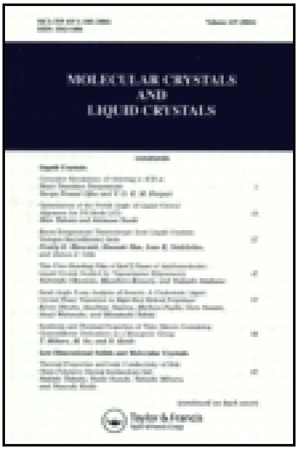

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Photogeneration and Transport of Charge in Vacuum Sublimed Linear Trans-Quinacridone Layers

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PHOTOGENERATION AND TRANSPORT OF CHARGE IN VACUUM SUBLIMED LINEAR TRANS-QUINACRIDONE LAYERS

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Abstract Results on steady-state and transient current photoconductivity in vacuum-evaporated films of linear trans-quinacridone (LTQUIN) are presented and discussed in terms of charge photogeneration and charge transport mechanisms. LTQUIN appeared to be a good photoconductor (photoconduction quantum yield Φ>0.2 e/photon) with hole effective mobility $\mu_h \approx 10^{-4}$ cm^2/V s being a decreasing function of electric field. The hydrogen bonds present in the solid LTQUIN lead to some particular features of its photoconduction at high electric fields.

INTRODUCTION

The investigation of photoelectronic properties of organic materials has been concentrated on compounds forming solid state due to relatively weak Van der Waals forces[1]. The search of possible applications of organic materials turned out the attention to other compounds characterized by good chemical, light and thermal stability. The wide class of organic dyes seems to be the most promising for applications in energy conversion systems[2,3], light sensors[2,3] or xerography[4]. Among dyes the quinacridones[5] are particularly good candidates for such applications due to their extremely good stability originated most probably from intermolecular H-bonds strenthening the crystal lattice. On the other hand, the presence of hydrogen bonds may influence electronic processes by a non-linear response to external electric fields due to electric-field dependence of the dielectric constant (see *e.g.* Refs. 6,7)

In an attempt to explore electronic properties of H-bonding molecular materials, photoconduction in vacuum-sublimed linear trans-quinacridone layers has been investigated in the present work. The results of this study demonstrate this compound to be a good photoconductor with some particular features reflecting electric field-induced changes in its dielectric behaviour.

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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.

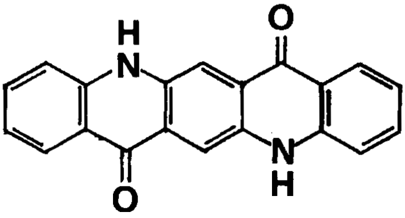

FIGURE 1 Linear trans-quinacridone (LTQUIN); structural formula.

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 of 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[8]; 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 ($\varepsilon = 6.3 \times 10^4$) and 524 nm ($\varepsilon = 5 \times 10^4$)

The photoconduction action spectrum when the positive electrode is illuminated is rather complicated depending on 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). Such a behaviour follows the theoretical predictions based on the model assuming simultaneous detrapping of charge by phonons and optical particles active in photoenhancement[9-11].

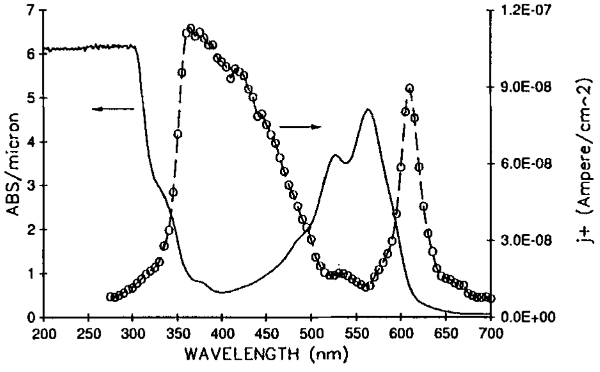

FIGURE 2 LTQUIN film 1.8 μm. Photoconduction action spectrum.
Field = $2x10^5$ V/cm, light intensity = $1.98x10^{12}$ phot/s cm^2.

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).

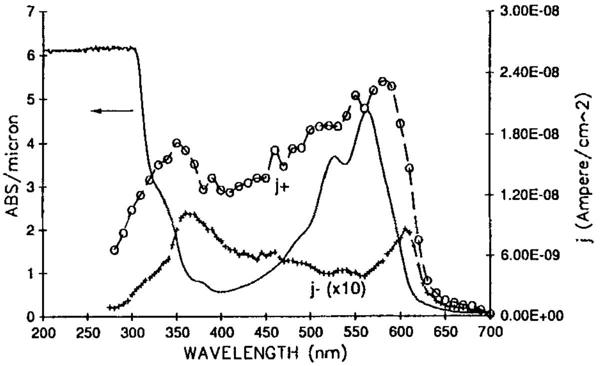

FIGURE 3 LTQUIN film 1.8 μm. Photocurrent action spectra.
Light intensity = $4.6x10^{10}$ phot/s cm^2.
(o) F = + $4x10^5$ V/cm, (+) F = - $4x10^5$ V/cm.

It is noteworth to say that the photoconductive effect in LTQUIN is very strong and the gain at fields higher than 2x10^5 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).

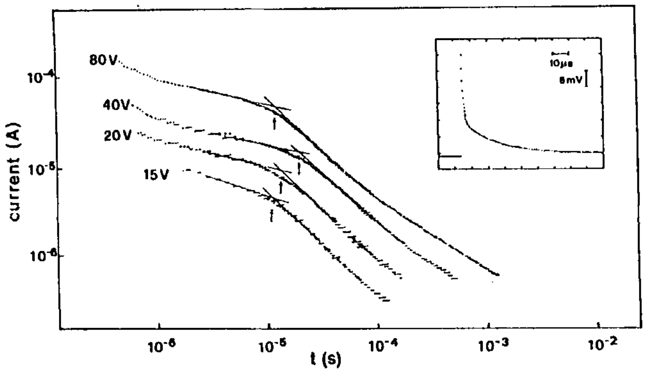

FIGURE 4 Experimental time evolution of the photocurrent on a log-log scale for different positive applied voltages; the arrows represent the transit times. Sample thickness is 2.8 μm. In the inset a representative photocurrent signal as it appears on the scope is reported.

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[12] in which the time dependence of photocurrent is:

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

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

were 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, just changing the input resistance on the oscilloscope and therefore the RC constant of the circuit 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).

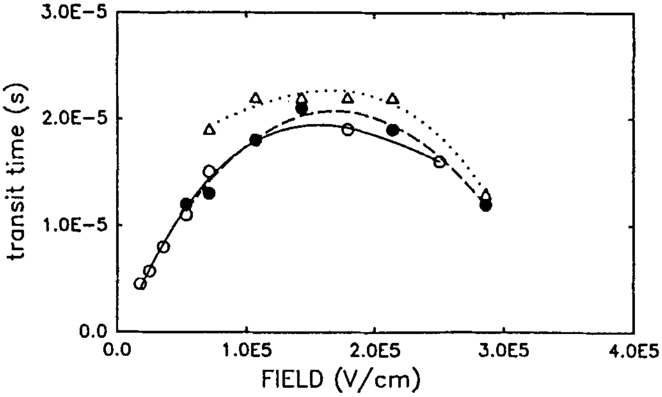

FIGURE 5 Field dependence of the transit time at three different light pulse energies: (o) $E = 3.4\times10^{13}$, (●) $E = 6.7\times10^{12}$ and (Δ) $E = 6.4\times10^{11}$ phot/cm^2.

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 $\int i dt \leq 10^{-2}$ 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 $\mu = d^2 / (F\ t_T)$, where d is the sample thickness, F the applied field and t_T the transit time, is plotted as a function of the applied field.

A weak 1/F decrease in the effective mobility above the field value ≈ 10^5 V/cm (at the maximum transit time) (see Figure 7) can be explained by a field-independent diffusion contribution to the carrier motion[13]: $\mu = \mu_{drift} + v_{df}F^{-1}$, where the pure drift mobility $\mu_{drift} = 2.1\times10^{-5}$ cm^2/Vs and the diffusion velocity $v_{df} = 12$ cm/s.

A strong initial decrease is due to the field increase of the transit time which is unusual feature not observed for aromatic compounds. This anomalous behaviour can originate from external field-induced internal polarization of the sample[6,7]. The direction and magnitude of the internal field is such that the small external field makes the total field (external+internal) smaller, leading to transit time increase.

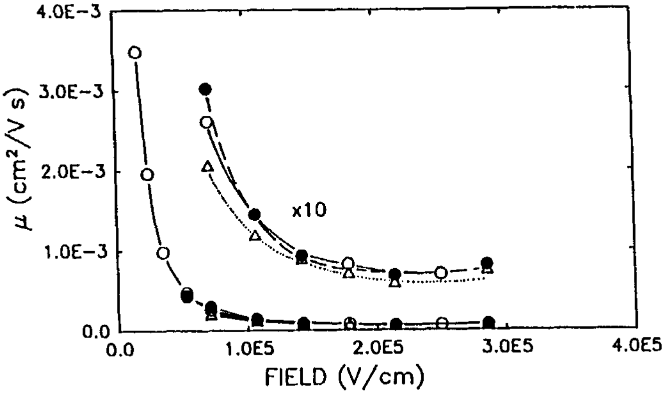

FIGURE 6 Field dependence of the hole mobility as derived from the transit time for three different light pulse energies. Symbols as for Fig. 5.

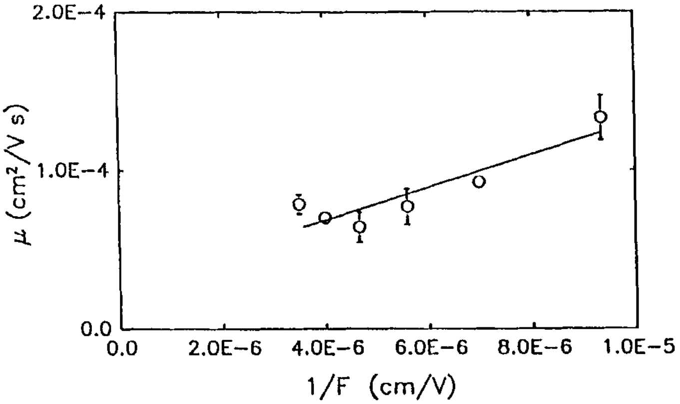

FIGURE 7 Effective mobility as measured by the transit time above $F \approx 10^5$ V/cm plotted vs. 1/F.

The influence of the applied field consists of the proton shift forming a high-polarity intermolecular charge-transfer species. This effect (possibly enhanced by photoexcitation) is supported by a large contribution of the second derivative of the absorption spectrum to the long-wavelength electroabsorption signal observed recently on LTQUIN thin films[14]. Though the non-linear response of t_T to F below $F \approx 10^5$ V/cm seems to be well explained by the above mechanism, some influence of space charge (especially at high light intensities) cannot be excluded since its presence is indicated by light intensity and voltage variation in the "forward" action spectra of the photocurrent (see Figures 2 and 3). A more detailed, quantitative analysis of results and pulse conductivity experiments, being in progress, are needed in order to resolve this question.

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