Photovoltaic Solar Cells Based on Rare Earth Bisphthalocyanine Complexes

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Photovoltaic Solar Cells Based on Rare Earth Bisphthalocyanine Complexes.

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We describe here the elaboration of photovoltaic cells based on rare earth bisph-thalocyanine complexes. Those p-type organic compounds have been use in Schottky and pn configurations. Depending on the lanthanide rare earth of the Pc_2Ln complexe, the absorption band characteristics of Pc and Pc_2Ln generates intense ,weak or no photocurrent. This observation can be directly related either to the size of the Ln atom or to the structural organisation of the Pc_2Ln thin films.

INTRODUCTION

Recent studies demonstrate the possibility to realize photovoltaic (PV) cells using organic semiconductors[1]. Organic compounds offer potential advantages in term of ease of processing and deposition, low processing costs and a nearly unlimited variability. Nevertheless, up to now organic PV cells have low conversion efficiencies, the best values (close to 1%) having been obtained with copper phthalocyanine and perylene in a pn heterojunction[2]. However, several ways can be considered to improve their efficiencies. PV cells have to combine a high optical absorption in the visible range, stability under illumination, in air and in the presence of moisture, and good

properties of charges transport. Significant effort has been expended in the design and synthesis of new materials with a view to controlling and enhancing materials properties. However, it has recently become apparent that other factors such as (i) molecular ordering within an organic thin film, and (ii) the nature of the interface formed following metallization of the semiconductor, can significant influence device characteristics.

One of the most efficient class of organic semiconductors for solid state PV conversion is that of phthalocyanines (Pc)[2]. These disk-shaped molecules absorb strongly over the visible range of light and also possess good transport properties. An alternative class of phthalocyanines is that of the complexes they form with rare earth elements[3]. These sandwich complexes Pc_2Ln also possess good transport properties which have been studied in field-effect transistors[4]. Nevertheless, their photovoltaic behavior has never been reported.

In this work, we report on photovoltaic cells based on various rare earth bisphthalocyanines: Pc_2Lu, Pc_2Gd, Pc_2La, Pc_2Eu and Pc_2Nd. Similarly to phthalocyanines, all Pc_2Ln absorb strongly in the visible range and behave as organic semiconductors. We have thus built PV cells having either a Schottky or pn configuration and checked the influence of the rare earth atom on the PV characteristics.

EXPERIMENTAL PART

The Pc_2Ln complexes are synthesized according to the method described by Moskalev[5]. It consists in heating a mixture of 1,2 dicyanobenzene and tris-acetate rare earth $Ln(CH_3COO)_3$ at 300°C in a sealed pyrex tube. The Pc_2Ln complexes are obtained in high yields as strongly colored powders melting or decomposing above 300°C. In spite of their poor solubility in organic

solvents, the Pc_2Ln complexes are first purified by extraction with dichloromethane in a Soxhlet apparatus. Further purification is realized by vacuum sublimation ($P=5.10^{-6}$ torr; $T=300°C$) during the film deposition step.
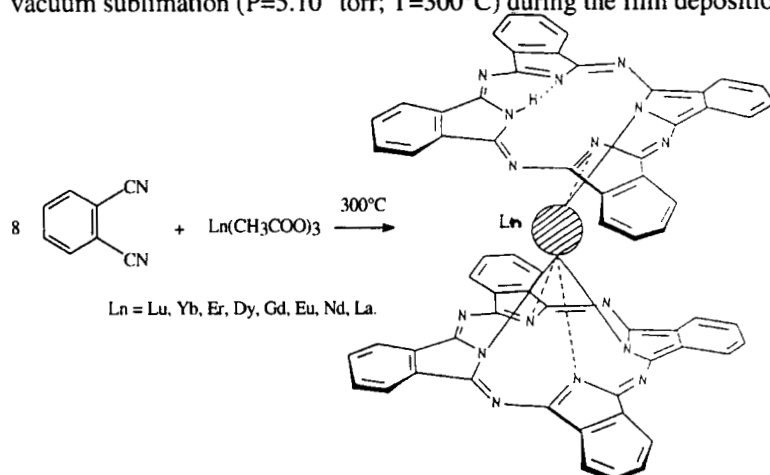
FIGURE 1   Synthesis and structure of bisphthalocyanine.

The Schottky and pn heterojunction PV cells are realized by the successive vacuum deposition (10^{-5}-10^{-6} torr) of the p- and n-type materials (or vice versa) onto a transparent glass substrate coated with SnO_2 ($\rho=10$ $\Omega/\square$; $s=15x15$ mm^2). For pn heterojunctions (see figure 2), the n-type
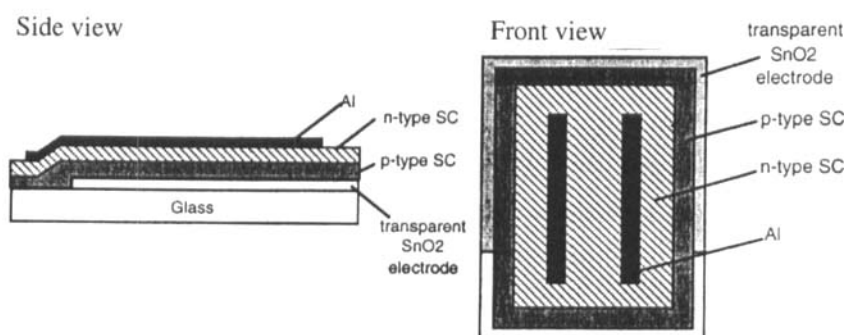
FIGURE 2   Structure of pn junction cell.

material[6] is N,N'-diphenyl 3,4,9,10-perylenetetracarboxylic-diimide (DPP), a perylene derivative whose structure is shown on figure 3. During deposition, the thickness of the organic layers (30-100 nm) is controlled by a quartz crystal microbalance. A semi-transparent aluminum layer (s=2x10 mm^2; thickness=20-30 nm) is then vacuum deposited through a mask as the top electrode of the PV device. By this procedure two identical independent cells can coexist on a single glass slide. The diodes are illuminated either through the transparent SnO_2 or semi-transparent Al electrode so that both interfaces with the organic layers can be probed.
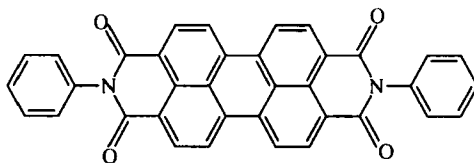

FIGURE 3   Structure of DPP.

The UV-visible absorption spectra of the various Pc_2Ln complexes are recorded on a Varian Cary 2415 spectrophotometer. The current-voltage characteristics of our PV cells in the dark and under white light illumination (P=80-100 mW/cm^2) are recorded in a Faraday box with a Hewlett-Packard 4140B picoammeter/DC source using two tungsten micro-electrodes. The action spectra ($i_{ph} = f(\lambda)$ of the Pc_2Ln based PV cells are obtained using a halogen photo optic lamp (36 V, 400 W), a Jobin-Yvon monochromator (1 nm/second scan rate) and a ATNE ADS 2 lock-in amplifier . The incident light frequency (80 Hz) is fixed with the help of a light chopper EGG 9479. The light beam is focused on the sample by a lens. The whole setup is run under software Keithley Das 1600. All action spectra are systematically corrected of the incident light intensity and sample area.

RESULTS AND DISCUSSION

The Pc_2Ln complexes present a sandwich structure (see Figure 1) where the rare earth atom Ln is between two Pc disks. In this 2:1 stoichiometry, the Ln atom is binded at six nitrogen atoms, one hydrogen atom bridging two nitrogen atoms of the macrocycle. Depending on the rare earth atom, a 3:2 stoichiometry can also be observed (Pc_3Ln_2). Such a stoichiometry appears progressively from lutetium to lanthane.

Lutetium bisphthalocyanine (Pc_2Lu) has been shown to be the first intrinsic molecular semiconductor[7,8]. At room temperature, its intrinsic charge carriers concentration is $n_i = 3.10^{14}$ cm^3, its mobility being $\mu = 10^{-4}$ $cm^2/V.s$ and its conductivity $\sigma_i = 5.10^{-5}$ $\Omega^{-1}.cm^{-1}$ [9]. Beside, Pc_2Ln can be doped with electron acceptors and electron donors to yield highly conducting materials. In the case of Pc_2Lu and Pc_2Tm, both n-type and p-type majority carriers are observed depending upon the ambient atmosphere. In absence of air, n-type conduction takes place p-type conduction is only observed under air [4].

We describe now the I-V characteristics of a PV cell based on gadolinium bisphthalocyanine Pc_2Gd as a typical example of the present study. Figure 4 shows the I-V curves of the {$SnO_2/Pc_2Gd(50nm)/DPP(30nm)/Al$} cell, both in the dark and under white light illumination. The asymmetrical profile of the I-V curve in the dark (V = -1.5 to +1.5 volts) evidences the rectifying behavior of the diode. A photocurrent appears under irradiation through either the Al or SnO_2 electrode. The open circuit voltage ($V_{oc} = 0.85$ V), short circuit current ($I_{sc} = 3.9\ 10^{-7}$ A/cm^2) as well as the maximum voltage ($V_{max} = 0.5$ V) and maximum current ($I_{max} = 2.1\ 10^{-7}$ A/cm^2) of this PV cell lead to a fill factor FF=0.27 according to the classical relationship:

$$FF = V_{max} \times I_{max} / V_{oc} \times I_{sc}$$

The conversion efficiency of the {SnO_2/Pc_2Gd(50nm)/DPP(30nm)/Al} cell (η = 10^{-4} %) can then be calculated by dividing the maximum power output (P_{max} = V_{max} x I_{max}) by the incident light power P_i:

$$\eta = (V_{max} \times I_{max})/P_i$$
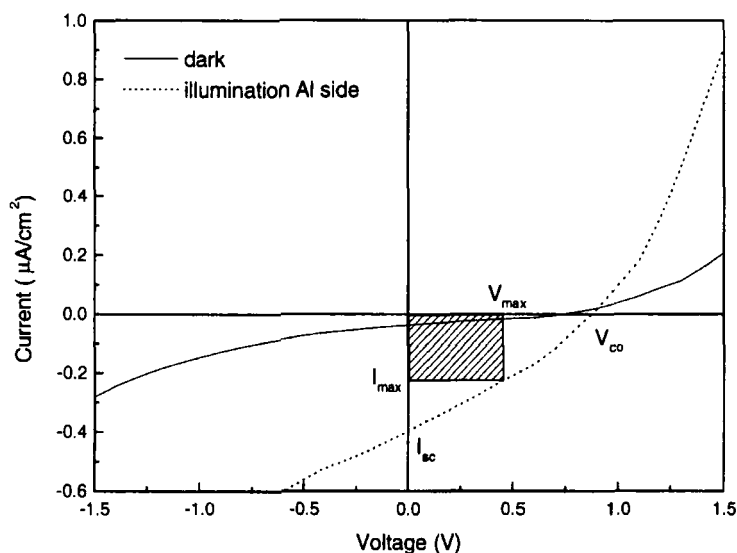
FIGURE 4   Current-voltage characteristics in dark and under illumination of the {SnO_2/Pc_2Gd(50nm)/DPP(30nm)/Al} photovoltaic cell.

Figure 5 shows a typical action spectrum recorded when illuminating the diode {SnO_2/Pc_2La(30nm)/DPP(40nm)/Al} through the SnO_2 and Al electrodes. Absorption spectra of the DPP and Pc_2La layers are shown for comparison in figure 5a. Absorption of these two compounds is intense and complementary in the visible range. We note that the photocurrent spectra obtained by illumination through either the SnO_2 or Al electrode have a

similar profile and correspond to the absorption spectra of the respective compounds. The photocurrent density generated through the SnO_2 electrode
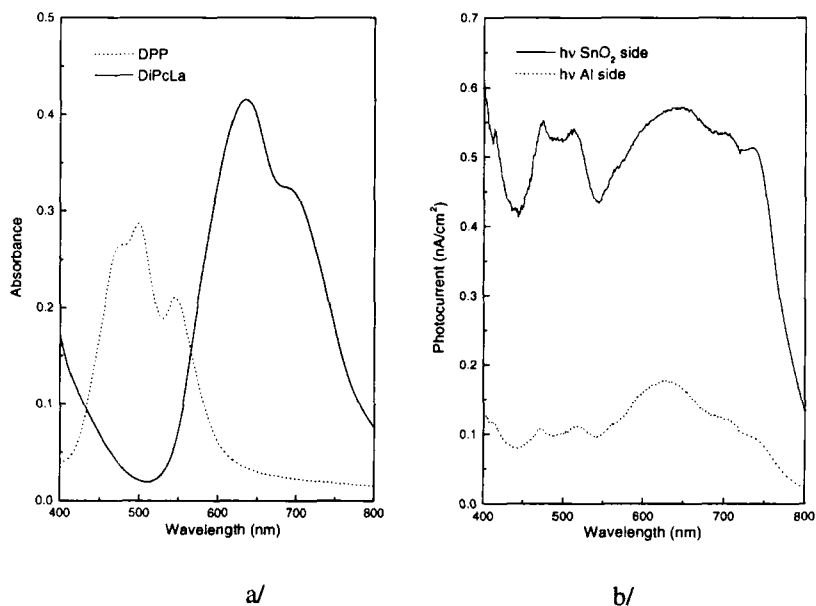

a/   b/

FIGURE 5   a/ Absorption spectra of DPP and DiPcLa films. b/ Photocurrent action spectra of the {SnO_2/Pc_2La(30nm)/DPP(40nm)/Al} photovoltaic cell.

is $i_{ph} = 0.5$ $\mu A/cm^2$ over the entire visible range. This value corresponds to the highest monochromatic efficiency ($\phi = 0.78\%$) obtained with photovoltaic cells based on Pc_2Ln complexes (see Table II). The monochromatic efficiency of the PV cell $\phi = (1242 \times I_{cc}/\lambda \times P_i) \times 100$ is calculated at the wavelength where photocurrent is maximum.

As another example, figure 6 shows the absorption spectrum of the lutetium complexe Pc_2Lu in thin film and its associated action spectra in the {SnO_2/Pc_2Lu(50nm)/DPP(50nm)/Al} diode under illumination through both SnO_2 and Al electrodes. In contrast to the lanthane complexe Pc_2La (see

above), the action spectra of the Pc_2Lu based diode do not show any photocurrent in the spectral region corresponding to the intense absorption characteristic of phthalocyanines and bisphthalocyanines. The observed photocurrent of the Pc_2Lu pn heterojunction over the 400-600 nm range is then clearly generated following absorption of light by DPP only.
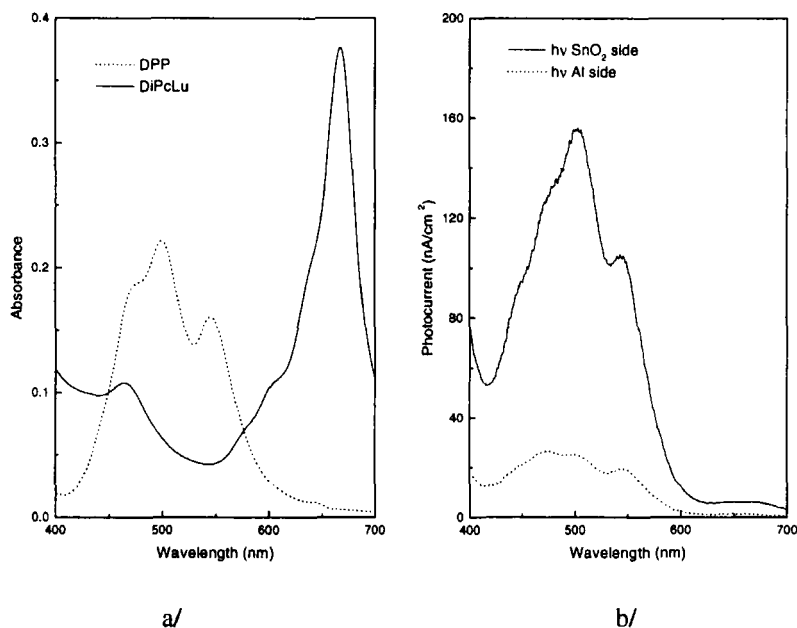

FIGURE 6   a/ Absorption spectra of DPP and DiPcLu films. b/ Action spectra of the {SnO_2/Pc_2Lu(50nm)/DPP(50nm)/Al} photovoltaic cell.

A similar observation can be done when the heterojunction is reverse so that the SnO_2 electrode is in contact with DPP instead of the Pc_2Ln complexe. Beside, this observation is confirmed in Schottky-type diodes such as {SnO_2/Pc_2La(150nm)/Al} and {SnO_2/Pc_2Lu(150nm)/Al}. In these devices, the intense absorption band of Pc_2Ln complexe generates a photocurrent only in the case of the lanthane rare earth ion. Finally, we note that for other

lanthane rare earths (Nd, Eu, Gd), the strong absorption band at 600-700 nm generates photocurrents whose intensity is intermediate between that of lanthane (intense photocurrent) and lutetium (no photocurrent). The main characteristics of all the PV cells under study are gathered in Tables I and II.

TABLE I I-V parameters (the open circuit (V_{oc}), short circuit (I_{sc}), fill factor (FF) and conversion efficiency) of photovoltaic cells based on rare earth bisphthalocyanine complexes.

Photovoltaic cells	V_{oc} (V)	I_{sc} (A/cm^2)	FF	η (%)
SnO$_2$/DiPcLa(150nm)/Al	0.24	2.08×10^{-10}	0.28	0.14×10^{-7}
SnO$_2$/DiPcLa(30nm)/DPP(40nm)/Al	0.42	2.06×10^{-7}	0.22	2.4×10^{-5}
SnO$_2$/DiPcNd(50nm)/DPP(40nm)/Al	1.72	2.35×10^{-7}	0.28	1.1×10^{-4}
SnO$_2$/DiPcEu(50nm)/DPP(40nm)/Al	0.48	1.08×10^{-8}	0.3	1.6×10^{-6}
SnO$_2$/DiPcGd(50nm)/DPP(30nm)/Al	0.85	3.98×10^{-7}	0.27	10^{-4}
SnO$_2$/DiPcLu(50nm)/DPP(50nm)/Al	0.39	6.57×10^{-8}	0.23	0.75×10^{-7}
SnO$_2$/DPP(100nm)/DiPcLu(350nm)/Al	0.045	1.07×10^{-8}	0.31	10^{-7}

TABLE II Monochromatic efficiency ($\phi = (1242 \times I_{cc}/\lambda \times P_i) \times 100$) of photovoltaic cells based on rare earth bisphthalocyanine complexes.

Photovoltaic cells	ϕ (%)
SnO$_2$/DiPcLa(150nm)/Al	0.09 at 706 nm
SnO$_2$/DiPcLa(30nm)/DPP(40nm)/Al	0.78 at 474 nm
SnO$_2$/DiPcNd(50nm)/DPP(40nm)/Al	0.028 at 520 nm
SnO$_2$/DiPcEu(50nm)/DPP(40nm)/Al	0.028 at 517 nm
SnO$_2$/DiPcGd(50nm)/DPP(30nm)/Al	0.044 at 471 nm
SnO$_2$/DiPcLu(50nm)/DPP(50nm)/Al	0.06 at 501 nm
SnO$_2$/DPP(100nm)/DiPcLu(350nm)/Al	0.084 at 465 nm

CONCLUSION

The use of rare earth bisphthalocyanines in Schottky and pn photovoltaic cells is reported here for the first time. The best conversion efficiencies (0.78% at 474 nm) are obtained with the lanthane complexe but remain far below that of monophthalocyanines. Depending on the lanthanide rare earth of the Pc_2Ln complexe, the 600-700 nm absorption band characteristics of Pc and Pc_2Ln generates intense (La), weak (Nd, Eu, Gd) or no (Lu) photocurrent. This observation can be directly related either to the size of the Ln atom or to the structural organisation of the Pc_2Ln thin films.

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