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Electroluminescence Studies in Pyrene Single Crystals†

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The observation of electroluminescence in pyrene single crystals is reported. Holes and electrons were introduced into the samples by contact injection using CuI and Na–Hg amalgam electrodes as hole and electron injectors, respectively. The radiation-recombination light intensity is found to be directly proportional to the current through the crystal. The yield for light emission is about 2×10^{-3} photons per injected electron-hole pair. The electroluminescence spectrum differs from the fluorescence spectrum of pyrene (excimer emission) by the appearance of fine structure, the relative heights of the various peaks being functions of the injecting current.

INTRODUCTION

Until now, recombination radiation in organic crystals was mostly studied in anthracene.[1–7] High concentrations of electrons and holes were obtained by contact injection using proper materials as electrodes. The measurements were carried out in both the pulsed and d.c. modes. The recombination radiation was found to have the same spectrum as that of the ordinary fluorescence of anthracene (modified on the short wavelength side by reabsorption in the crystal[1]). It was well established that the light emission results from the radiative decay of singlet excitons produced by recombining electron-hole pairs. The yield for light emission was about 0.4 photons per injected electron-hole pair. The measurements yielded also the values of the electron-hole and triplet exciton—triplet exciton recombination-rate constants.

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In the present paper we report on the observation of recombination radiation in pyrene. We used CuI and Na–Hg amalgam electrodes as hole and electron injecting contacts, respectively. For high current densities, the light emission intensity was found to be directly proportional to the current density, which is also the case for anthracene.[1] In pyrene, however, the yield is very low, being only 2×10^{-3} emitted photons per injected electron-hole pair. Moreover, the recombination radiation spectrum is markedly different from the fluorescence spectrum (excimer emission). In the former spectrum, well-defined peaks are observed, the relative intensities of which varying with current density.

EXPERIMENTAL

The measurements were carried out on pyrene crystals grown either by sublimation, or from the melt by the Bridgman method. In both cases the starting material was purified by zone refining in an inert atmosphere of about 60 zone passes. The sublimation-grown crystals were in the form of platelets (50–100 μ in thickness) oriented parallel to the (a, b) plane. The melt-grown crystals were cut parellel to the (a, b) plane by a wire saw and then polished to the desired thickness ($\sim$0.5 mm). Before application of the contacts, the melt-grown samples were briefly etched in benzene. A Na–Hg amalgam contact served as an electron injector,[8] while a CuI contact was used to inject holes into the sample. The latter electrode was prepared as follows: A copper layer of about 1000 Å in thickness and 0.1 cm^2 in area was evaporated onto one face of the sample. Subsequently, this face was exposed to iodine vapour for about 5 minutes. Apart from being hole injectors, the CuI electrodes so obtained have the important advantage of being transparent in the range $\lambda > 0.41\ \mu$, which is almost the entire range of interest of the excimer emission of pyrene.[9] The emitted recombination radiation of pyrene could therefore be observed either from the side or through the CuI contact. After mounting of the crystal in its cell, and application of the amalgam contact, the crystal holder was transferred to a vacuum chamber to prevent oxidation of the amalgam. The optical system for detecting the emitted light consisted of a Jarell–Ash double monochromator followed by a P.A.R. photomultiplier type IP-28-A cooled to liquid nitrogen temperature. The monochromator slit width was 2 mm which permitted a spectral resolution of about 50 Å. The total emitted light was measured through a side window, towards which the crystal holder could be turned. The fluorescence emission of pyrene was measured by the same system, excitation taking place by light from a mercury lamp passed through a Corning glass filter 7-37 ($0.32\ \mu \lesssim \lambda \lesssim 0.39\ \mu$).

The currents through the crystal were measured on a series resistor by a Cary 31 vibrating-reed electrometer. The photomultiplier output was amplified by a Kiethley 621 electrometer and recorded by a Yokogawa type 3077 X-Y recorder. The optical transmission of the CuI contact (and the crystal) was measured by a Beckmann D.K. spectrophotometer.

RESULTS

The role of the contacts in the light-emission process was determined by the set of the experiments represented in Figure 1. The sample in this case was a vapour-grown platelet 45 μ in thickness. The current and the integrated light-emission intensity are plotted on a log-log scale as functions of the applied d.c. voltage. Curves (a) and (b) are the respective characteristics obtained with a hole-injecting CuI electrode in the positive polarity and a counter (non-injecting) mercury contact. The injection properties of CuI are evidenced by the superlinear increase of the current density with increasing voltage (curve (a)). The current density in the entire voltage range is seven to ten orders of magnitude smaller than those for a trap-free insulator,[10] indicating the presence of a large density of hole traps in the sample. At very high voltages some light emission is observed (curve (b)) indicating that the mercury contact becomes slightly electron injecting at those voltages. The yield for light emission is around 3×10^{-5} emitted photons per injected hole. On reversing the voltage, the currents are smaller by as much as two to three orders of magnitude, and no light emission could be observed.

In curves (c) and (d) of Figure 1 are shown the results of similar experiments carried out after the mercury contact is replaced by a Na–Hg amalgam. This amalgam was previously[8] found to be a good electron injector. The result is a three-orders-of-magnitude increase in the currents (curve (c)), and about a two-orders-of-magnitude increase in the light-emission yield (curve (d)). As is seen from the curves, the light-emission intensity is approximately proportional to the current in the high-current range, yielding a fairly constant yield of $\sim 2 \times 10^{-3}$ photons per injected charge carrier. (It is slightly less than linear at lower currents.) The linear dependence here, as well as that observed in anthracene,[1,2] and naphtalene[11] may be accounted for by the high electron-hole recombination rate constant K making the charge-carrier lifetime at the recombination zone small compared to its transit time. For such cases, the current becomes the rate-limiting factor for light emission. In anthracene K has been estimated as $\sim 10^{-6}$ cm^{3}sec^{-1}. A comparable value is expected for pyrene in view of the similarity in the free-carrier mobility in the two cases.[12] However, while for anthracene the yield is reported to be roughly of the order of one photon for every pair injected[1,2]

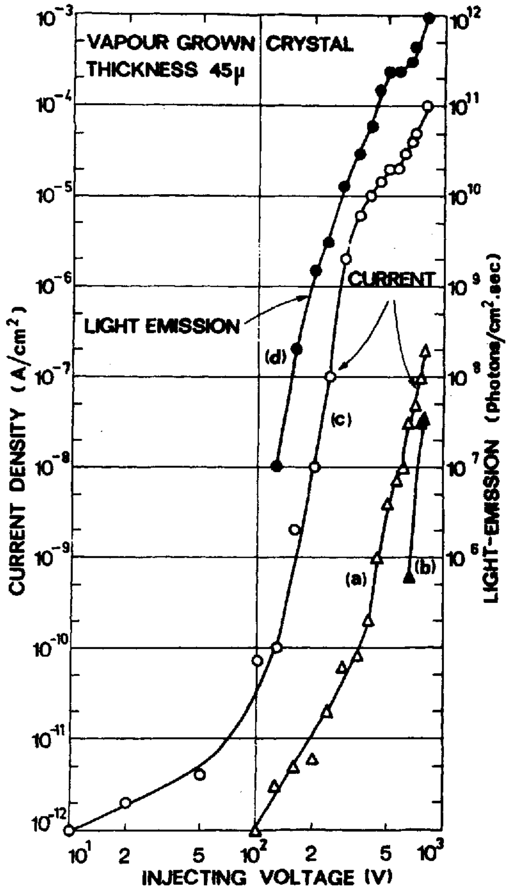

FIGURE 1 Log-log plots of current density (open symbols) and light emission intensity (full symbols) *vs.* d.c. injecting voltage. Triangles correspond to the positive electrode being CuI and the negative being mercury; circles correspond to a replacement of the mercury electrode by a Na–Hg electron injecting amalgam. The accuracy of the absolute magnitude of the light flux marked on the right ordinate is within a factor of two or so. Note that the absica scale is blown-up by a factor of two.

we find in pyrene a yield two to three orders of magnitude lower. It appears therefore that in pyrene non-radiative electron-hole recombination processes dominate. The dominant mechanism of recombination in anthracene is that an electron-hole pair first produces a singlet exciton which then decays radiatively. In order to establish that the low yield in pyrene is not a result of a low yield for the latter process, we measured the yield of the prompt fluorescence in the crystal. This was found to be close to unity (0.7 ± 0.3,

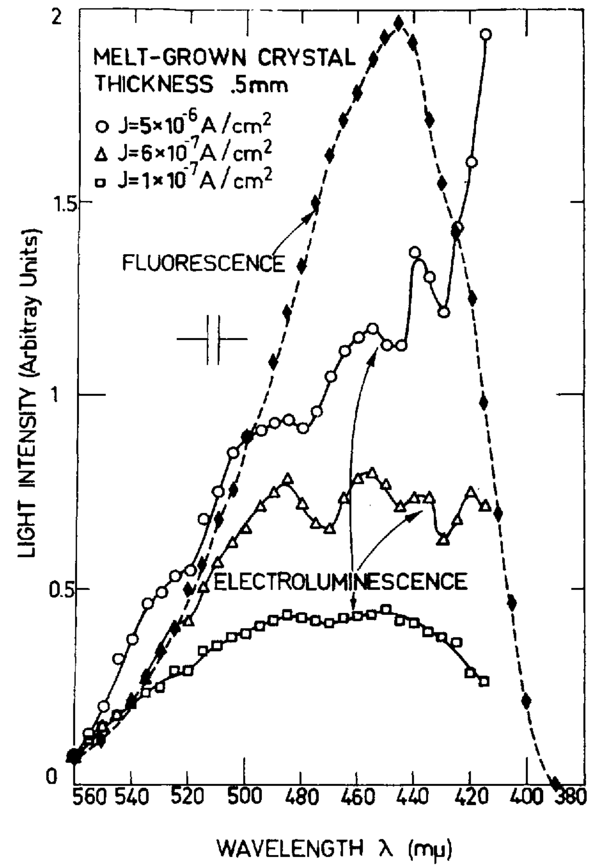

FIGURE 2 Fluorescence and electroluminescence spectra of pyrene.

very similar to the value obtained for pyrene solved in ethanol[13]). The reason for the low yield must thus lie in the process of singlet-exciton production.

In Figure 2 the spectrum of the fluorescence for a melt-grown pyrene crystal is shown together with spectra of the recombination radiation obtained on the same crystal for different current densities. All curves are normalized to a common value at $\lambda = 560$ mμ. Although the recombination radiation appears roughly at the same wavelength range as the fluorescence, the two types of spectra are markedly different. Well-defined peaks appear in the spectrum whereas the fluorescence emission of pyrene[9] is a broad structureless band (dashed curve in Figure 2). The height of the peaks change with current: for higher currents, the peaks at shorter wavelengths become more intense. No wavelength shifts of the peaks could be observed. Thus the model which explains the electroluminescence in anthracene seems inappropriate to pyrene.

DISCUSSION

In anthracene both fluorescence and electroluminescence are attributed to the same process, namely, the radiative decay of singlet excitons. This is evidenced by the similarity in both the spectral shape and the value of the quantum yield. In pyrene, the fluorescence is attributed to a similar process. (It is somewhat different from that of anthracene in that the emission spectrum appears as a broad structureless band with a considerable red shift from the singlet–singlet absorption. It is believed to originate from an excited dimer state which has no stable dimer ground state.[14]) The electroluminescence emission, on the other hand, bears little if any resemblence to the fluorescence. It appears likely, therefore, that it originates from an entirely different process. There are two obvious points of difference between the two types of emission. Firstly, the fluorescence originates very close from the illuminated surface, the absorption depth of the exciting light being very small ($\lesssim 1000$ Å). In contrast, the electroluminescence eminates from the bulk material. Secondly, there is a difference in the mode of excitation. In the fluorescence process there is no doubt that singlet excitons are directly produced by the exciting light. Recombination of injected hole-electron pairs, on the other hand, does not necessarily produce singlet excitons. Both the shape of the electroluminescence spectrum and the extremely low yield indicate, in fact, that this must indeed be the case. The recombination may proceed directly across the gap or via some traps, the latter process being the more likely one in view of the observed structure. At the same time the low yield indicates that non-radiative recombination is the dominant process. To some extent the present results resemble those of electroluminescence in tetracene-dope anthracene crystals.[15] There, the free-trapped carrier recombination was found to be the dominant recombination mechanism. At the same time, the yield was only about 10% and the dependence of the light-emission intensity on the current was different for difference wavelengths.

More work is necessary in order to ilucidate the role of surface and bulk effects on the one hand, and the nature of the radiative recombination displayed in the electroluminescence structure on the other. The use of samples of higher purity may lead to an increased yield and to the appearance of the singlet spectrum.

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