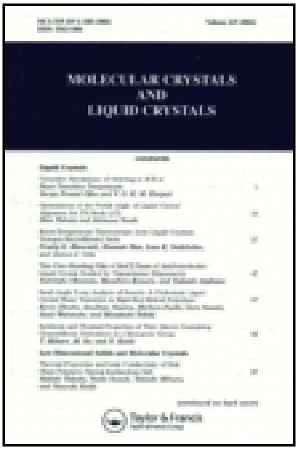

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Double Injection and Electroluminescence in p-Terphenyl Single Crystals

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Double Injection and Electroluminescence in *p*-Terphenyl Single Crystals

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Double injection currents in *p*-terphenyl are followed by light emission from decaying singlet excitons produced by the recombining electron-hole pairs. Only one singlet exciton is produced out of ~100 recombinations, the other recombinations are non-radiative. The current densities with gold and Na-Hg amalgam as hole and electron injecting contacts, respectively, approached the limit of volume-controlled currents, but were limited to well defined spots covering only 10^{-3}–10^{-4} of the contacts area.

I INTRODUCTION

Studies of electroluminescence in organic crystals have been carried out most extensively on anthracene,[1] but on other materials as well.[2–4] The low-mobility, organic crystals are characterized by efficient energy losses to phonons in the course of the electron-hole mutual approach towards recombination. Therefore, a direct radiative transition across the energy gap is very unlikely. Furthermore, photons emitted by any such transitions would have been immediately reabsorbed by lower energy excitonic transitions. The studies in anthracene showed[1] that each injected electron-hole pair produces either singlet or triplet excitons according to their multiplicities ratio (1:3). The singlet excitons then decay radiatively with the spectral distribution of the ordinary fluorescence. Studies in pyrene[3] showed quite different characteristics. The light emission yield was very low, only 10^{-3} photons per injected carrier, while the crystal fluorescence quantum yield is close to unity. The spectrum slightly resembled the ordinary fluorescense, but it showed additional structure, which changed with the current. Extension of the range of studied materials is thus very desirable.

II EXPERIMENTAL

The measurements were carried out on vapour-grown thin (10–100 μ) platelets of *p*-terphenyl crystals. The samples' large surfaces were parallel to the crystallographic (a, b) plane.[5] A Na–Hg amalgam and evaporated gold were used as electron and hole injecting contacts, respectively. The gold contact, of area $\simeq$ 0.1 cm^2, was made very thin ($\lesssim$500 Å), and was partly transparent to the emitted recombination radiation. The sample, after being mounted in its cell and application of the Na-Hg amalgam contact, was transferred to a vacuum chamber to prevent oxidation of the Na-Hg amalgam. The vacuum chamber had several quartz windows, towards which the crystal holder could be rotated for optical measurements. The fluorescence and electroluminescence spectra as viewed through the gold were measured with a Jarell-Ash double monochromator followed by a P.A.R. type 1P28 photomultiplier. The photomultiplier output current was measured with a Keithley model 153 microvoltammeter and recorded with a Moseley model 7030 AM recorder. The crystal fluorescence was excited with u.v. light of wavelength λ = 3300 Å obtained from a 2500 Watt Oriel Xe arc lamp followed by another Jarell-Ash monochromator. The voltage across the crystal was supplied by a Keithley model 246 high voltage supply and the currents were measured with a Keithley model 616 digital electrometer.

III RESULTS AND DISCUSSION

Gold and Na-Hg amalgam in contact with anthracene are known as good hole and electron injectors, respectively.[1,6] They are not as good carrier injectors to *p*-terphenyl. Particularly the Na-Hg amalgam showed no indication of electron injection at low fields when a conducting glass (SnO coated quartz) was used as a counter electrode. Gold was slightly hole injecting, and this was evidenced by a super linear voltage dependence of the current flowing through the crystal when the gold contact was made positive (again, with a counter conducting-glass electrode). Some current-voltage characteristics with various contact combinations are shown in Figure 1 on a log-log scale (the abscissa is blown-up 4 times compared to the ordinate). The open and full circles indicate the currents obtained with a gold contact against mercury, when the gold was made positive, or negative, respectively. At low voltages both I–V curves are superlinear, indicating that both contacts were hole-injecting. The break in the curve for positive gold marks the onset of electron injection by the mercury. The injected electrons reduce the positive space charge of the injected holes and enable higher injection rates. The currents at higher voltages were followed by

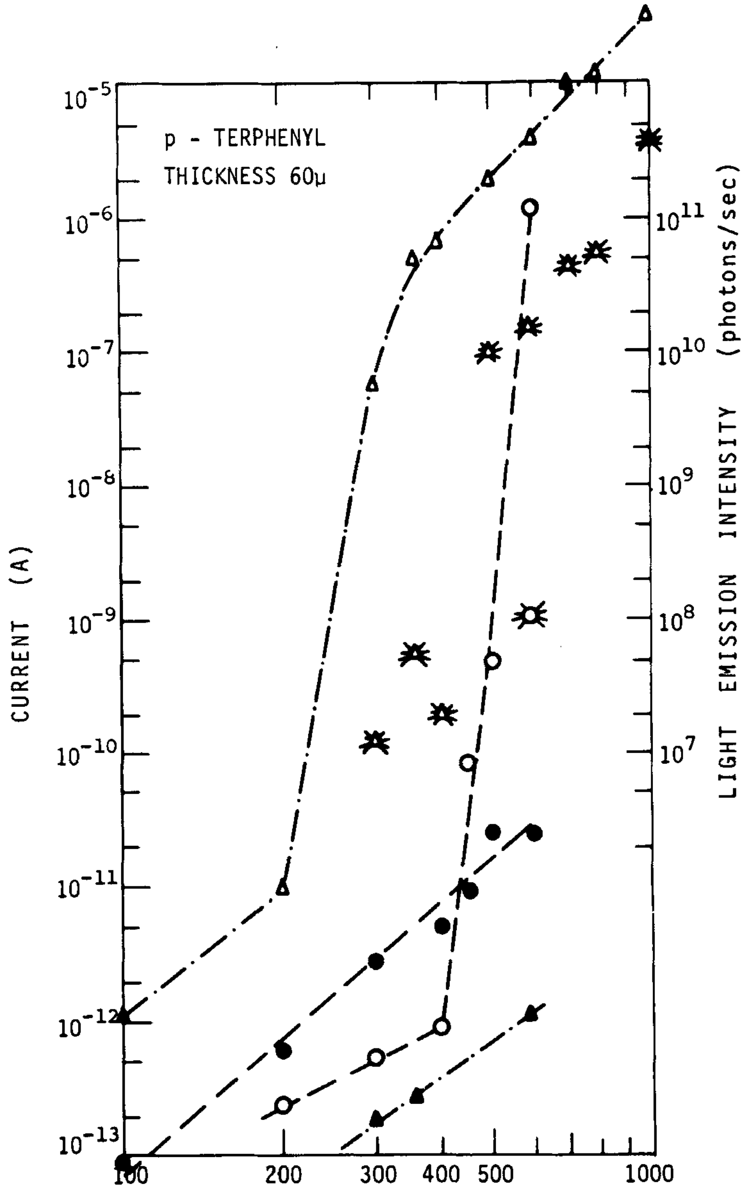

FIGURE 1 Log-log plots of current and light emission intensities as functions of voltage for different contact combinations. The current scale is given on the left ordinate and the light emission scale on the right. The abscissa is blown-up 4 times compared to the ordinate. Circles represent results obtained with gold against mercury contacts and triangles represent results obtained after the mercury contact was replaced by a Na-Hg amalgam. Open and full symbols, respectively, indicate a positive or a negative polarity of the gold contact. "Starred" symbols represent the light-emission intensity.

emission of recombination radiation as indicated in Figure 1 by the "starred" open circle. The scale for the light emission rate is marked on the right ordinate.

After making the above measurements, the mercury contact was replaced by a Na-Hg amalgam. The resulting current vs voltage curves are shown in Figure 1 by open and full triangles for the gold contact being positive, or negative, respectively. When the Na-Hg amalgam contact was positive (i.e., negative gold) the currents became more than an order of magnitude smaller compared to their respective value with the positive mercury. This is consistent with the interpretation of the latter currents as originating from hole injection by the mercury: The replacement of the mercury by a lower work-function contact material (the Na-Hg amalgam) has quenched the hole injection from that side. The residual currents could be caused by electron injection from the gold. In the other polarity (open triangles in Figure 1) the break in the curve occurs at a lower voltage (200 V, instead of 400 V for gold against mercury contacts combination). In this case the effect of reduction of the negative contact work function has enhanced the double injection currents, and the much higher currents are followed by light emission ("starred" open triangles).

The spectral distribution of the emitted light is shown in Figure 2 together with the ordinary crystal fluorescence spectrum. The two spectra are essentially identical, both result from radiative decay of singlet excitons. The

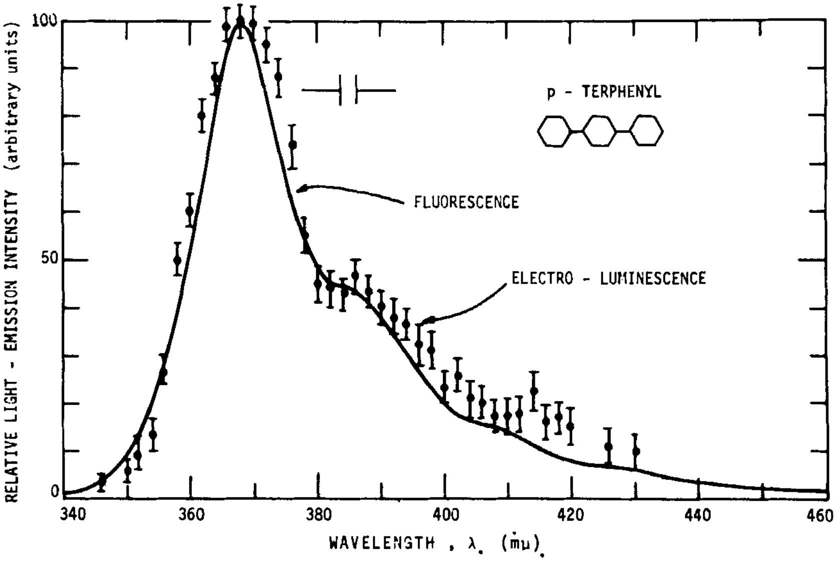

FIGURE 2 Fluorescence and electroluminescence spectra of *p*-terphenyl.

structure is due to splitting of the singlet ground state by molecular vibrations of energy 0.17 eV. Both spectra are similar to the fluorescence spectrum obtained with ultra-thin samples[7] but broadened, and modified on the short wavelength side by reabsorption in the crystal.

At low current injection rates ("contact-limited" currents), an injected carrier may cross the sample with little chance to undergo recombination with an opposite-sign carrier. Neglecting trapping, the electron and hole recombination lifetimes τ_n and τ_p, respectively, are given by

$$\tau_n = \frac{1}{Kp}; \tau_p = \frac{1}{Kn}, \tag{1}$$

where n and p are the electron and hole volume concentrations, respectively, and K is the recombination rate constant. In low mobility materials, such as *p*-terphenyl,[8] K may be expressed by Langevin's formula[1]

$$K = \frac{q\mu}{\varepsilon_r \varepsilon_0}, \tag{2}$$

where q is the electronic charge, ε_r is the crystal relative dielectric constant, ε_0 is the permittivity of free space and μ is an effective electron-hole relative mobility. Neglecting anisotropy effects, μ satisfies μ_n, $\mu_p < \mu < \mu_n + \mu_p$, where $\mu_n (= 0.35 \text{ cm}^2/\text{Vsec})$ and $\mu_p (= 0.8 \text{ cm}^2/\text{Vsec})$ are the electron and hole mobilities,[8] respectively. The electron and hole transit-times across the sample, t_n and t_p, respectively, are given by

$$t_n = \frac{L^2}{\mu_n V}; t_p = \frac{L^2}{\mu_p V}, \tag{3}$$

where L is the sample thickness and V is the applied voltage. The currents remain contact-limited as long as $\tau_n \gg t_n$ and $\tau_p \gg t_p$. When injection rates increase such that $\tau_n \sim t_n$ and $\tau_p \sim t_p$, the currents attain their maximum value and become "volume controlled." An expression for the maximum current density is derived by equating the transit and recombination times. The maximum current density J_{VC} is approximately given by[1]

$$J_{\text{VC}} \approx \frac{\varepsilon_r \varepsilon_0 (\mu_n + \mu_p) V^2}{L^3}. \tag{4}$$

When the actual currents satisfy Eq. (4), one may reasonably conclude that every injected carrier recombines inside the bulk. For smaller, "contact-limited" currents, the fraction of recombining carrier is approximately given by the ratio of the actual current density to the calculated "volume controlled" current density given by Eq. (4).

The high-voltage double injection current-voltage plot in Figure 1 (open triangles) shows a fourth power voltage dependence of the currents rather than a square voltage dependence as in Eq. (4). Also, the current densities are many orders of magnitude smaller. At first sight, both facts suggest that the contacts are incapable of supplying the maximum possible current. However, a major modification should be performed concerning the effective current carrying area. Careful inspection of the crystal during application of the voltage revealed, that not all of it was homogeneously fluorescing. The light emanated from well-defined spots, between 30 to 50 spots in that particular sample at 1000 V. The number of luminous spots increased with the voltage, and many of the spots were continually flickering. A crude estimate sets the diameter of each luminous spot as about 10–20 μ. Thus, the effective current-carrying area, identified by the luminous spots, was only 10^{-4}–10^{-5} cm^2. Accordingly, the actual current density at 1000 V was as high as 0.1–1 A/cm^2, a value approaching the limit given by Eq. (4) (1–2 A/cm^2). The fourth power dependence is partly because more luminous spots are "turned on" upon voltage increase. Perhaps it also reflects an increase in dimensions of each spot. It was, however, impossible to make any quantitative estimates of such changes.

From the above it appears that the fraction of injected carriers that undergo recombination is about 10^{-1}–1 in our case. The light emission efficiency, which is approximately constant in the voltage range 500 V–1000 V, is only $\sim 10^{-3}$ (emitted photons per injected carrier). Then only about one recombination out of a hundred result in the emission of a photon. The efficiency of light emission by decaying singlet excitons is very close to unity,[9] and they are the origin for the observed light emission. Therefore, the above is also a figure for the efficiency of singlet excitons generation. Most of the electron-hole recombinations ($\sim 99\,\%$) are non-radiative.

Returning to the nature of current injection, it is clear that the contacts used were basically very bad carrier injectors. However, possibly surface irregularities causing higher local fields, and/or variations of surface states properties enabled the occurrence of carrier injection in parts of the contacts area.

IV SUMMARY

This work is a study of double injection currents and recombination radiation in *p*-terphenyl. Gold and Na-Hg amalgam contacts were used as hole and electron injectors, but efficient injection took place in only 10^{-3}–10^{-4} of the contacts area. In that area the current densities approached the limit of volume-controlled currents. The recombination radiation has the same spectral distribution as the ordinary crystal fluorescence, both result from the radiative decay of singlet excitons. The major proportion of electron-hole recombinations is non-radiative. Only about one singlet exciton is produced per about 100 recombination events.

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