place when the concentration of crystal-

forming substance in solution reaches the crystallization point. In our case of composite molecules (aryl-alkyl molecules), the crystallization point is different for the aryl and alkyl parts. Our system has only one relatively strong interaction between molecules in solution and it is related to the  $\pi\pi$ -interaction responsible for stack formation. This means that when aryl solvent evaporates in drying process the  $\pi\pi$ -interaction plays the major role in crystallization and it begins with oligomeric stack (small supramolecules) formation that consist of several molecules bound by  $\pi$ -interaction. There needs to be a balance between evaporation of two solvents, with the aryl solvent going out of system first being followed by the alkyl solvent. This order allows us to achieve a target functional structure: stacks of molecules with alkyl chains orderly positioned (crystallized) around the core aryl stack.

Therefore, aryl solvents need to have lower evaporation point than alkyl solvents. The actual values should be found by experimental work with compounds that exhibit the target crystalline structure.

#### 5.2. Crystallization in Homeotropic Alignment

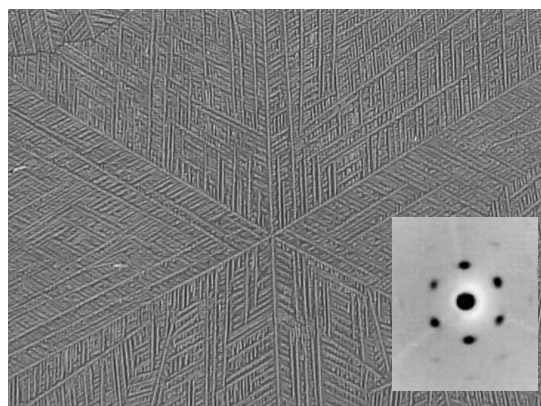
Homeotropic alignment is produced through thermotropic liquid crystal phase of the material. Several published articles describe homeotropic alignment of alkyl-substituted polyaromatic compounds obtained with gradual cooling from temperatures higher than the corresponding clearing point [5], [7], [8].

The isotropic melt contains non-associated species. Monomeric molecules thermodynamically favor a large surface contact and the subsequent layer of molecules grows epitaxially onto the first molecular layer. In other words, molecules must aggregate, but the corresponding driving force must be suppressed till the final stage of deposition. This process can be controlled by temperature and/or proper solvent.

Depending on properties of the material the appropriate deposition technique is chosen:

- If the material melts within the desired temperature range, then the material is deposited on the substrate and molecules are homeotropically aligned upon cooling from the clearing point;
- If the material does not melt within the desired temperature range, then the material is deposited from a mixture of high boiling point solvents, and molecules are self-organized into vertical columns upon slow drying at elevated temperatures.

We demonstrated the first approach on DBA components and triads (DBABD). For example, coronene having two hexyl and two tricosane side-chains melts at 130°C with isotropization temperature 210°C. It's cooling from clearing point at the rate of 5°/min results in a perfect homeotropic structure.



**Figure 4. Coronene homeotropically aligned films (x10)**

The films possess defect-free homeotropic molecular orientation on the area of several sq. cm. Optical measurements demonstrated that the films are isotropic in the plane ( $n_x = n_y$ ), with  $\Delta n = n_x - n_z = 0.3$ .

The second approach was applied to coronene with shorter side-chains being non-melting at temperatures below 300°C and n-pellers. When deposited in a mixture with high boiling-point solvents (dibutylphthalate, hexadecane, tetralin, etc.), the compound realized homeotropic alignment. "Out of plane" optical anisotropy ( $\Delta n$ ) with film thicknesses ranging between 50 to 1000 nm was measured to be  $\Delta n = 0.2$ .

We have also demonstrated the second approach using porphyrin-naphthalene n-peller having  $(C_{11}H_{23})_2$  and  $CH_2Phe(OC_{16}H_{33})_2$  side-chains which does not melt below 300°C. Deposition from a mixture with dibutylphthalate (1:1) having a high boiling point results in homeotropically aligned films (Fig. 5). The isotropization temperature of the coating liquid is 180°C which makes deposition possible on the plastic substrates. "Out of plane" optical anisotropy of film thickness ranging between 50 and 1000 nm was found to be  $\Delta n = 0.2-0.4$ .

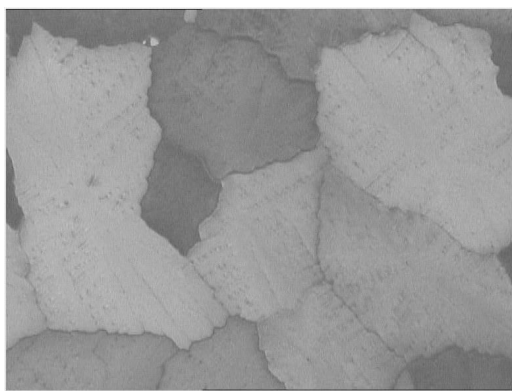


Figure 5. N-peller homeotropically aligned films (x10)

DBA with porphyrin as a donor and naphthalene as an acceptor is not found to be efficient materials for solar cell application.

The same technique was applied to perylene-porphyrin n-peller bearing the  $CH_2Phe(OC_{16}H_{33})_2$  side-chains. This mixture with hexadecane and tetralin (1:1.2:0.8) has a clearing point at 230°C and the ordered molecular structure was obtained by controlling the cooling rate. After cooling at a 10°C/min the recrystallized film underwent orientational ordering resulting in discotic-nematic molecular structure. However, using a 2°C/min rate led to a partially homeotropic columnar phase.

Partial homeotropic alignment was also achieved with a coating liquid of N-peller/Dibutylphthalate/Sulpholane = 1/1/1. "Out of plane" optical anisotropy of a 50-nm thick films was  $\Delta n = 0.05-0.10$ .

## 6. Solar cells

Different molecular packing of the film is reflected by corresponding photo response. We have studied cells made of ITO/CuPc/n-peller/Al design.

Glass substrates with low resistance ITO (10 Ohm/sq.) were used. The ITO layer was etched forming 3-5 mm-width stripes. Prior to deposition, the substrates were treated with plasma and washed with iso-propanol.

A selective layer of copper phthalocyanine (CuPc) of 10 nm thickness was deposited by Meyer rod technique and then annealed in  $N_2$  at 250°C during 30 minutes. An active layer of perylene-porphyrin n-peller of 50 nm thickness was then deposited by Meyer rod technique using the following coating liquids:

1. 5% toluene
2. N-peller/Hexadecane/Tetralin = 1/1.2/0.8
3. N-peller/Dibutylphthalate/Sulpholane = 1/1/1.

After the deposition, recrystallization of mixtures 2 and 3 was performed by cooling the samples down from 250°C at the rate of 10°C/min. When the temperature reached 100°C the samples were placed into an oven preheated to 150°C and baked for 30 minutes. The baked samples were washed by soaking in hexane and then dried by compressed air. Aluminium contact layer was then sputtered in vacuum by thermal evaporation.

Corresponding photocurrents measured under illumination of ca. 10 mW/cm<sup>2</sup> are indicated in the Table 2.

Table 2. Photo response versus molecular ordering of the active layer

#	Molecular ordering	$I_{sc}$ , $\mu A/cm^2$
1.	Isotropic	0.3–0.7
2.	Discotic nematic	10–20
3.	Disordered homeotropic	300–400

## 7. Conclusion

Cryscade Solar is developing a novel DBA solar energy harvesting technology that combines two unique solutions. First, separation of carriers at the event of light absorption in precisely defined molecular structures. Second, stacking of molecules, providing escape paths for separated carriers in segregated "pipes" formed by donors and acceptors. This keeps charges separated for transportation along isolated electron and hole channels to corresponding electrodes.

We have found a process for arranging DBA molecules on substrates in the form of vertical columns. Homeotropic alignment of molecular packing has strong influence on photocurrent of solar cell. DBA columns are electrically insulated from neighbors due to extended peripheral alkyl chains surrounding each molecular vertical stack.

Efficiency is highly sensitive to change in degree of crystallization. This high sensitivity, in turn, provides control over optimization process.

We presented findings on the first ever prototype of a solar cell with control over all essential parameters of efficiency: absorption band, lifetime of separated charges and carriers' mobility. We believe that DBA crystalline photovoltaic material in homeotropic orientation of monocrystals is ideally suited for creating the most efficient and inexpensive solar cells on the industry.

## 8. References

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