

ORGANIC PHOTOCONDUCTOR TTF-TCNQ (TETRATHIAFULVALENE- TETRACYANOQUINODIMETHANE): A POTENTIAL ROOM TEMPERATURE INFRARED DETECTOR AT 10 μm

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Abstract

The absorption properties of charge transfer organic semiconductor TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) films deposited on KBr single crystal, quartz and glass substrates in far infrared have been investigated. An absorption edge at $\sim 10 \mu\text{m}$ was observed. Photoconductivity, photoconduction efficiency and gain and photocarrier's lifetime have been measured. The results show an electric field dependent photoconductivity. At an applied voltage of 14 V the photoconductivity reaches $1.2 \times 10^{-2} (\text{ohm}\cdot\text{cm})^{-1}$ which is almost the same as that of its DC dark conductivity, i.e. $1.8 \times 10^{-2} (\text{ohm}\cdot\text{cm})^{-1}$. Low temperature results show that the performance of the detector does not improve, but the field dependency, which was shown at room temperature, did not occur at low temperatures. The laser power dependency of the photocarriers showed that a single photon absorption process is involved. Slight deviation from linear dependency could be attributed to trapping in the band gap. It was concluded that the material may potentially be used as a CO_2 laser detector.

Introduction

The possible application of organic compounds to a variety of optical devices such as photorefractive waveguides, photoelectrochemical solar cells, xerographic photoreceptor in photocopiers and electronic printers has encouraged scientists to further investigate the optical properties of these materials. One of these compounds is organic conductor TTF-TCNQ with two types of conductivity, as a semiconductor at room temperature and

below 60 K as a metal, with conductivity changes in the range of $10^{-7} (\text{ohm}\cdot\text{cm})^{-1}$ to $10^{+5} (\text{ohm}\cdot\text{cm})^{-1}$ [1].

The optical properties of organic salts with the main emphasis on TTF-TCNQ have been studied since the early seventies [2]. The work carried out by Tanner and Jacobson [3] suggested that TTF-TCNQ has a very strong frequency dependent conductivity in far infrared which peaks at 1000 cm^{-1} at room temperature. They concluded that the conductivity change in infrared would yield an energy gap of 0.14 eV. They also showed that the conductivity increased by a factor of 10 when measured below 65 K.

Keywords: CO_2 laser; Infrared detector; Organic conductors; Photoconductor (organic); Photoconductor efficiency

Materials and Methods

TTF-TCNQ is a quasi one-dimensional organic conductor [4,5]. In the crystal structure, TTF-TCNQ large molecules are stacked on top of each other with closed-packed spacing in the stack or chain direction ($b=3.819\text{ \AA}$) and much larger spacing between molecules in the other two crystallographic directions ($a=12.298\text{ \AA}$, $c=18.468\text{ \AA}$). The molecular structure of the constituents and the ac plane of the crystal structure are shown in Figure 1. At room temperature, the conductivity along the chain b axis is $\sigma_b=600\text{-}900\text{ (ohm-cm)}^{-1}$, the ratio of the b axis conductivity to that of the a -axis direction where the current flows between unlike molecules σ_b/σ_a is $\sim 10^3$ at 300 K and increases to a maximum of 6×10^3 near 60 K [6]. Although extensive work has been carried out on the optical properties of TTF-TCNQ (see chapter 5 in ref. [2]) the application of the material as a photoconductive detector has not been investigated.

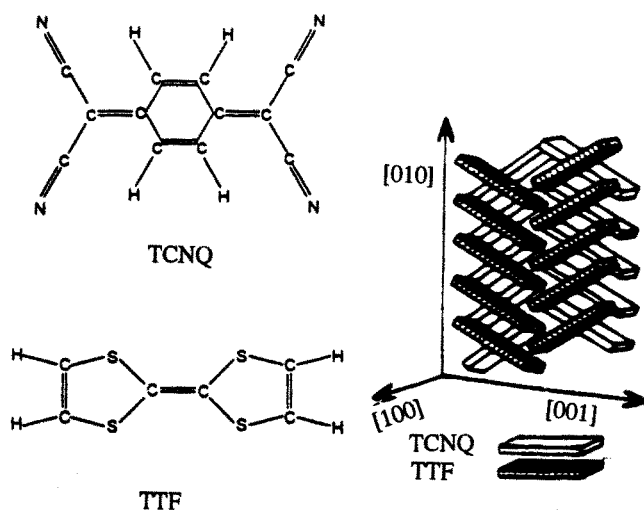


Figure 1. Molecular constituents and views of the crystal structure of TTF-TCNQ normal to the ac plane in the (100) direction (following Fig. 1, p. 89, [2])

Excitation spectrum at infrared (up to 1000 cm^{-1}) has been reported [8]. However, its absorption at $10\text{ }\mu\text{m}$ and the modest low dark conductivity along the normal to b axis makes it interesting to be considered as a photoconductive layer, when grown along the b axis. Epitaxial growth of TTF-TCNQ has shown that the films grow on a cleaved (100) face of rock salt and maintain the crystalline orientation [9]. Therefore, it seems that a thin layer of this material, $0.5\text{-}1\text{ }\mu\text{m}$, deposited on a crystalline substrate, should exhibit a reasonable photoconductivity at wavelengths around the energy gap. In this paper, we report on the fabrication of TTF-TCNQ photoconductor thin layers and their ability to perform detection when irradiated by a low power CO_2 laser at $10.6\text{ }\mu\text{m}$.

The salt was synthesized by mixing solutions of TTF in acetone and TCNQ in acetonitrile, filtering and then drying the mixture. The dark black powder was sublimated onto commercially obtained KBr substrates at a temperature $\sim 180^\circ\text{C}$ under a vacuum of 10^{-7} torr. The 1 mm thick single crystal KBr substrates were cut into 1 cm^2 dimensions along the (100) surface, and were polished on both sides. The thickness of the layers was monitored in the deposition system to better than a few angstroms. Metallic contacts were formed with a raster shape aluminum contact with an interspacing of $\sim 1\text{ mm}$. Prior to formation of the metallic contacts, the absorption spectra of each of the layers were measured. The effective photoconductive surface in between the contacts which absorb radiation was $\sim 5\text{ mm}^2$. The $V\text{-}I$ characteristic of dc voltage applied showed a good ohmic contact. The illumination of the surface was carried by an air-cooled CO_2 waveguide laser operating in CW mode at $10.6\text{ }\mu\text{m}$ with a maximum power of 1.4 watts . For irradiation at low temperatures, an infrared dewar with a silicon window was used. To measure photocurrent signal, a lock-in amplifier and a chopper operating at 630 Hz were used. At higher applied voltages a digital oscilloscope was employed. The circuit by which the photoconductivity measurements were made is shown in Figure 2.

In Figure 3 absorption spectrum of $1\text{ }\mu\text{m}$ thick film

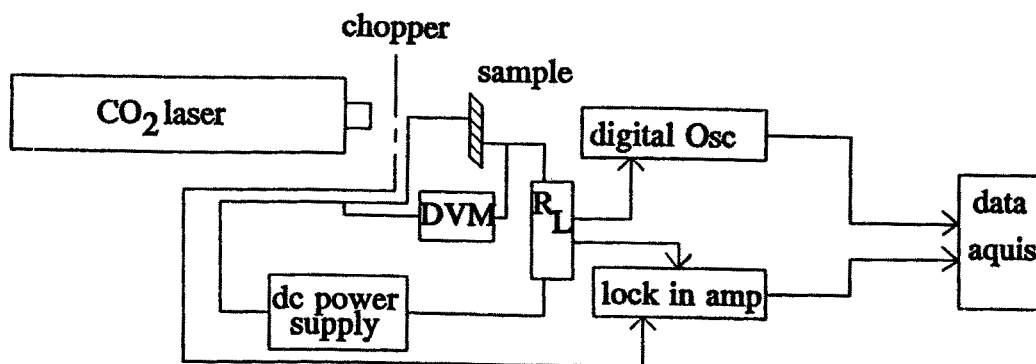


Figure 2. Experimental set-up for measuring photovoltage and photocurrent across a load resistance R_L

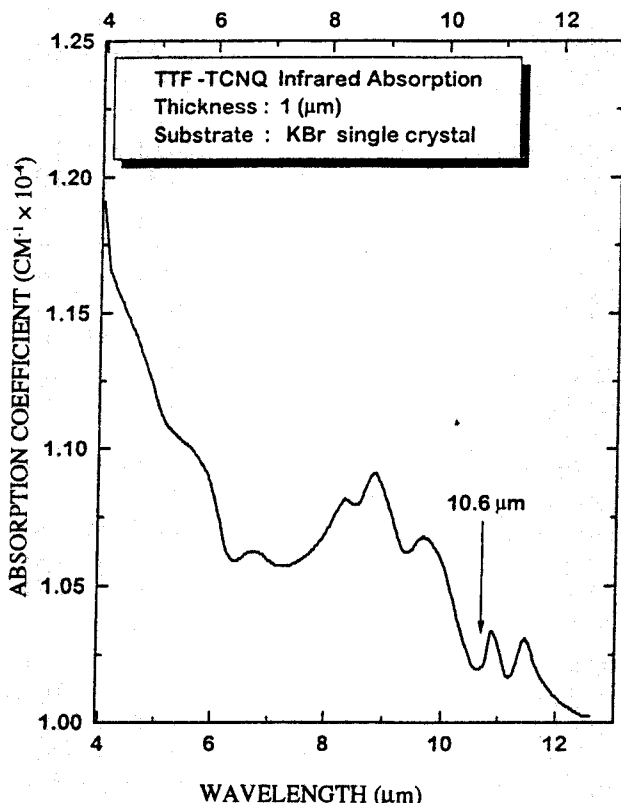


Figure 3. Infrared absorption of a 1 μm thick TTF-TCNQ layer deposited on (100) face of a KBr single crystal. The absorption edge at a wavelength of 10.6 μm is shown by the arrow

deposited on KBr substrate taken between 2500-300 cm^{-1} is shown. The spectrum exhibits an absorption edge at approximately 10 μm with absorption coefficient of $1.05 \times 10^4 \text{ cm}^{-1}$ which is in agreement with the spectroscopic work carried out earlier [3,10] by Jacobson *et al.* At low temperatures, however, there are many reports of a low energy gap ranging between 180 cm^{-1} to 300 cm^{-1} [11, 12, 13, 14].

Photoconductivity of the same sample at room temperature and at 77 K is shown in Figure 4. The data shows a change of photoconductivity with applied electric field at room temperature whereas at low temperatures, it remains approximately constant. At room temperature the increase in conductivity could be attributed to higher injection efficiencies [14], which in reality means higher collection efficiency. At low temperatures, however, the lower energy gap causes saturation in photocarrier injection occurs at very low electric fields.

Photoconductivity and photoconduction efficiency may increase with large applied electric fields, when the prepared sample has a low dark conductivity at room temperature. One of our samples which was prepared on glass substrate did show a very low dark current at room temperature,

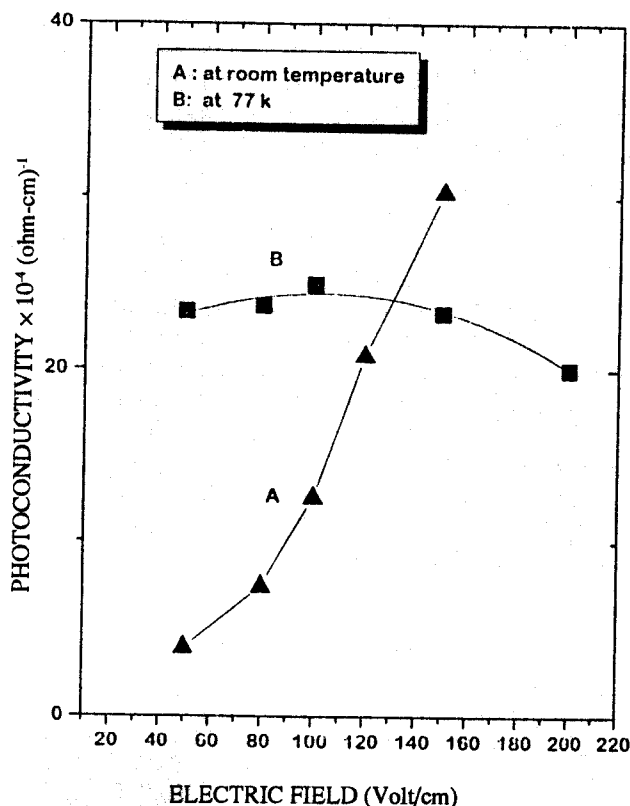


Figure 4. Measurement of photoconductivity against applied electric field at: (A) room temperature, and (B) at 77 K

hence it could withstand high electric fields. In fact the experiment with different substrates showed that the room temperature resistivity of TTF-TCNQ solid layers decreased with layer crystallinity. We observed that the resistivity of the layers deposited on glass, oriented quartz crystals, and on oriented (100) KBr single crystals decreased respectively. Figure 5 displays the photocurrent and the dark current under applied voltages of up to 700 volts for one of the samples prepared on glass substrates. The inset shows the difference in the load resistance voltage at a bias voltage of 250 volts. A difference of 14 volts induced by the incident beam is clearly seen.

In our experiment, the inter-spacing of the metallic contacts was 1 mm. By using smaller inter-spacing metallic contacts, we should be able to apply larger electric fields at a given bias voltage and reach higher efficiencies. One technique of reducing the dark current is to control the perimeter for a given optically active area. This would give an indication of whether there is surface leakage current with this material. From our dark current measurements we have calculated a dc conductivity of $1.85 \times 10^{-2} (\text{ohm-cm})^{-1}$. The maximum photoconductivity at room temperature in Figure 5 is $\sim 1.2 \times 10^2 (\text{ohm-cm})^{-1}$, which

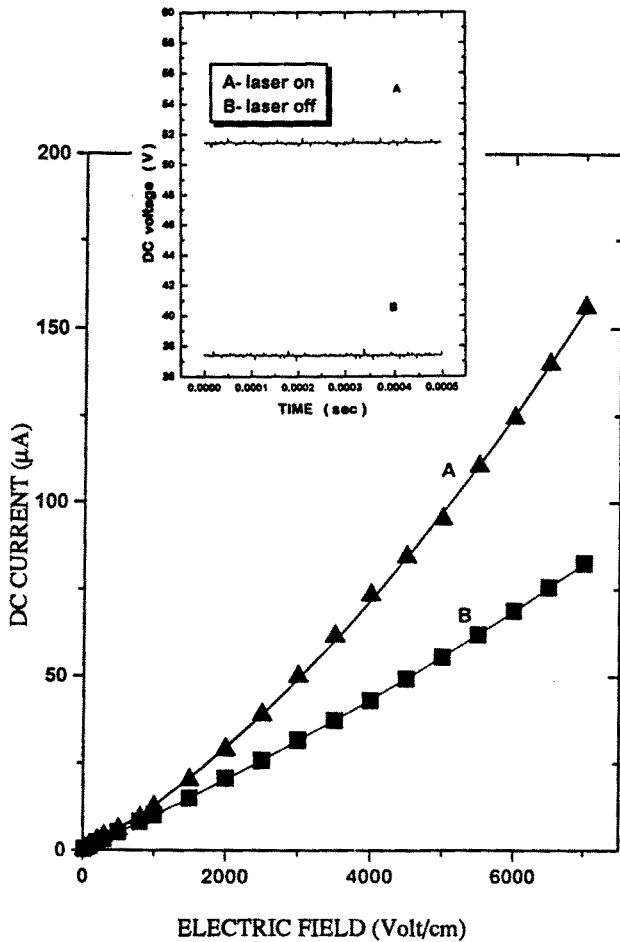


Figure 5. Measurement of DC current with: (A) laser on, and (B) laser off, plotted against applied electric field. The inset shows the change in DC voltage across a 1 MΩ load resistance at an applied electric field of 2500 V/cm

is comparable to its dc value showing that the material would have the same response to excitation by electric field or by photons at room temperature. In Figure 6, current decay of the photogenerated signal across 1 MΩ load was measured using an electronic shutter in front of the laser. The decay shows a slow recombination with a time constant of ~ 200 msec. which clearly indicates the presence of traps in the forbidden gap. The inset in Figure 6 shows the rise time which is in the same order confirming that generation recombination could have taken place via trapping centres in the energy gap.

In a semiconductor with an absorption coefficient α , the density of photogenerated carriers pair is [15]:

$$n_o = \frac{\alpha I_o \tau}{\hbar \omega} \quad (1)$$

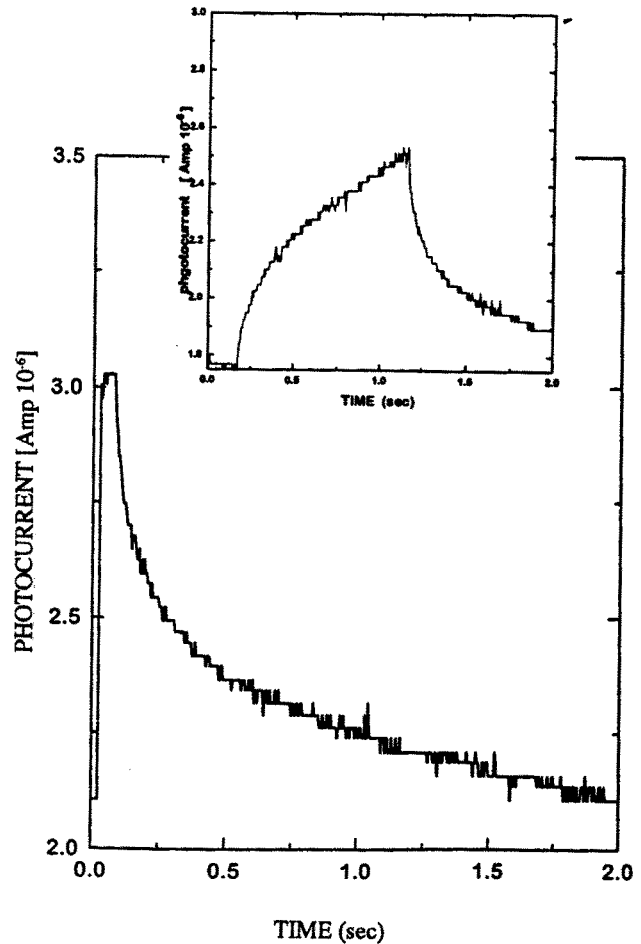


Figure 6. Measurement of photovoltage decay with an electronic shutter located in front of the laser. The inset shows the rise time for the same sample

where I_o is the irradiance of the incident beam, τ is the lifetime of the carriers and $\hbar\omega$ is the energy of the incident photons in joules. Now if we consider n as the density of photogenerated carriers collected at the terminal, considering $n = J_{ph}/quE = \delta/qu$ and also assuming that $\mu = v_d/E = d/\tau E$ then the quantum efficiency η can be written as:

$$\eta = \frac{\delta_{ph} E \hbar \omega}{\alpha I_o d q} = \frac{\eta}{\eta_0} \quad (2)$$

where δ_{ph} is the photoconductivity which can be obtained from experimental results, d is the length of the path in which photocarriers travel, μ is the carrier mobility, and v_d is the drift velocity. The quantum efficiency, η should increase rapidly with the applied electric field. Figure 7 shows the behavior of η , with electric field, measured at

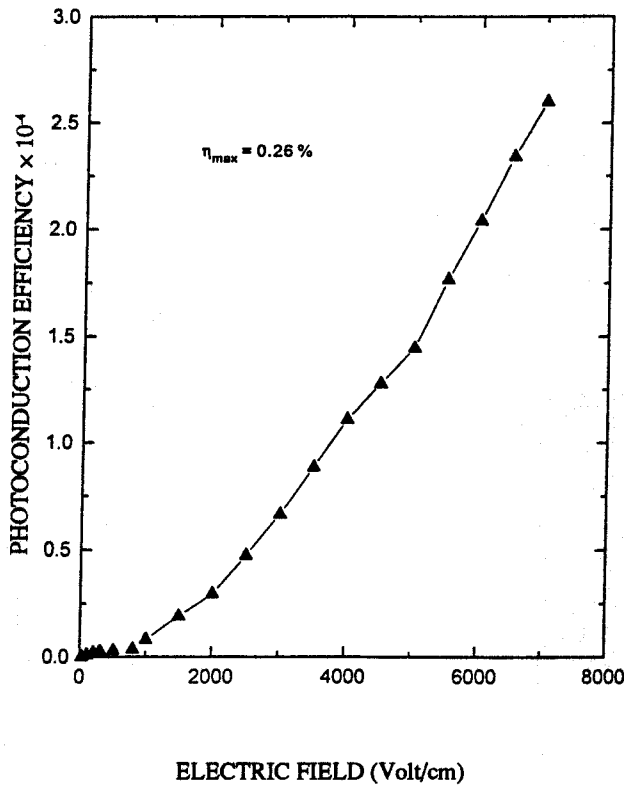


Figure 7. Photoconduction efficiency calculated from equation (2) as a function of applied electric field

room temperature. The quantum efficiency η , in equation (2) for photoconductive detector, has to be corrected for its dependency on the photoconductive gain, G .

Photoconduction gain may be defined as the ratio of the lifetime of the photocarriers to the transition time for carriers [16], i.e. the time required for that carrier to move between the electrodes:

$$G = \frac{\tau}{\tau_r} = \frac{l_d}{d} = \frac{\mu \tau V}{d^2} \quad (4)$$

where τ is the lifetime, μ the carrier's mobility, V the applied voltage and d is the electrode's spacing. The gain is therefore dependent upon the lifetime of the carriers and their mobility. Photoconduction gain can be less than or greater than unity depending upon whether the drift length L_d is greater or smaller than interelectrode's spacing d . Values of L_d greater than L imply that a free charge swept out at one electrode is immediately replaced by injection of an equivalent free charge carrier at the opposite electrode, thus a free charge carrier will continue to circulate until recombination at an ionized atom takes place.

To obtain a larger photoconduction gain, one desires high carrier lifetime, large mobility and high electric field

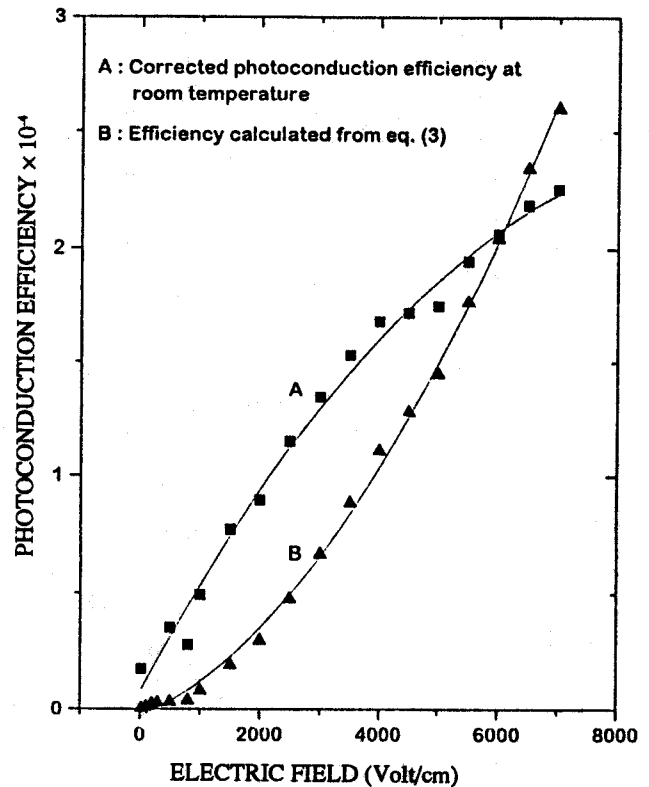


Figure 8. Comparison of the corrected photoconduction efficiency data and that of Figure 7.

strength in the photoconductor. The mobility is usually limited by neutral impurity scattering and since in the present experiment the impurity concentration is high, (and high concentration of impurities is essential to maintain high resistivity of the layer), little can be done to improve mobility. Lifetime can be maximized by elimination of the compensating impurities of the opposite type of the major ionized molecules. This reduces the number of ionized impurity sites that are recombination centres at which the carriers can terminate their lifetime. The limitation on electric field strength is impact ionization breakdown. This occurs when free charge carriers, accelerated by electric field, attain kinetic energy sufficient to ionize neutral molecules by inelastic collision. It occurs at some critical field strength and is accompanied by a drop in the detector's resistance and a complete loss of photosignal.

Regarding equation (3), the photoconduction efficiency calculated by equation (2) can be corrected for its dependency on photoconduction gain, i.e. τ/τ_r . In Figure 8, the effect of such a correction is shown. Data indicate that at lower applied electric fields, the corrected photoconductive efficiency n_c is larger than n , meaning that photoconductive gain is smaller than unity. At an electrical field strength of around 6000 V/cm these two curves cross, which is the electric field intensity required

to obtain a value of photoconductive gain $G=1$. The results therefore suggest that in order to obtain $G=1$ in a thin film TTF-TCNQ photoconductive layer, a minimum field intensity of 6000 V/cm is necessary.

Based on the data shown in Figure 4, a photoconductive gain of 6.3×10^{-3} was obtained for samples prepared on KBr substrates. This value is larger by a factor of 20 than that of visible organic photoconductors reported in references [16, 17, 18, 19, 20, 21]. In comparison, one can suggest that TTF-TCNQ is a reasonably sensitive photoelectric material.

The responsivity of an infrared photoconductor detector is defined as the ratio of the photovoltage signal generated at the load resistance to the power of the beam incident onto the surface of the detector. Figure 9 shows the responsivity as a function of the biasing voltage, obtained from the sample prepared on a glass substrate. The inset is the low voltage responsivity. Both data show a fairly linear increase in the detector responsivity with the applied electric field. Such dependency has been

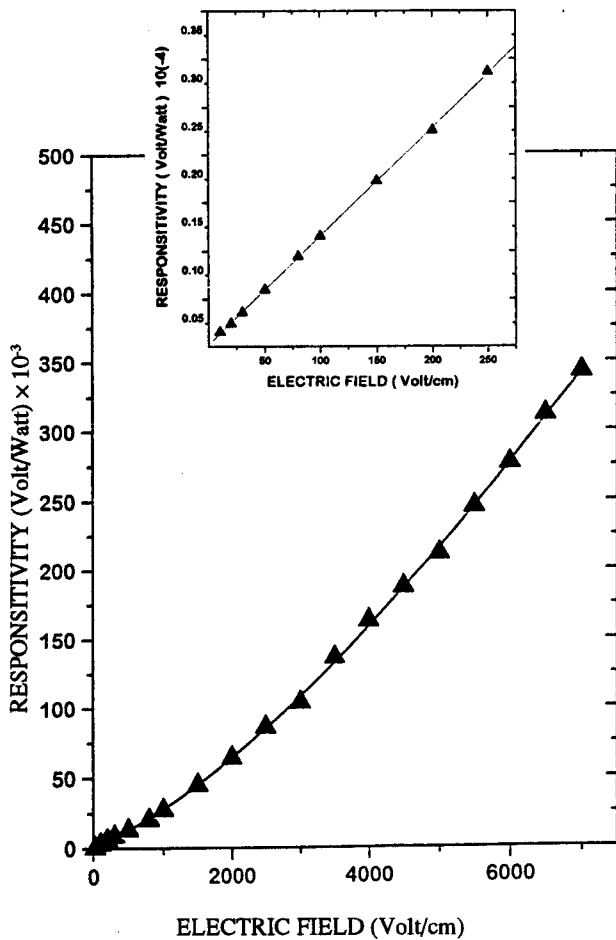


Figure 9. Presentation of the change in photoresponsivity. The inset is the low voltage responsivity.

observed for the well-known semiconductor infrared detectors such as HgCdTe [23,24].

The increase in responsivity is due to the increase in the sweepout factor which will have a larger value at higher electric fields [25]. A square root dependency of the responsivity of HgCdTe at 80 K has been observed [25]. Our results, however, do not show such a dependency but show linear dependency at low voltages and a weak exponential increase at higher fields. Our results on responsivity are consistent with the other field dependent data presented in this work. Regarding the magnitude of the responsivity of TTF-TCNQ thin films to that of the known semiconductors such as GaAs (10^3 - 10^4 V/w at 77 K, [26]), InSb (0.5-20 V/w at 1.65 K, [27]), HgCdTe (10^5 V/w at 80 K, [28]) and extrinsic Ge with gold impurity (10^2 - 10^3 V/w at 77 K) which show good performance at low temperatures only, this organic material could not compete with semiconductor infrared detectors, but it could be noted for its room temperature parameters given in this research work.

Power dependency of the photogenerated signal was measured between 100 mw to 900 mw. The change in the photocurrent signal with laser power fit very well in relation such as:

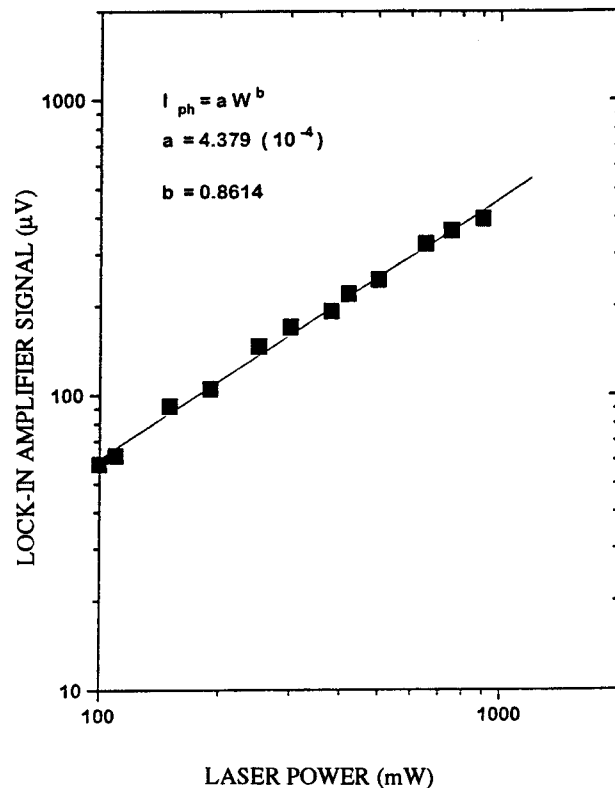


Figure 10. Power dependency of the photogenerated signal across a 100 K load resistance, and at a bias voltage of 15

$$I_{ph} = \alpha W^b \quad (4)$$

where a and b could be obtained from the data. A fitting value for $b=8614$ and $a=4.34 \times 10^{-3}$ give a very small deviation from linearity. This clearly indicates that photoabsorption is a single photon process and that small deviations could be caused by saturation in electron-hole pair generation.

Conclusion

The experimental results presented in this paper give evidence for relatively high photoconductivity of TTF-TCNQ thin films, compared with other organic materials. The advantage of this material is long carrier lifetime at room temperature, and simplicity of fabrication. However, the low mobility of the carriers ($\sim 10^{-5}$ cm²/v-sec) is a limiting factor for its photoresponsivity. This can be overcome by increasing the applied electric field on the material. Furthermore, it could be suggested that an MIS structure of this material would be useful in the investigation of detector performance under larger electric fields.

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