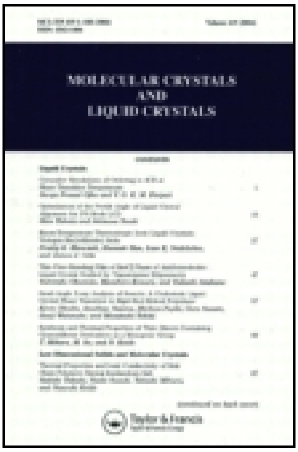

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Transient Photocurrents in Evaporated Films of Linear Trans-Quinacridone (LTQUIN)

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TRANSIENT PHOTOCURRENTS IN EVAPORATED FILMS OF LINEAR TRANS-QUINACRIDONE (LTQUIN)

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Abstract Transient photocurrent measurements on LTQUIN, a good photoconductor in the wavelength region between 200 and 600 nm, show an anomalous behaviour with respect to other organic photoconductors. Photoconductive action spectra are also reported.

Keywords: quinacridone, photoconductivity, polycrystalline solid films, charge transport

INTRODUCTION

Photoconductive effects in organic materials have long been known and are in fact utilized in xerography[1]. Recently some attempts have been made to build photovoltaic cells both all organic[2,3] and in combination with inorganic semiconductors[4,5].

Any organic compound to be used in fields like energy conversion, light sensors or xerography should meet the basic requirements of good chemical, light and thermal stability, and high absorption in the visible. The wide class of organic dyes seems to be the most promising for the above-mentioned applications, and among them, the quinacridones[6] could be good candidates; their extremely good chemical, light and thermal stability strongly suggest a study of their photoelectronic properties. Moreover, quinacridones are peculiar among photoconductors for having intermolecular H-bonds in the solid-state. Until now, investigations of the photoelectronic properties of organic materials have been limited to aromatic compounds with weak intermolecular interactions due to van der Waals forces. The presence in these dyes of intermolecular H-bonds, which are much stronger than van der Waals interactions, represents quite a new situation in this field, and should have some influence on the electrical properties of these systems.

Transient photocurrent measurements on the title compound have been performed in order to obtain information on the microscopic processes of charge transport determining the final macroscopic behaviour of these materials.

EXPERIMENTAL PROCEDURE

The title compound ($C_{20}H_{12}N_2O_2$, M.W. 312.33), whose structural formula is shown in Figure 1, is infusible and was purified by vacuum sublimation at about 420°C.

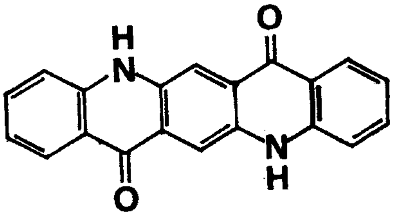

FIGURE 1 Linear trans-quinacridone (LTQUIN); structural formula.

Films were obtained by vacuum (10^{-2} Pa) vapour deposition at a controlled rate. Thin films (0.2 μm) for optical measurements (Perkin Elmer λ9 spectrophotometer) were deposited on a quartz substrate. The film thickness was measured using a Tencor Alpha Step 200 surface profiler.

Both steady state and transient experiments were performed on the following sandwich cell arrangement: semitransparent Al electrode deposited onto a polished quartz plate / 0.5 - 3 μm LTQUIN film / semitransparent top Al electrode deposited onto the LTQUIN film (electrode area = 0.78 cm^2). The sample, during the measurements, was mounted in an evacuable chamber.

Steady state experiments were performed using a 900 watt xenon lamp and a monochromator and monitoring, by means op a Keithley 485 picoammeter, the light induced conductivity changes in the sample under an electric field. The light intensity was measured with an EG&G power meter.

Transient photoconductivity experiments were made using the time-of-flight (TOF) technique[7]; as the light source, a pulsed nitrogen laser having an average maximum energy of 3 mJ/pulse at 337 nm and a pulse duration of 8 ns was employed. The laser energy was measured by means of a Laser Precision energy meter. The transient photocurrents were detected and analyzed by means of a Tektronix 468 digital oscilloscope interfaced with an Apple II computer.

RESULTS AND DISCUSSION

Steady state measurements

Solid LTQUIN absorption spectrum (Figure 2) shows a large band between 410 and 620 nm with two pronounced maxima at 560 nm ($\varepsilon = 6.3\times10^4$) and 524 nm ($\varepsilon = 5\times10^4$)

The photoconduction action spectrum when the positive electrode is illuminated is rather complicated, and depends on many factors, i.e. film thickness, light intensity and applied voltage. The experiments indicate that the decrease of the light intensity accompanied by an increase of the applied electric field changes the photoconductive behaviour from totally antibatic to quasi-symbatic with respect to the first absorption band (Figures 2 and 3).

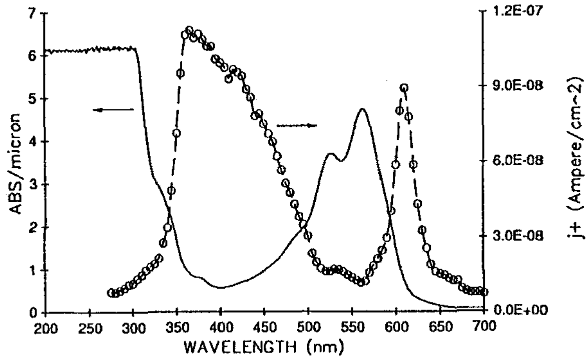

FIGURE 2 LTQUIN film 1.8 μm. Photoconduction action spectrum. Field = 2×10^5 V/cm, light intensity = 1.98×10^{12} phot/s cm^2.

The negative action spectrum, on the contrary, is completely antibatic in any experimental condition, pointing out that holes are the majority charge carriers (Figure 3).

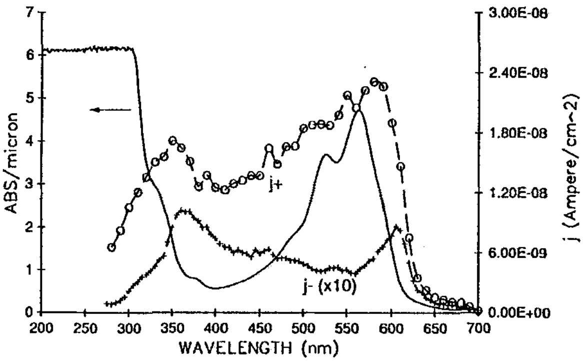

FIGURE 3 LTQUIN film 1.8 μm. Photocurrent action spectra.
Light intensity = 4.6×10^{10} phot/s cm^2.
(o) F = + 4×10^5 V/cm, (+) F = - 4×10^5 V/cm.

It is noteworthy to say that the photoconductive effect in LTQUIN is very strong, and that the gain at fields higher than 2×10^5 V/cm is near unity.

Transient measurements

All the experiments were performed at room temperature and pressure and with the illuminated electrode positively biased.

The shapes of the photocurrent signals obtained shining a laser light pulse on the LTQUIN samples didn't show any clear bending in the current decay, thus preventing the direct acquisition of the transport parameters over the entire electric field ranges investigated (inset in Figure 4).

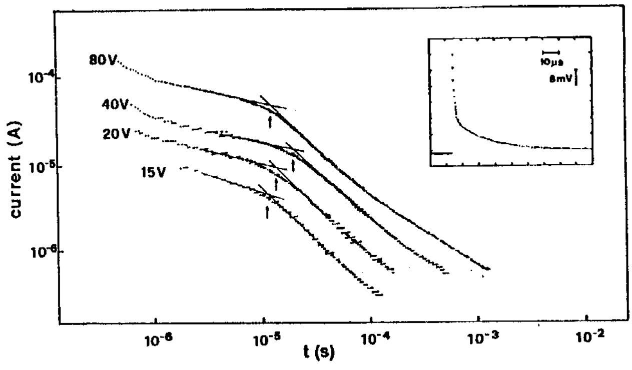

FIGURE 4 Experimental time evolution of the photocurrent on a log-log scale for different positive applied voltages; the arrows represent the transit times. Sample thickness is 2.8 μm. In the inset a representative photocurrent signal as it appears on the scope is reported.

By replotting the photocurrent signal on a double logarithmic scale (Figure 4), it was possible to obtain the transit time and consequently the effective mobility of the majority carriers (holes). Following the theoretical model for dispersive transport[8] in which the time dependence of photocurrent is:

$$I(t) \propto t^{-(1-a_i)} \qquad \text{for} \qquad t \leq t_T$$

$$I(t) \propto t^{-(1+a_f)} \qquad \text{for} \qquad t \geq t_T$$

where a_i and a_f are coefficients ≤ 1 and ≥ 0, the transit time t_T is indicated on the time scale by the slope change from $-(1-a_i)$ to $-(1+a_f)$.

In order to have a large enough time range, the curves in Figure 4 were obtained superimposing, in the log-log, scale subsequent single photocurrent signals in the same experimental conditions in which the input resistance on the oscilliscope and therefore the RC constant of the circuit were changed in order to cover a time range from 10 ms down to 500 ns.

Measurements at different electric fields were performed on a LTQUIN film

2.8 μm thick in which the light is completely absorbed in the first 0.5 μm (1/6 of the total thickness).

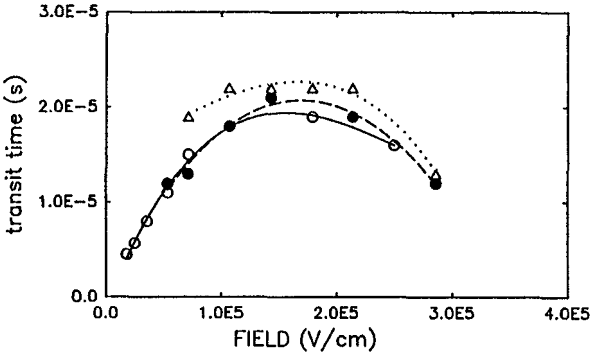

FIGURE 5 Field dependence of the transit time at three different light pulse energies: (o) E = 3.4×10^{13}, (●) E = 6.7×10^{12} and (△) E = 6.4×10^{11} phot/cm^2.

In Figure 5 the field dependence of the charge carriers transit time is reported. Three experimental runs were made at three different values of the light energy hitting the film surface and only in the highest energy case the condition:

$$\int i\,dt \leq 10^{-2}\ \mathrm{CV}$$

was not fulfilled and the space charge produced by the light pulse could not be neglected.

The plot shows a decrease of the transit time with the electric field, as expected, for fields higer than 2×10^5 V/cm and an anomalous behaviour at lower fields, in particular a transit time increasing with increasing field has never been reported.

In Figure 6 the mobility, μ, derived from the usual relation:

$$\mu = d^2 / (F\,t_T)$$

were d is the sample thickness, F the applied field and t_T the transit time, is plotted as a function of the applied field.

While for field values higher than 1.5×10^5 V/cm the mobility can be considered to mantain a constant value (7×10^{-5} cm^2/V s) in the entire range of the light energies used, it decreases, with increasing field, in the low field region. A low field mobility decrease is reported in the literature for some polycrystalline materials [9-17] but in our case the results cannot be straightaway interpreted in terms either of intergrain hindrance in the drift movement of the carriers due to a perturabation in the distribution of distances between localized states[15,18] or of local intergrain barriers created by trapped charge[13,19] or of the field independent diffusion contribution to the carrier movement[17].

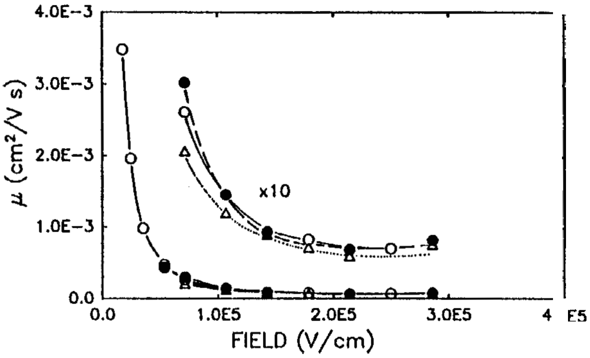

FIGURE 6 Field dependence of the hole mobility as derived for the transit time for three different light pulse energies. Symbols as for Fig. 5.

This anomalous charge transport behaviour might be due, in our experimental conditions, to a non constant electric field through the bulk, with the electric field profile remarkably changing when the external applied field changes. An aqueous blocking contact should eliminate this problem.

Furthermore it is worthwhile remembering that LTQUIN molecules, in the solid phase, have a partially ionic character, due to intermolecular H-bonds. How this ionic character influences the charge transport is, at present, not understood.

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