

# Optical and Electrical Properties of Vacuum Evaporated Sexithiophene Thin Films

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## ABSTRACT

Optical and Electrical Properties of Vacuum Evaporated Sexithiophene Thin Films have been studied in the present work. The optical properties of Sexithiophene layers have been studied by absorption spectroscopy and fluorescence. From the optical studies, it has been observed that sexithiophene can be absorbed in the visible region and the electronic transitions have been occurred in the absorption spectra and fluorescence spectra. The weak fluorescence of 6T thin film would be an asset to the photovoltaic conversion of solar energy. The total conversion efficiency of the fabricated cells has been calculated as  $\eta = 0.7 \cdot 10^{-2}\%$ . It is found that this very poor yield has been obtained mainly due to two factors. The first concerns the rate of photogeneration of free charges in the organic semiconductor since the excitons formed by light absorption of strong Frenkel excitons. The second is due to the small overlap of the absorption spectrum with the emission spectrum of the lamp. This manifest in the low lifetime of free carriers  $\tau = 4.3 \mu\text{s}$  from compared to the transit time  $187 \mu\text{s}$  which weakened due to the low carrier mobility.

**Keywords:** Organic materials, Optical Properties, Electrical properties, Photovoltaic.

## 1. INTRODUCTION

Conjugated organic materials are usually perfect insulators in the dark, but they become quite well conductors once enlightened. When a thin layer of organic semiconductor is sandwiched between two dissymmetric (with different work functions) then there exists an intrinsic electric field which is responsible of the driving force in the so called photovoltaic electronic excited states called excitons play an important role in transporting energy they are

electron-hole pairs bound by Coulomb attractive interaction, the creation yield of free carriers resulting from ionization of photogenerated excitons is strongly dependent on the effective applied field as described by Onsager's theory<sup>3-4</sup>. The optical excitations mostly lead to transitions in the visible spectrum sometimes in the UV. The photocurrent in such structures likely originates from ionisation of those tightly bound frenkel excitons usually met in organic materials. We are interested to oligomers comprising six units of thiophene (6T) and having a flat structure in the solid phase<sup>5</sup>.

## 2. EXPERIMENT

ITO (Indium Tin Oxide) glass slides have been used for the fabrication of diodes and quartz plates to study the optical characterizations like absorption and photoluminescence. The etching of the ITO blades by covering the suitable part with an adhesive tape and keeping them into a solution of 4N dilute hydrochloric acid. This allows us to have a blade partially covered with the ITO layer in order to subsequently avoid short-circuits, when taking the contacts on the aluminum electrode. The substrates obtained are cleaned according to a standard procedure consisting of 4 steps namely 1. ultrasonic bath in purified acetone for 15 minutes, 2. absolute ethanol bath for 15 minutes, 3. drying by argon flow, 4. drying in an oven at 150 ° C. for 30 minutes. These steps are essential for the accurate functioning of diodes. The surface state of the ITO is of great importance specially in its electronic properties such as its work output that can vary from a few tenths eV just by accurately cleaning its surface. Sexithiophene single crystals on ITO slides were grown from the vapor phase in a home-made vertical evaporator which consists of a 5-cm-diam glass tube, round closed at one end and fitted at the other to a gas stopcock. The powdered material was disposed at the bottom of the tube, and the crystals collected on a glass slide equipped with an appropriate collector and placed at the center of the tube. The tube was introduced in a vertical furnace, with the collector slightly above the inner rim of the furnace. The growth was conducted under argon reduced pressure (~500 Pa), at a temperature of 210 °C. The crystals, which appear as thin (~10 μm) orange plates with lateral dimensions up to 5 mm, were picked up from the collector after one or two days.

## 3. RESULTS AND DISCUSSION

### 3.1 UV-Visible absorption spectroscopy

Fig.1 shows the structure of Sexithiophene. The UV-Vis absorption spectra in the spectral range of UV-Visible (200 to 800nm), corresponding to energies between 1.5 eV and 6 eV is shown in Fig.2. In this field of energy absorbed photons induce electronic transitions as opposed to vibrational transitions observed in the infrared range.

The measure is to raise the spectral reference (baseline) and thereafter it falls within the spectrum by placing the sample on the optical path of the monochromatic light upstream of a detector. The absorption spectrum is given in optical density which is by definition

$$\text{D.O.} = \log \left( \frac{I_0(\lambda)}{I(\lambda)} \right)$$

From the absorption spectrum of sexithiophene thin layer, it may be noted that the 6T does not absorb light at low energies (long wavelengths) and the absorption edge is located around 550 nm. A more detailed representation of energy by adjusting the absorption bands by Gaussian functions, shows that the absorption edge is located exactly at 2.24 eV which corresponds to the optical gap of 6T. It is noted that the energy gap between the replicas vibronic 0.17 which is equivalent to the energy of vibration C=C binding. On the other hand, the transition to the high level of the bursting of Davydov is located 3,37 eV .

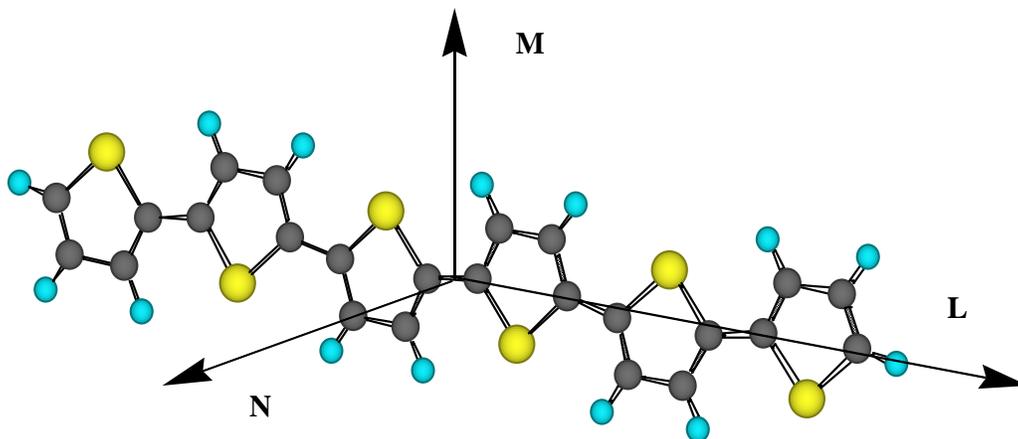


Fig. 1: Structure of Sexithiophene

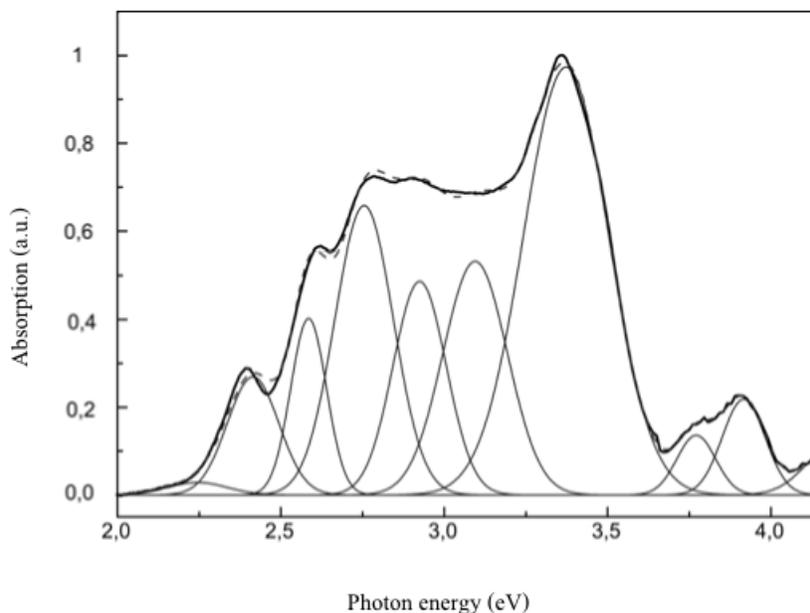


Fig. 2: Fit (dashed) absorption spectrum of 6T (solid line).

### 3.2 Photoluminescence Studies

The fluorescence spectrum of the thin layer of 6T was done using a spectrophotometer (Perkin-Elmer). 6T thin film deposited by vacuum evaporation on a quartz plate is placed in the spectrophotometer under  $45^\circ$  incidence. A Xenon lamp illuminates the entrance of the excitation monochromator that selects a wavelength at its output. The light emitted by the sample first passes through a filter that eliminates the excitation wavelength, is then collimated through a lens onto the entrance of the monochromator analysis. The signal delivered by the photomultiplier is recorded on a computer. The fluorescence spectrum obtained is shown in Figure 3. It is observed from the figure that there are presence of two fluorescence bands at 610 and 650 nm and a third of lower intensity around 720 nm. The light emitted by the thin layer of 6T is located in the red-orange region shows a weak signal may shows a weak signal may be an advantage for photovoltaic conversion. Figure 2 shows the fit of the fluorescence spectrum represented by four energy bands. Note here that the energy difference between two successive bands is that is quite consistent with the vibrational energy of the double bond  $C = C$ . The other by the transition to the ground state is not detectable because it is prohibited.

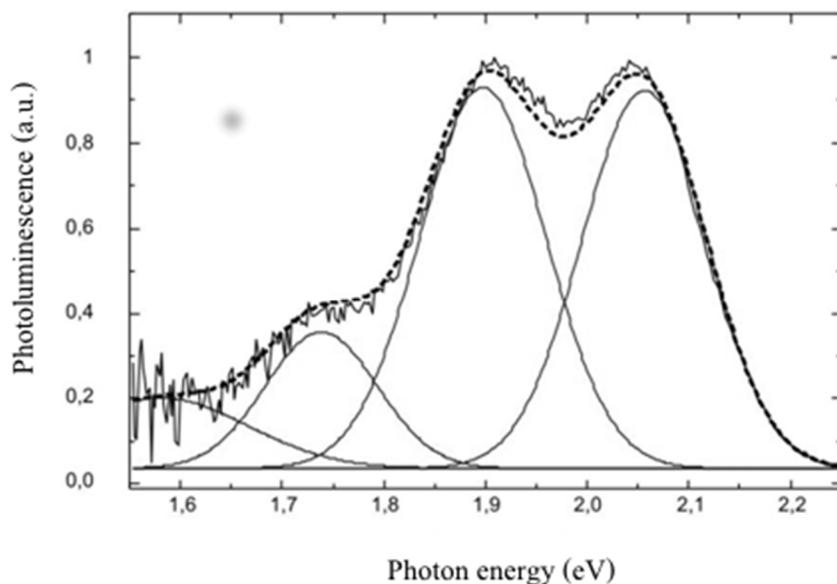
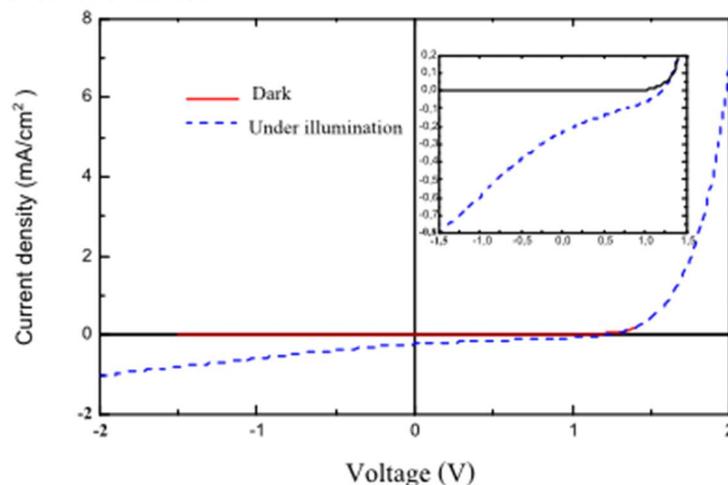


Fig. 3: Fit (dashed) of the photoluminescence spectrum of sexithiophene thin film (solid line).

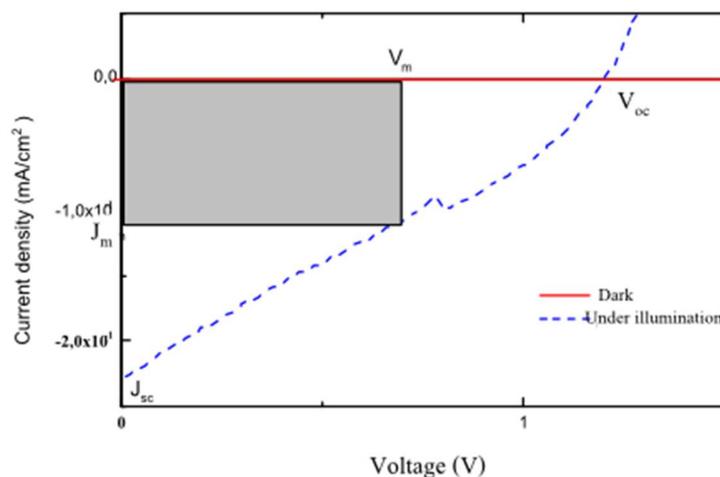
### 3.3 Electrical Properties

I-V measurements of the samples both in the dark and under illumination have been done. All measurements were made at temperature's room by scanning the voltage between two competing values and measuring the current at each applied voltage.

The sample is connected by one of its terminals to a programmable voltage generator (HP 33120A) as the external voltages not far and the number of accumulation. In measurements under illumination, the sample is illuminated by a tungsten-halogen lamp (ORIEL 66181) to which we have a heat filter (SHOTT KG2) to avoid heating the sample during the measurement. A cylindrical lens focuses the beam onto the active portion of the cell. Figure 4 shows the current-voltage characteristics of the cell ITO/6T/Al in the dark and under illumination. By examining the characteristic in the dark, it is observed that the cell has a rectifying character which proves that it is a diode. On the other hand, the characteristic under illumination differs significantly from that in the dark, this is proof that the fabricated cells have good photovoltaic behaviour.



**Fig.4** Current- voltage characteristics of the cell ITO/6T/Al In the dark and under illumination The inset shows that the photocurrent depends strongly on the applied voltage.



**Fig. 5** Magnification image

Figure 5 shows the rectangle of maximum power and the different parameters of the cell. For a power of incident light  $1\text{ W/cm}^2$ , the cell efficiency is  $7,7 \cdot 10^{-2} \%$ . This yield is very low compared to yields obtained with cells based on silicon and reach values one hundred times larger. This low value can be explained mainly by two factors. The first concerns the rate of photogeneration of free charges in the organic SC since the excitons formed by light absorption are of Frenkel type, that is to say very strongly bound excitons. The second, specific to 6T is due to its absorption spectrum which has two major drawbacks for photovoltaics: first by observing the absorption spectrum of 6T superimposed on the issuing of the lamp that most of the light emitted by the lamp is not absorbed and that the sample absorbs a fraction of the incident light. On the other hand, the OD (optical density) is low because the molecules are rod-shaped with a very large long axis compared to the other two axes are arranged almost perpendicular to the substrate surface, this has the effect of reducing the interaction of light with the layer of 6T reducing the absorption of light.

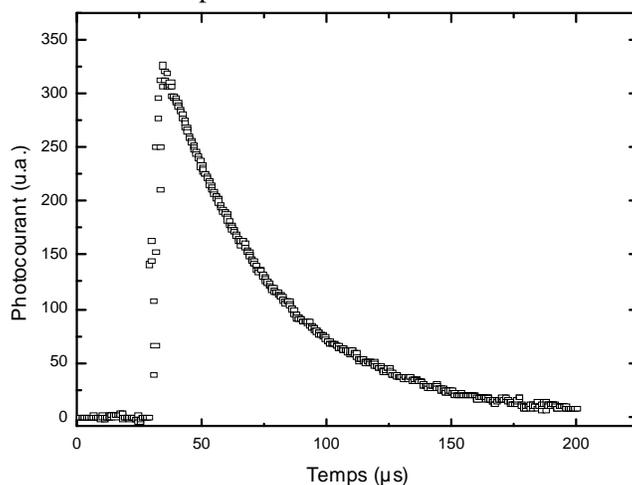
Analysis of these features gives the following photovoltaic parameters in Table.1:

**Table 1. Photovoltaic parameters**

$V_{CO}$ (V)	$J_{cc}$ ( $\text{mAcm}^{-2}$ )	$V_m$ (V)	$J_m$ ( $\text{mAcm}^{-2}$ )	FF
1.2	0.23	0.7	0.11	0.27

### 3.4 Study of the photocurrent transient pulse laser

The study of the transient photocurrent is a powerful tool that allows access to the kinetics of photogeneration of free charges in semiconductors. The experimental device consists of a neodymium laser (Nd: YAG) laser pulses of 7 ns duration at 532 nm. The pulse is focused through a cylindrical lens on the active part of the sample that is connected to a fast oscilloscope Tektronix 7912AD. All laser oscilloscope is controlled by a computer with a program that allows to average the decline of photocurrent on several measures. Figure 6 shows the variation of the transient photocurrent versus time on a linear scale.



**Fig. 6 Transient photocurrent.**

Indeed, in general, the kinetics of photogenerated carriers created by light is described by the following equation<sup>6,7</sup>:

$$\frac{\partial n_{ph}}{\partial t} = G - \beta n_{ph}^2 - \frac{n_{ph}}{\tau} \quad (I)$$

$n_{ph}$  Where is the density of free photo carriers created by the laser pulse, the term G represents the generation rate and the other two terms represent the "disappearance" charges. In this equation, the quadratic and linear terms correspond to kinetic bimolecular and monomolecular.  $\beta$  is called bimolecular recombination coefficient and  $\tau$  is the lifetime of free carriers.

In the present case, as the pulse is extremely short (7 ns) compared to the time scale on which we observe the photocurrent ( $\mu s$ ) can quite overlook the generation<sup>5</sup> term in equation (II) which simplifies to:

$$\frac{\partial n_{ph}}{\partial t} = - \beta n_{ph}^2 - \frac{n_{ph}}{\tau} \quad (II)$$

The term is dominant when the bimolecular rate of generation is very large in the case of a powerful light pulse strongly absorbed. Otherwise this is the monomolecular term wins<sup>9</sup>. In this case equation (III) becomes:

$$\frac{\partial n_{ph}}{\partial t} = - \frac{n_{ph}}{\tau} \quad (III)$$

The solution of this equation is  $n_{ph} = n_0 \exp\left(-\frac{t}{\tau}\right)$  of the form which is in agreement with the initialling of the photocurrent variation with time (Figure 6). Indeed, by observing the absorption spectrum of 6T can immediately realize that we are in the case of a light pulse absorbed very little (532nm), which translates into a low rate of photogenerated charges .The fit of Figure 6 gives a value of  $\tau = 43\mu s$  . On the other hand, the transit time of charges through the layer can be estimated from the following equation

$$\tau_{tr} = \frac{d}{\mu E}$$

Where the thickness of the active layer, E is is the electric field intrinsic reigned in the layer and  $\mu$  the mobility of charges in the 6T. For  $d = 150 \text{ nm}$ ,  $E \approx 4 \cdot 10^4 \text{ Vcm}^{-1}$  and  $\mu \approx 2 \cdot 10^{-6} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  the transit time is of the order  $187 \mu s$  . This time is much higher than the lifetime of free carriers which is an additional argument to explain the poor performance of our cells. It therefore appears that the determining factor is the low carrier mobility<sup>8</sup>.

#### 4. CONCLUSION

Optical and Electrical Properties of Vacuum Evaporated Sexithiophene Thin Films have been studied in the present work. The optical properties of Sexithiophene layers have

been studied by absorption spectroscopy and fluorescence. From the optical studies, it has been observed that sexithiophene can be absorbed in the visible region and the electronic transitions have been occurred in the absorption spectra and fluorescence spectra. The weak fluorescence of 6T thin film would be an asset to the photovoltaic conversion of solar energy. The total conversion efficiency of the fabricated cells has been calculated as  $\eta = 0.7 \cdot 10^{-2}\%$ . It is found that this very poor yield has been obtained mainly due to two factors. The first concerns the rate of photogeneration of free charges in the organic semiconductor since the excitons formed by light absorption of strong Frenkel excitons. The second is due to the small overlap of the absorption spectrum with the emission spectrum of the lamp. This manifest in the low lifetime of free carriers  $\tau = 43 \mu\text{s}$  from compared to the transit time  $187 \mu\text{s}$  which weakened due to the low carrier mobility.

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