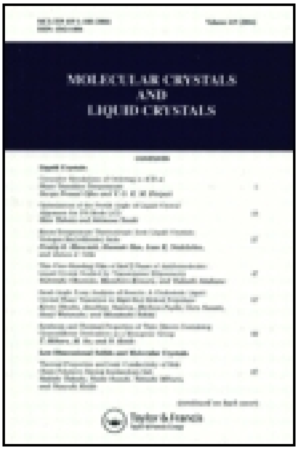


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Organic P-N Junction Solar Cells

G. A. Chamberlain [a]

[a] Shell Research Ltd., Thornton Research Centre, P.O. Box 1, Chester, CH1 3SH

Version of record first published: 17 Oct 2011.

To cite this article: G. A. Chamberlain (1983): Organic P-N Junction Solar Cells, Molecular Crystals and Liquid Crystals, 93:1, 369-379

To link to this article: http://dx.doi.org/10.1080/00268948308073540

Mol. Cryst. Liq. Cryst., 1983, Vol. 93, pp. 369–379
0026-8941/83/9304-0369/$18.50/0

Printed in the United States of America

ORGANIC P-N JUNCTION SOLAR CELLS

G.A. CHAMBERLAIN
Shell Research Ltd., Thornton Research Centre,
P.O. Box 1, Chester CH1 3SH

Abstract A number of solid state organic solar cells have been prepared and tested in simulated sunlight. Photovoltaic effects were consistent with the formation of a rectifying junction at the interface between a triphenylmethane dye (n-type) and a merocyanine dye (p-type). The most efficient device consisted of a sandwich of thin layers of indium-tin oxide/malachite green/a benzothiazole-rhodanine merocyanine/Au on Pyrex. Exposure of the cell to chlorine vapour in the absence of air improved the sunlight efficiency to 0.12%. Investigations of the photocurrent action spectrum, rectification and capacitance have given mechanistic information on the photovoltaic energy conversion processes.

INTRODUCTION

In the search for cheap, efficient and reliable solar cells, the potential for organic semiconductors is currently being assessed. A greater understanding of the photovoltaic mechanism, together with molecularly engineered and chemically doped systems, have led to the development of metal-insulator-organic semiconductor cells with efficiencies approaching 1%[1]. The mechanism is thought to involve the creation of excitons in the organic material by light absorption. The excitons can produce charge carriers (electrons and holes) by electron transfer to dopant sites. The charge carriers can then either recombine or become separated in the built-in field at the metal-semiconductor interface and give rise to a photocurrent at short circuit or photovoltage at open circuit. However, theoretical calculations[1] on promising aluminium/merocyanine cells indicate that the ultimate efficiency of these devices in sunlight is only about 4% even if the carrier generation and collection steps proceed with unit probability. The sunlight efficiency is limited by the incomplete absorption of solar radiation within the short built-in field region[2], typically about 20-30 nm. If , however, the built-in field width is increased to 50 nm and the organic layer absorption is broadened to cover the entire visible spectrum then efficiencies of around 10% should be within reach, given that there are no additional losses in carrier generation and collection processes[1]. With this approach in mind, we have have prepared some organic p-n heterojunction cells and have determined some of the features that limit their efficiency.

EXPERIMENTAL

The p-n cells consist of four solid layers - a substrate of NESA glass, n-type triphenylmethane dye, p-type merocyanine dye and gold. The NESA glass (an indium-tin oxide coated Pyrex glass from Bomert, Teves and Blankley Ltd. of Croydon) was cleaned and degreased in an ultrasonic bath of Decon solution, and then heated in a roaring gas flame for about ten seconds. After cooling, one drop of a concentrated solution of triphenylmethane dye (Kodak) in dichloromethane was spin coated at 3000 r.p.m. Electrical contacts of indium were applied using a soldering iron and the coated substrate was evacuated to 10^{-6} Torr. The thickness of the triphenylmethane dye is difficult to estimate but is probably less than 100 nm.

Merocyanine dye, synthesised using the method described by Brooker et al.[3], was evaporated to a thickness of about 50 nm onto the surface, followed by a 20 nm layer of gold. A sandwich cell of about 2 cm^2 area was so formed in which the gold and indium-tin oxide layers were staggered to avoid short circuiting. The cells were doped by exposure to about 10^{-4} Torr chlorine gas for a few seconds. Capacitance, spectral and current-voltage measurements were made without breaking the vacuum as described in Ref. 2. An area of 0.064 cm^2 was illuminated through the NESA glass with a fibre-optic.

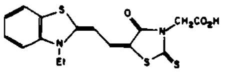
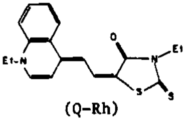
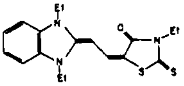
RESULTS

PHOTOVOLTAIC EFFECTS AND RECTIFICATION

The photovoltaic output and sunlight efficiencies of six cells of different n-type and p-type dye combinations are shown in Table 1. Before exposure to chlorine gas, the conversion efficiency of each cell was $<< 10^{-4}$%. After doping the photovoltaic output increased rapidly to the steady values recorded in Table 1 and remained stable at these levels for at least several days. In the dark negligible current and voltage were observed. However, on venting the vacuum chamber with ambient air the photocurrent rapidly decreased and significant dark currents and voltages were observed as degradation took place.

The most efficient device consisted of malachite green (n-type)/benzothiazole-rhodanine (BTh-Rh) merocyanine (p-type). The short circuit photocurrent was linear in light intensity up to the solar intensity used, in common with the other cells, so it was assumed that electron-hole recombination was not an important loss mechanism. We

TABLE I Photovoltaic data on chlorine-doped organic p-n heterojunction cells.

n-type dye (triphenylmethane)	p-type dye (merocyanine)	I_o (mW cm^{-2})	I_{sc} (mA cm^{-2})	V_{oc} (V)	F.F.	η (%)
malachite green	 (BTh-Rh)	75	0.24	0.66	0.56	0.12
malachite green	 (Q-Rh)	62	0.13	0.40	0.30	0.025
methyl violet	BTh-Rh	50	0.037	0.84	0.25	0.016
methyl violet	Q-Rh	50	0.624	0.25	0.30	0.09
methyl violet	 (Bim-Rh)	48	0.312	0.53	0.32	0.11
basic fuchsin (rosaniline)	Q-Rh	80	0.055	0.019	0.25	0.0003

decided to investigate this particular cell in more detail. The current-voltage characteristics in Figure 1 show strong rectification at voltages above ∿ 0.5 V with the NESA electrode biassed negatively. The rectification ratio at 0.8 volts was 100. In sunlight, a fill factor of 0.56 was recorded. This is one of the highest values reported for organic cells, and is consistent with the strong rectification observed. However, all the other cells had inferior rectification and fill factors.

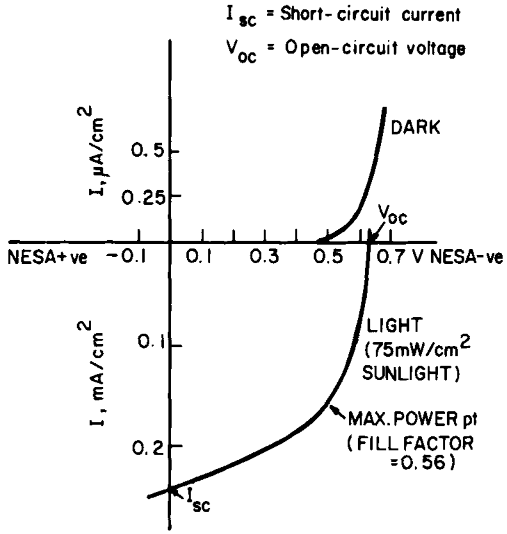


FIG. 1 — Current-voltage characteristics of the cell NESA/malachite green/Bth-Rh merocyanine/Au after chlorine doping in the dark and in 75mW/cm^2 sunlight

PHOTOCURRENT ACTION SPECTRA

The photocurrent action spectrum for illumination through the NESA electrode from 400 to 720 nm for the malachite green/BTh-Rh cell in Figure 2 showed a large peak at 500 nm, attributable to absorption by the merocyanine. The absorption spectra of each dye are shown in Figure 3 for comparison. A minimum in quantum yield (based on incident light) was observed at wavelengths corresponding to the absorption peaks of the malachite green. These results are consistent with the formation of a rectifying junction at the interface of the two dyes, since the malachite green

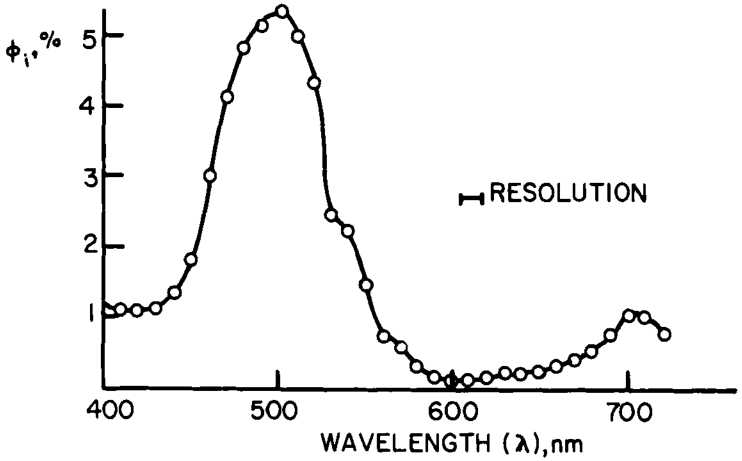


FIG. 2 — Photocurrent action spectrum of the cell NESA/malachite green/merocyanine Bth–Rh/Au after chlorine doping

The quantum yield ϕ_i is given by the ratio of the number of electrons flowing at short circuit to the number of incident photons at each wavelength interval

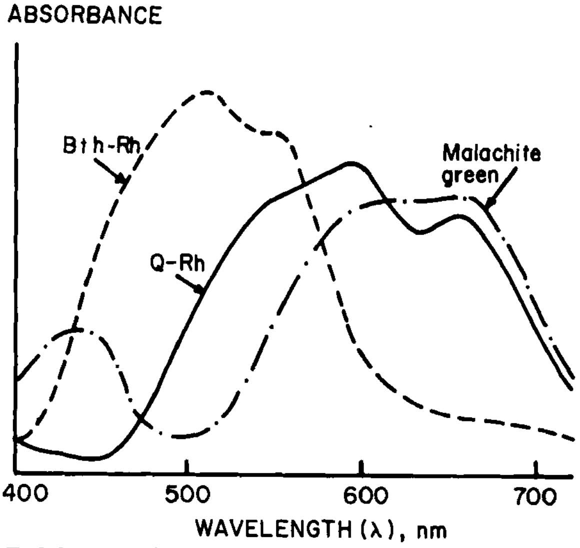


FIG.3 — Visible absorption spectra of thin solid films of merocyanines and malachite green

essentially filters out the strongly absorbed photons in the range 580 nm to 690 nm before they reach the rectifying junction. Absorption by the malachite green around 500 nm is weak whereas absorption by the merocyanine is strong, so the filtering action is not as pronounced and a larger quantum yield is observed. Similar observations were made for the methyl violet/Bim-Rh cell.

CAPACITANCE MEASUREMENTS

Capacitance measurements as a function of applied bias in the dark for the NESA/malachite green/BTh-Rh/Au cell were made at frequencies less than 1.6 Hz. Above this frequency the capacitance became voltage independent. A plot of $1/C^2$ versus applied bias at 0.086 Hz and at 25°C is shown in Figure 4.

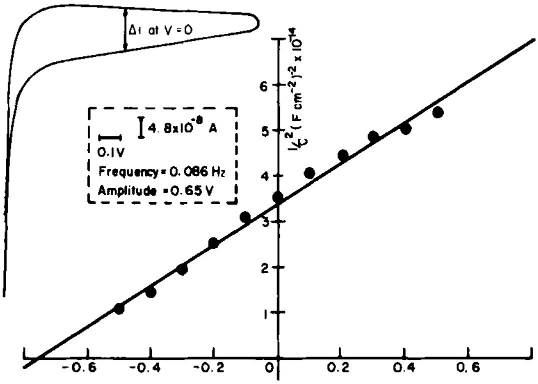


FIG. 4 — Mott-Schottky plot for ITO/malachite green/merocyanine (Bth-Rh)/Au cell at 25°C
Inset: original I/V data at 0.086 Hz

Over the linear portion the differential capacitance is related to the voltage by the equation[4],

$$\frac{1}{C^2} = \frac{(\varepsilon_n p + \varepsilon_p n)^2 2(V_{bi} \pm V)}{(\varepsilon_n n + \varepsilon_p p)\varepsilon_n \varepsilon_p \varepsilon_o q p n A^2} \qquad (1)$$

where ε_n, ε_p and ε_o are the permittivities of the n-type and p-type dyes and vacuum respectively, p and n are the carrier concentrations in the p-type and n-type dyes respectively, q is the electronic charge, V_{bi} is the built-in potential, V is the applied bias and A is the total area. When $1/C^2 = 0$, $V = V_{bi}$, and when $V = 0$ the capacitance per unit area equals $\varepsilon_o \varepsilon_n \varepsilon_p / (\varepsilon_p x_n + \varepsilon_n x_p)$ where x_n and x_p are the built-in field widths in the n-type and p-type dyes respectively. In our analysis we have assumed that $\varepsilon_n \sim \varepsilon_p \sim 4$, and it follows that the slope is then equal to $2(p + n)/\varepsilon\varepsilon_o qnp$. x_n and x_p are then also given by[4],

$$x_n = \left(\frac{2p\varepsilon\varepsilon_o V_{bi}}{qn(n + p)}\right)^{\frac{1}{2}} \qquad (2)$$

and $$x_p = \left(\frac{2n\varepsilon\varepsilon_o V_{bi}}{qp(n + p)}\right)^{\frac{1}{2}} \qquad (3)$$

The relative voltage supported in each of the organic semiconductors is,

$$\frac{V_n}{V_p} = \frac{p}{n} \qquad (4)$$

From Figure 4 we obtain $V_{bi} = 0.76$ V and $x_n + x_p = 65$ nm. Using Eq. (1)-(4) and a carrier density of 10^{18} cm^{-3} in the merocyanine[2], the following parameter values were calculated: $n = 8.5 \times 10^{16}$ cm^{-3}, $x_n = 60$ nm, $x_p = 5$ nm, $V_n = 0.70$ V and $V_p = 0.06$ V.

DISCUSSION

The results show that substantial improvement in sunlight conversion efficiency over previous similar devices[5,6] can be obtained by doping with Cl_2. If the devices are kept under vacuum then the stability is also remarkably good. We have shown[2] that doping with Cl_2 does not change the dark conductivity of these merocyanine thin films. The same observation has been made with our triphenylmethane films. We have suggested previously[2,2] that Cl_2 forms charge transfer complexes with merocyanines at specific adsorption sites, thereby creating localised potential energy minima in the solid state energy bands of the film. Excitons can dissociate into charge carriers at these sites by electron transfer to the lowest unoccupied energy level of the complex. We expect that chlorine diffusion into the n-type dye will be limited by the conditions of our doping technique, since this dye is overcoated by merocyanine which also has a greater affinity for chlorine, and it is probable that excess chlorine may become trapped at the interface between the two dyes. The observation that the action spectrum in Figure 2 shows a peak corresponding to merocyanine confirms that the efficiency of charge carrier generation and collection is much larger in this dye. If charge generation and collection is limited to the built-in field region x_p in the merocyanine (5 nm), then the internal quantum yield based on light absorbed by the merocyanine at 500 nm is 54% (i.e. 5.36%/[fraction of light transmitted by NESA and malachite green][fraction of light absorbed by BTh-Rh at 500 nm] = $5.36\%/0.7 \times (1 - \exp(-3 \times 10^5 \times 5 \times 10^{-7}))$. Cells of greater sunlight efficiencies could be made, therefore, if a more efficient n-type dye could be found. Another important factor is spectral matching of the dye absorption spectra. The efficiency of the malachite green/Q-Rh cell is lower because Q-Rh absorbs in the same portion of the visible as malachite green so potentially usable photons are filtered out before they reach the merocyanine. We note, however, that methyl violet appears to be more efficient than malachite green because of the higher photocurrents reported in Table 1 for the Q-Rh cell.

The maximum photovoltage generated by the cell cannot exceed the built-in voltage V_{bi}. The relative position of the Fermi energies of the two organic semiconductors before contact determine the value of V_{bi} in the cell. Conversely, if the Fermi energy of one organic semiconductor and V_{bi} are known, then the Fermi energy of the other semiconductor can be calculated. In the malachite green/BTh-Rh cell, the Fermi energy of BTh-Rh is about 5.4 eV[2,7] and $eV_{bi} = 0.76$ eV; therefore the Fermi energy of our malachite green film is about 4.6 eV relative to the vacuum level.

For efficient cells, it is important to maximise V_{bi} in order to provide a large driving force for the separation of photogenerated carriers, as well as to satisfy the requirement of large V_{oc}. However, the magnitude of V_{oc} at a given light intensity and the variation of photovoltage with photocurrent are strongly dependent on current-controlling mechanisms in the junction, such as interface states and traps. These factors have been studied by investigating the temperature dependences of the capacitance and the current-voltage characteristics and will be reported elsewhere.

REFERENCES

1. G.A. Chamberlain, Solar Cells (1982) in press.
2. G.A. Chamberlain, J. Appl. Phys., 53, 6262 (1982).
3. L.G.S. Brooker, G.H. Keyes, R.H. Sprague, R.H. Van Dyke, E. Van Lare, G. Van Zandt, F.L. White, H.W.J. Cressman and S.G. Dent, Jr., J. Am. Chem. Soc. 73, 5332 (1951).
4. S.M. Sze, Physics of Semiconductor Devices (Wiley-Interscience, New York, 1969), p.140.
5. K. Kudo and T. Moruzumi, Japan J. Appl. Phys., 20, L553 (1981).
6. H. Meier, Organic Semiconductors (Verlag Chemie, Weinheim, 1974), p.429.
7. G.A. Chamberlain and R.E. Malpas, Faraday Disc. Royal Soc. Chem., 70, 299 (1980).