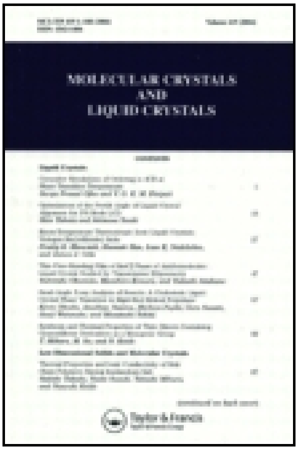

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Some Aspects of the Role of Solid State Chemistry in the Performance of Organic Solar Cells

Don L. Morel [a]

[a] Exxon Research and Engineering Company, P.O. Box 8, Linden, New Jersey, 07036, U.S.A.

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Some Aspects of the Role of Solid State Chemistry in the Performance of Organic Solar Cells

DON L. MOREL

Exxon Research and Engineering Company, P.O. Box 8, Linden, New Jersey 07036, U.S.A.

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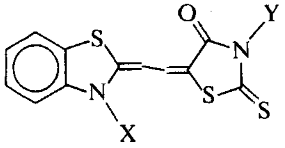
Photovoltaic solar cells having sunlight efficiencies of order 1% have been fabricated using organic materials as the photoactive medium.[1] The best results to date have been achieved with dyes of the merocyanine family. Two of the principal dye structures that have been investigated are shown below.



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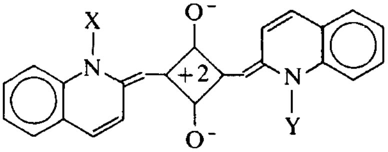

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Though the devices exhibit classical photovoltaic behavior in many respects, there are several operational idiosyncrasies which require modifications to conventional theories and ensuing expectations in performance. Furthermore, the added dimension of chemical substitution provides a means of varying and fine tuning the critical parameters of operation which is not possible in conventional inorganic devices. An investigation of the interrelationships among critical device parameters and chemical structure has been undertaken. The effects of chemical manipulation are evident from the initial light absorption process through the delivery of power to the external load.

Though absorption is essentially a molecular phenomenon, collective effects can be realized in the solid state if appropriate packing arrangements and ensuing molecular overlap can be effected. The absorption profile is still basically Gaussian in nature and not bandlike. The

location of the absorption peak can however be shifted to maximum solar overlap by adjusting the chromophore length. Based on total absorption, structure II dyes can be equated to materials having a bandgap of 1.8 eV which represents a maximum theoretical solar efficiency in excess of 20%. Because of other peculiarities in performance, further qualifications must be placed on this analogy.

The process of current generation involves several additional steps beyond standard bandlike behavior. Excitation may involve the production of an exciton which first diffuses to a high field region and then is broken down into a free carrier pair by the action of the field. In addition to being field dependent, the efficiency of the process is also energy dependent. Quantum efficiencies approaching unity are realized in the blue or Sorét spectral region. This process may be more bandlike in nature. The spectral location and performance of each of these mechanisms is dependent upon dye chemistry.

While conventional band models can be used to discuss barrier formation and voltage development, some consideration must be given to redox potentials in analyzing device performance. By judicious choice of electrodes V_{oc}'s as high as 1.25 volts can be realized which is very high for conventional photovoltaic devices.

While stability is a major concern for these devices, it appears that proper care in encapsulation and design can result in substantial improvement in lifetime. It also appears that there is a positive correlation between stability and efficiency whose basis may lie in minimization of the time that molecules spend in the excited, reactive state.

INTRODUCTION

Organic materials have found successful applications in devices involving interaction with light. Two such areas are conventional photography and electrophotography. Because of the similarities of the mechanisms involved in these and the conversion of light energy into electrical energy through the photovoltaic process, it is of interest to investigate the potential of organic materials for the production of solar cells. Sunlight efficiencies of order 1% were recently reported for solar cells based on merocyanine dyes.[1] It is the purpose of this paper to briefly discuss the operation of these devices and to outline the role of solid state chemistry in their performance.

THEORY OF OPERATION

While conventional device theory serves as a guideline for discussing device performance, many modifications are required because of the complexities introduced by the peculiarities of charge generation and transport in organic materials. Solar cells are power generating devices and it is necessary to consider the generation of both current and voltage. As a first approximation, it is convenient to assume the applicability of the band theory of solids so that one can use conventional band diagrams in discussing these parameters. The first problem that arises then is the identification of a band gap. Since a band edge in the conventional sense does not exist for these materials, for purposes of this discussion we will identify the band gap with the location of peak absorption for the material. The bands themselves are narrow and are likely more readily identifiable with the chemical concepts of oxidation and reduction potential levels. The concept of fermi level is also relegated to subordinate status in that these materials are very insulating in the dark. With these assumptions, one can construct an energy level diagram for these devices as shown in Figure 1a which gives rise to the band scheme shown in Figure 1b. In this case the material is completely depleted with the band bending determined by the electrodes. One of the metal electrodes is semitransparent so that light can reach the organic layer. The maximum voltage the device can develop under illumination is given by

$$V_{\max} = \frac{(\phi_1 - \phi_2)}{e} \tag{1}$$

where ϕ_1 and ϕ_2 are the work functions of metal 1 and metal 2 respectively.

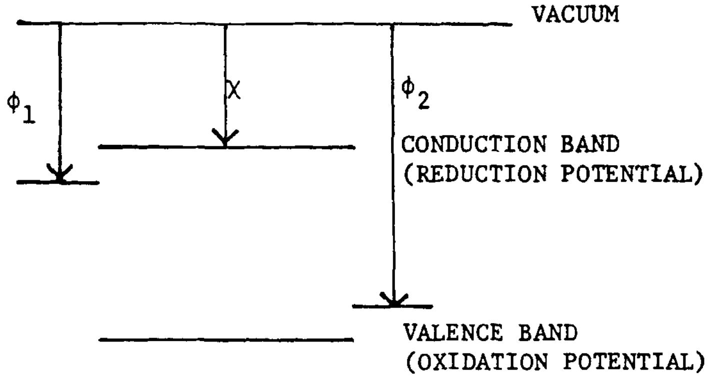


FIGURE 1a Assumed energy level scheme. ϕ_1 and ϕ_2 are the work functions of the electrodes; χ, electron affinity.

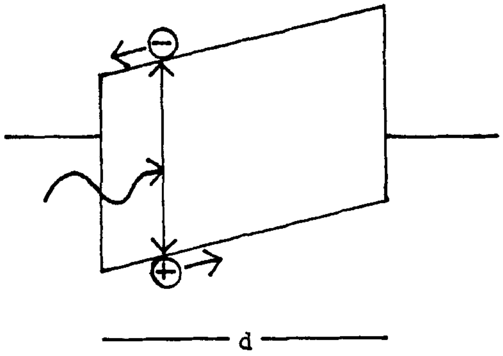


FIGURE 1b Resulting band diagram from scheme 1a.

In the case where the material is either thick enough or conducting enough so that it is not completely depleted, the effective fermi level will then be a factor in the band bending that occurs. Also, it is advantageous to include an oxide layer between the semitransparent metal and the organic layer to form an MIS structure. Both of these factors however are beyond the scope of this discussion.

Current generation in this scheme is exactly analogous to that of a material having a field V/d impressed across it, where d is the thickness of the material and V is the voltage developed under the given conditions of illumination and loading. The expression for the current is

$$I = \eta L e g \tag{2}$$

where η is the quantum efficiency, L is the absorbed photon flux, e is the unit of electronic charge, and g is the gain which is to a first approximation given by τ/T where τ is the carrier lifetime and T the transit time. The transit time is a function of the carrier mobility μ and is given by $d^2/V\mu$ in this case.

The power generating capability of the device is finally limited by the concept of fill factor, FF, which is a measure of the ability of the device to deliver current and voltage simultaneously to a load. As seen in Figure 2 the ideal theoretical limit of the device is to deliver its maximum current capability and voltage capability simultaneously. These quantities are referred to as short circuit current, I_{sc}, and open circuit voltage, V_{oc}, which are measured under shorted and fully loaded conditions respectively. In actuality one increases at the expense of the other as the load is varied resulting in the load curve designated by the solid line in Figure 2. The fill factor for the device is related to the fractional area of the ideal theoretical rectangle ($I_{sc} \times V_{oc}$) that the actual load curve encompasses. Ordinarily losses associated with the fill factor are attributable to shunt and series resistances which are shown in

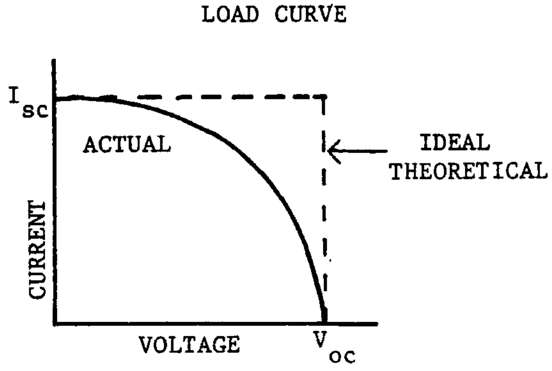


FIGURE 2 Ideal theoretical and actual power curves.

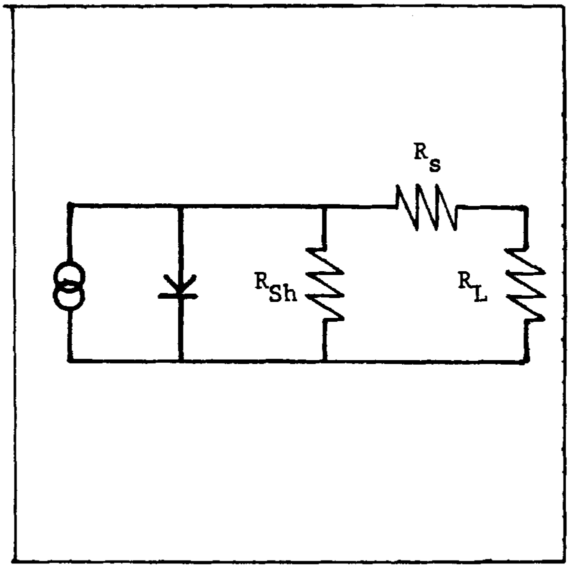


FIGURE 3 Solar cell schematic diagram. R_L, load resistance; R_s, series resistance; R_{Sh}, shunt resistance; ⊖, current generator.

the schematic diagram for a device in Figure 3. However, over and above these, for organic materials one has the possibility of field dependent quantum efficiencies and mobilities to contend with as the internal fields change under varying loading conditions.

Finally one can write an expression for the sunlight efficiency as

$$\mathrm{SEE} = \frac{I_{sc} V_{oc} \times \mathrm{FF}}{\mathrm{L}} \times 100\% \tag{3}$$

(L = solar intensity) which is power out/power in. Although each of the three contributing parameters in the above expression is important, I_{sc} will be focused upon as the primary means of evaluating chemical manipulation in the discussion which follows.

DEVICE FABRICATION AND STRUCTURE

The devices are made in a sandwich cell configuration using Corning 7059 glass as the substrate material. The semitransparent metal or metal oxide electrode is vapor deposited onto the substrate and then is overcoated by the organic layer. Most of the dyes used in this study were sublimable in high vacuum and were put down in that fashion. Those that were not were cast

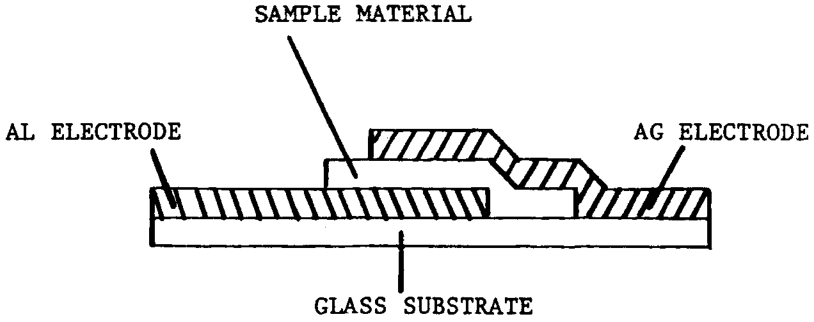


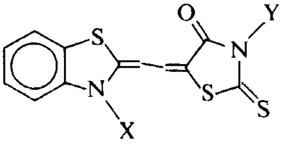
FIGURE 4 Cross sectional view of device structure.

from solution using a spin coating technique. The thickness of the organic layer was usually in the range of several hundred to several thousand angstroms though working devices down to 50 Å were fabricated.

The resulting device configuration is shown in Figure 4. The active area is the region of overlap between the two electrodes which is typically 1 cm^2. Most of the materials were tested with Al as the semitransparent electrode and Ag as the counter electrode.

RESULTS AND DISCUSSION

The results presented below will be for devices made from the two basic structures shown below. While the highest efficiencies achieved thus far have been with structure I dyes, structure II dyes offer higher potential efficiency because of their broader absorption profiles. The thin film absorption spectrum of each of these is shown in Figure 5 along with the solar intensity



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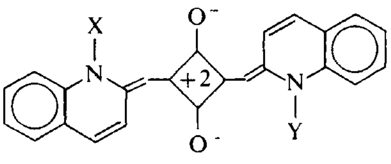

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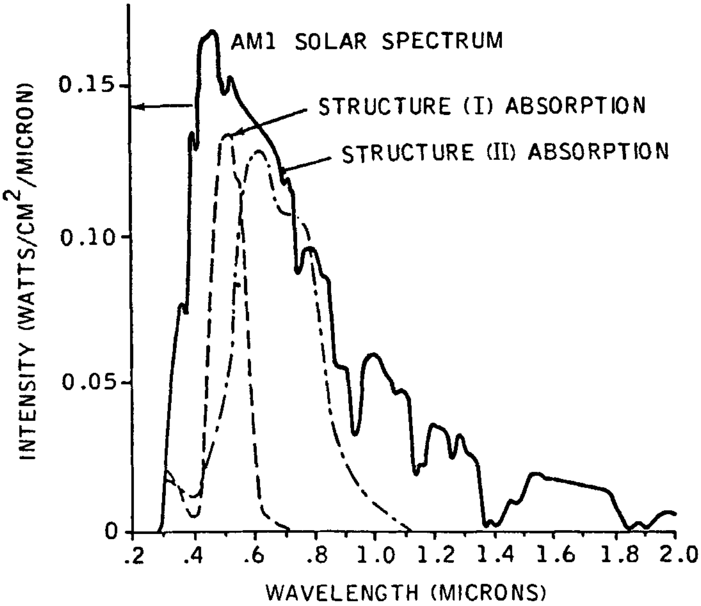

FIGURE 5 Absorption spectra for type I and type II structures superimposed on the solar spectrum.

spectrum. As can be seen, structure I dyes exhibit a narrow absorption profile (~ 100 nm) and can make effective use of only ~ 15% of the total solar output. While increasing the film thickness could boost this value up to ~ 30%, the interdependence on other performance factors limits the film thickness to values that result in the 15% figure. This limited absorption range is then the first order limit on the theoretical solar efficiency for the material. While this value is somewhat low, structure II dyes exhibit an absorption breadth of 2–3 times that of structure I dyes. Although the oscillator strengths of the absorptions are comparable (7–8 based on the product of width at half max times extinction coefficient), because of the magnitudes of the extinction coefficients with type II structures it is possible to realize high absorption percentages with non-compromising thicknesses so that the greater absorption breadth is effective. In fact, based on the total absorbed light for an effective thickness, type II structures can be equated with "conventional" materials having a band gap of 1.8 ev. The maximum theoretical solar efficiency for such a material is in excess of 20%. Needless to say, because of the other complexities involved such a one to one comparison on this basis may not be strictly applicable, although as a first order approximation the implications are attractive.

It is interesting to note that unlike structure I dyes, the thin film absorption of structure II dyes is a solid state phenomenon. That is, the thin film absorption of structure I dyes is just a slightly broadened and shifted version of its solution spectrum while that of the type II dye represents a 3–4 fold increase in absorption breadth over its solution spectrum. It appears then that the performance of type I structures is essentially molecular in nature, while that of type II structures may involve collective or lattice type mechanisms as evidenced by the "collective" nature of the absorption process. The origin of this behavior lies in the packing characteristics of the molecules in the solid state and their ability to form active entities of a multimolecular nature.

Although type I structures suffer from limited absorption breadth, the situation can be significantly improved by incorporating into the film more than one species either as a mixture or as a multi-layered array. A convenient way of doing this is by combining structure I dyes whose peak absorptions are shifted with respect to each other. This can be accomplished by altering the chromophore length by varying the number of alternating bonds between the rings. A plot of this effect is shown in Figure 6. As can be seen, the shift is monotonic and of order ~75 nm/bond. A combination of these structures would again result in a very broad absorption profile.

The absorption of light is only the initial step in the process of current generation. There are many potential loss factors for the absorbed energy which do not contribute to power generation. Organic materials seem to

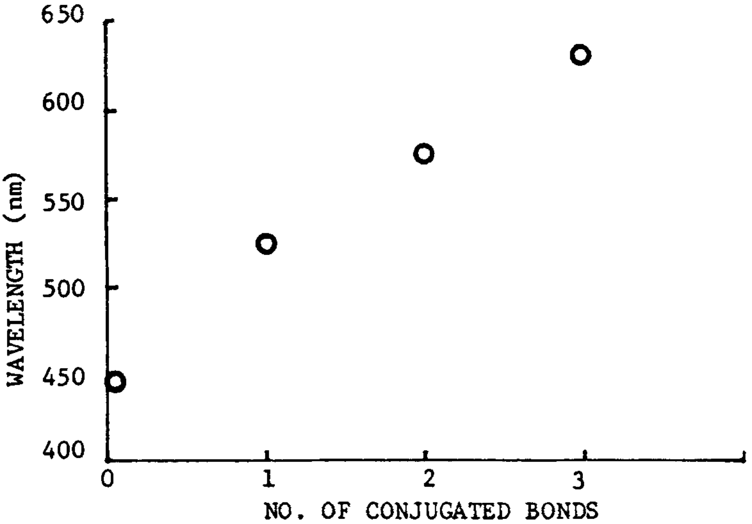

FIGURE 6 Location of peak absorption vs. the number of conjugated bonds in the interring chain for type I structures.

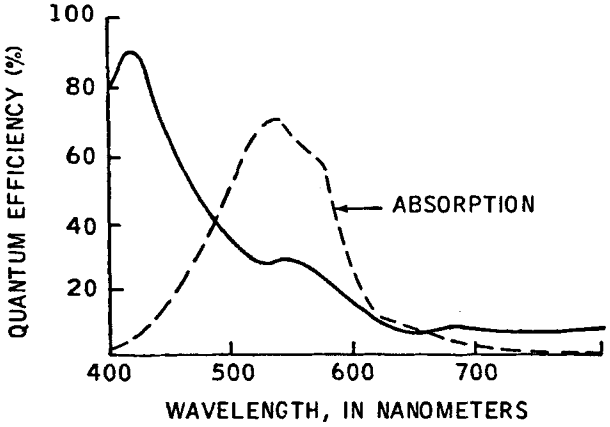

FIGURE 7 Quantum efficiency action spectrum vs. absorption spectrum for type I structures.

have more than their share of these.[2] In addition to the standard losses associated with carrier transport, there appear to be intermediate loss mechanisms associated with the generation, transport and dissociation of excitons. This is exemplified by the quantum efficiency action spectrum for a structure I dye shown in Figure 7. The increasing efficiency with decreasing wavelength is believed to be attributable to increasing ease of exciton dissociation with exciton energy.[3] This is a topic of very great importance to the performance of these devices and is deep rooted in the chemistry and structure of the organic medium. In particular, the high efficiencies in the blue or Soret region may be due to a current generation mechanism more in line with conventional band to band type processes. Of further importance is the possibility of shifting this high efficiency region further into the visible region so as to better match the solar spectrum. Preliminary results suggest that this can be done by judicious manipulation of ring structure.

V_{oc}'s up to 1.25 volts have been achieved with structure I dyes between Al and Ag electrodes. This seems to be consistent with the effective energy levels involved[4] and the theory outlined above. Use of other electrode couples seems to also support this theory.[2] Use of the Al/Ag couple with type II dyes however only results in V_{oc}'s of order 0.4 volts. Two possible explanations for this are that:

1) barrier formation is controlled by surface states, or

2) the structure II dyes are not completely depleted as are the structure I dyes.

In the latter case the barrier would be determined by the dye fermi level which might be unfavorably located for high voltage generation.

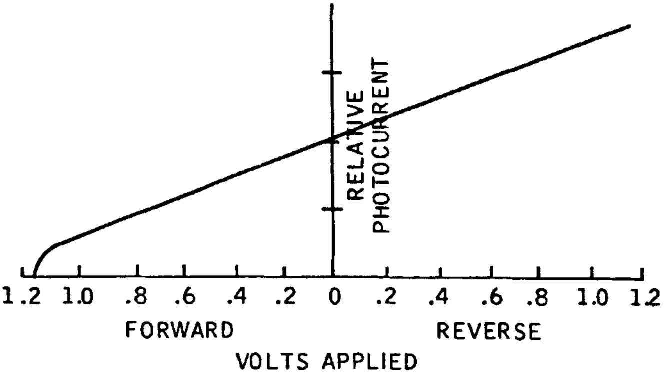

FIGURE 8 Photocurrent bias dependence.

Fill factors for these devices are in the range 0.25–0.3 and again appear to be limited by phenomena associated with the organic nature of the system. Careful study seems to indicate that although dark resistivities are high, device output is not necessarily limited by series resistance because of the highly photoconducting nature of the films. The mechanism responsible for the slope of the power curve again seems to be associated with the exciton intermediate, and in particular the field dependent nature of its dissociation probability. The power curve for a device made from a structure I dye is shown in Figure 8. The nearly linear dependence is ordinarily characteristic of a series resistance limitation, however, in this case the dependence is thought to be attributable to a field dependent quantum efficiency. That is, in addition to their dependence on photon energy, the dissociation probability of excitons into charge carriers is also dependent upon field. As the load is varied, the internal voltage generated by the device is varied within the device itself which alters the internal field distributions and hence the efficiency with which excitons are dissociated into charge carriers. This type of field dependent, energy dependent carrier generation mechanism is commonly observed in other organic and in some inorganic systems.[5] One of the challenges of this approach is to develop appropriate electrode and photoactive material combinations such that sufficient fields are always present to effect efficient carrier generation. The ability to do this will require detailed study of the active mechanisms and the development of techniques for their manipulation.

The expected stability of a device is always a concern during its development, and this is especially true for one which employs organic components. UV light is a known nemesis for organics, and this is certainly a consideration in this case. However, through the use of UV filtering encapsulants it is possible to eliminate this problem. The absorption of visible light by these dyes may also lead to potential instability. That is, the charge rearrangement that occurs in an excited molecule may make it more reactive than when it is in its ground state. The key to this problem is to keep foreign reactive species out of the film and to minimize the time that the dye spends in the excited state. Oxygen, and in particular, singlet oxygen seems to be the predominant culprit in this case. Preliminary results indicate that the elimination of oxygen leads to significant improvement of stability for devices made with type I dyes. While some degradation still occurs in these, at least part of it appears to be reversible. It also appears that the more efficient devices are more stable. This may be due to the fact that energy and charge is transported more rapidly through these, and hence the constituent molecules spend less time in the excited, reactive state. Such a symbiotic relationship between efficiency and stability would be a welcome one and would greatly facilitate the eventual use of these structures as practical devices.

Acknowledgments

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