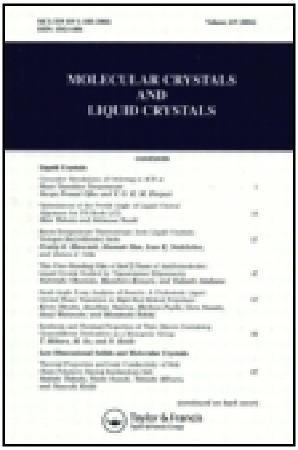

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Pulsed and Steady State Electroluminescence of Pentacene Doped Anthracene Crystals[†]

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The steady state and pulsed current-voltage-electroluminescence intensity dependences have been measured for pentacene-doped anthracene crystals over the temperature range 300–200°K. Prompt and delayed electroluminescence from both host and guest are produced. The overall electroluminescence efficiency with respect to input power is much less than for neat anthracene crystals, though efficiency is still high, ~10% with respect to crystal current.

For several years electrochemical electrodes have been used to produce electroluminescence in anthracene from the recombination of the injected electrons and holes.[1,2] This electroluminescence can be modified in intensity and/or energy distribution by doping the crystals with any materials which will act as a carrier trap.[3] Providing the dopant has a reasonably large fluorescence quantum efficiency, electroluminescence emanating from both anthracene and the dopant can be observed. Also because electron-hole recombination must finally produce both singlet and triplet excitons, it is possible that electroluminescence will show a time behaviour relating to the lifetime of these excitons, $\sim 10^{-9}$ sec and $\sim 10^{-3}$

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[§] National Research Council of Canada Postdoctorate Fellow 1971–72; present address: Mitsubishi-Kasei Institute of Life Sciences, 11 Minami oya, Machida-shi, Tokyo, Japan sec respectively; that is, prompt and delayed electroluminescence. However it has been seen that the bulk properties of a molecular crystal are easily pertubed by included molecules, for example inert gas molecules.[4] These additional traps caused by the guest may not be strongly evident in the spectral distribution of electroluminescence but will change the temporal dependence of electroluminescence, particularly that due to the long-lived host triplet exciton. We have studied the electroluminescence of anthracene-pentacene mixed crystals to note the influence of these traps, for it was anticipated that the triplet exciton lifetime in these crystals would be small, comparable or less than that in the corresponding anthracene-tetracene crystal.

The crystal ingots were melt grown in a Bridgmann type furnace[5] under helium gas from highly purified anthracene containing $\sim 10^{-4}$ mol/mol pentacene (Princeton Organics). Steady state measurements of the current-voltage (J-V) dependence, electroluminescence spectral distribution-current dependence were made over the temperature range 300–200°K. Using a pulsed voltage supply,[6] the time dependence of the pentacene and anthracene fast (nsec) and slow (msec) components of electroluminescence were observed. Each wavelength region was selected by combining appropriate optical filters. The cooled 9558 EMI photomultiplier used as detector was coupled with a time everaging computer to increase signal: noise ratios when required.

SINGLE INJECTION CURRENT-VOLTAGE-TEMPERATURE DEPENDENCE

As expected, steady state space charge limited hole and electron current-voltage-temperature curves all showed the presence of considerable trapping. At room temperature currents were $10^4 \sim 10^6$ times smaller than predicted trap free currents.[7] These results indicated the presence of an exponential energy distribution of electron traps plus a specific trap of ~0.44 ev. This depth agrees with the electron trap depth estimated from early literature values for the difference in electron affinities of anthracene and pentacene, Δ Ag = 1.2–0.74= = 0.45 ev.[8] but is in disagreement when recent magnitudes of these constants are used, Δ Ag ~ 0.7 ev.[9,10] Similarly an estimation of a hole trap at ~0.6 e.v. can be made from the respective ionization energies,[8] however the experimental results of hole current-voltage temperature dependences only showed the presence of exponential traps.

The magnitude of these specific trapping levels for pentacene are important when it is recognised that electron-hole recombination will certainly occur on such sites. Since the band gap in pure anthracene crystals is ~ 4.0 ev,[11] then recombination in a pentacene trap could make available a maximum energy of ~ 3.4 ev. This 3.4 ev is greater than that of the first excited singlet state of anthracene, ~ 3.1 ev,[12] and hence anthracene fluorescence produced directly from an electron-hole recombination in such a trap cannot be excluded.

VOLUME CONTROLLED CURRENT VOLTAGE-TEMPERATURE (J–V–T) DEPENDENCE

The volume controlled current (double injection) was always greater than that observed for single carrier injection, but was still in the order of 10 times smaller than predicted by Child's Law[7] for largest observed currents. Typically, $J \propto V^m$ was found, with m $3 \rightarrow 6$ depending upon the crystal, and also J decreased exponentially with respect to T^{-1} over the temperature range 200–300°K, i.e. $J \propto \exp(-1/kT)$.

CRYSTAL CURRENT-ELECTROLUMINESCENCE INTENSITY AND SPECTRAL DISTRIBUTION DEPENDENCE

Typical electroluminescence spectra are shown in Figure 1. The optically excited fluorescence spectrum of the same crystal is seemingly composed only of fluorescence due to anthracene because of both inefficient energy transfer to pentacene molecules and the relatively smaller pentacene fluorescence quantum efficiency. However components due to anthracene, 453 mμ and 480 mμ, and pentacene,[13,14] 612 mμ and 668 mμ, are easily recognized in electroluminescence. With high crystal currents, as the temperature was decreased to ~ 200°K, little change in relative intensity of the pentacene peaks occurrends, and no additional peaks appeared. The 0–0 singlet emission of anthracene becomes visible due to the decrease of reabsorption, together with a broad background emission, maximum ~ 480 mμ. If this background emission is subtracted the ratio of anthracene:pentacene electroluminescence decreases markedly as the temperature is lowered. At each specific temperature, the intensity of both anthracene (453 mμ) and pentacene (612 mμ) electroluminescence increased superlinearly with respect to the crystal current, and no saturation of pentacene emission with crystal current was evident. These results all indicate that the pentacene-anthracene system behaves similarly to a tetracene-anthracene mixed crystal system at room temperature,[15] but at lower temperatures the appearance of a background anthracene-defect electroluminescence[16] indicates the anthracene lattice has been considerably perturbed by the inclusion of the large pentacene molecules.[3,4] Indeed defects with exciton trap depths equal to that of the guest pentacene are evident from the spectra in Figure 1. Because a change in trap distribution would have a great influence, even at room temperature, on the time dependence of both the pentacene and anthracene components of electroluminescence, pulsed voltage measurements were made.

PULSED VOLTAGE-ELECTROLUMINESCENCE INTENSITY DEPENDENCE

Two separate electrode combinations were used for pulsed experiments, namely electrode combinations giving rise to either forced injection[4] or double injection. The general behaviour of both the crystal current and electroluminescence intensity transients were similar to those obtained for pure anthracene crystals.[4] No difference was found for either the pentacene or anthracene electroluminescence transient components even in their fast rise times,~1μsec which were always equal to that of the applied voltage pulse. This shows that carrier recombination gives rise to prompt electroluminescence emanating from both the guest and host in contrast to anthracene-tetracene. This result is to be expected from the SCLC results, for recombination in a pentacene trap may still provide sufficient energy to produce an excited anthracene singlet exciton. Delayed electroluminescence was also observed for though the voltage pulse decay was ~ 10^{-5} sec kV^{-1}, a considerable tail was observed which had a decay time in the millisecond region. Two components were found present in this slow decay, one of which was removed by applying a reverse bias voltage to the crystal and was thus due to carrier detrapping, Table I. The decay time of the electroluminescence slow components was ~2.5 msec, with bias voltages of ~ 5 kV cm^{-1}, and was unchanged as this bias voltage was increased.

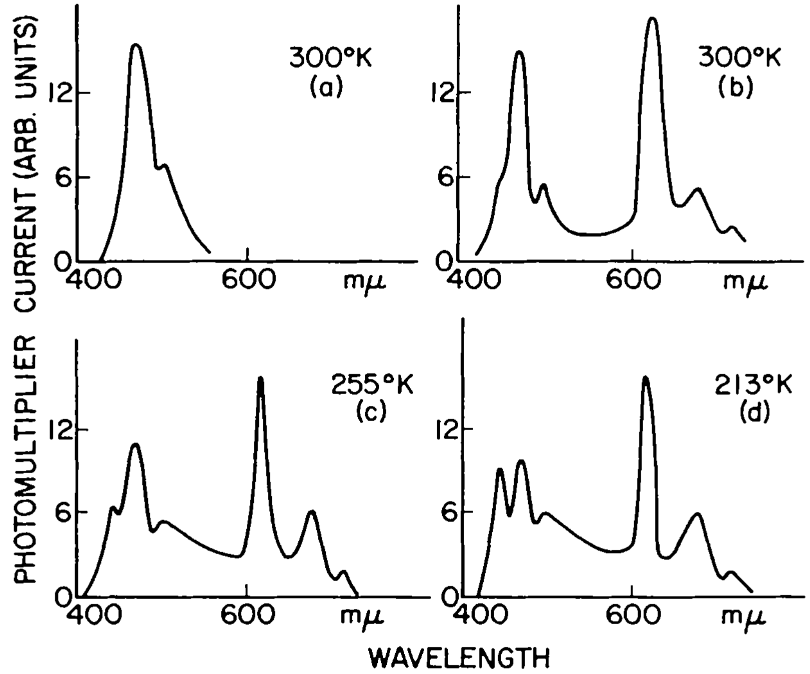

FIGURE 1 Comparison of the temperature dependence of observed electroluminescence spectra (b,c,d,) and a room temperature fluorescence spectra (a) for a pentacence doped anthracene crystal.

TABLE I

Applied voltage	Crystal current amps	Total electro-luminescence (relative units)	Slow component intensity	Ratio I_{slow}/I_{total}
Delayed Anthracene Emission				
4000	8×10^{-6}	300	12.6	0.042
3000	3×10^{-6}	55	3.7	0.067
2000	1.1×10^{-6}	22	3.3	0.15
1500	5×10^{-7}	12	2.5	0.21
1000	8×10^{-8}	1.0	0.4	0.43
Delayed Pentacene Emission				
4000	8×10^{-6}	350	38.5	0.11
3000	3×10^{-6}	90	13.4	0.15
2000	1.1×10^{-6}	26	8.3	0.32
1500	5×10^{-7}	3.8	1.5	0.41

Typical results comparing the relative intensity of the delayed anthracene and pentacene electroluminescence compared to the total anthracene and pentacene electroluminescence.

Thus the anthracene-pentacene mixed crystal system illustrates the ease in doping organic crystals to control electroluminescence spectra. Similar to an anthracene-tetracene crystal, the electroluminescence spectra at room temperature with reasonably high crystal currents consist principally of light characteristic of the dopant. However in contrast to anthracene-tetracene systems prompt and delayed electroluminescence from both pentacene and anthracene is observed. It is probable that differences in crystal quality can account for this different behaviour, however time resolution cannot separate host and guest electroluminescence under all circumstances. For anthrecene-pentacene crystals, relatively high electroluminescence efficiencies, 10%, are obtainable when electroluminescence intensity is considered as a function of crystal current. However, the electroluminescence efficiency as a function of power input is much less than observed in neat crystals. This decrease in efficiency is caused by the increased density of carrier traps. These traps are not only due to the dopant itself but also are produced by the pertubation of the crystal lattice by the dopant, the latter may be the most important.

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