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ELECTRICAL CONDUCTION AND LOW VOLTAGE BLUE ELECTROLUMINESCENCE IN VACUUM-DEPOSITED ORGANIC FILMS

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Bright blue (400–500 nm) recombination electroluminescence (EL) has often been observed from anthracene crystals with solid electrodes; external quantum efficiencies of 1%–8% have been seen and the theoretical efficiency is approximately 40%. The power efficiency has always been greatly degraded by the high voltages necessary to obtain reasonable currents through the comparatively thick crystals used. We report the preparation, and the structural, electrical and EL properties of approximately 0.6 μm vacuum-deposited anthracene films through which large steady state current densities can be passed at rather low applied voltages. The films showed the critical optimization effect, various structural and electrical properties exhibiting sharp singularities when the films were prepared at substrate temperatures within a narrow range near −60 °C. EL visible in normal room lighting was obtained at applied voltages of only about 30 V and up; in thinner films, EL could be seen in a darkened room at only about 12 V. This is apparently the first time that clearly visible EL has been reported from an organic material at voltages significantly less than 100 V. Broadly similar results were obtained for perylene and 1,12-benzperylene films; EL does not appear to have been observed before from these substances in any form. We discuss in some detail the prospects for practical EL devices based on organic films. In view of our results, and of the great improvements which are now probably feasible, we conclude that the prospects are promising; if these improvements can be realized, such devices could include high efficiency blue light-emitting diodes, and large-area broader wavelength systems for illumination applications.

1. INTRODUCTION

While inorganic electroluminescence (EL) has been widely studied and applied, organic materials have received much less attention. Nevertheless, certain organics such as anthracene could be superior to inorganics in some applications. Both holes

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and electrons have been injected into anthracene with high efficiency, and when these carriers (injected from opposite sides of a single crystal) recombine, blue (400–500 nm) EL is produced with rather high efficiency. Early work (refs 1 and 2, for example) utilized liquid solutions as the injecting electrodes, which obviously presents practical problems. More recently, however, a variety of solid electrodes has been made to inject large electron currents into anthracene, examples are Al/Al_2O_3, Si/SiO_2, alkali metals (which may also be liquid) or their compounds with anthracene, and carbon fibres or powdered graphite. Similarly, large hole currents can be injected by such materials as gold, indium, SeTe, pastes of gold, silver or platinum, powdered graphite, Nesa glass and CuO,I In some cases, these materials can inject carriers on their own, while in other cases strong injection of the opposite carrier by the other electrode is required The EL observed when an electrode from each group is placed on opposite sides of a pure or doped anthracene crystal has been studied quite extensively[3-17]

Of particular interest from a practical standpoint are several reports[3-6] in the last decade where very high currents have been achieved, accompanied by bright blue EL with high external quantum efficiencies η (photons out per electron–hole pair in), η values of 1%–8% have been seen, even though the light was often observed through a semitransparent electrode Other investigators have also observed such high efficiencies at rather lower current densities, using solid[7 15] and liquid[18] electrodes, while doping the anthracene with tetracene[4,5,9,16 20] or pentacene[8,17] shifts the EL from the blue into other portions of the visible spectrum, but appears to yield comparable η values. The theoretical[3] η for anthracene itself is approximately 40%, at least in the absence of deep traps[21]. The lifetime of anthracene EL cells, even with corrosive electron-injecting contacts, can be long[22], so that, if adequate brightness can be obtained for reasonable applied voltages, anthracene or a related compound could possibly be the basis of the first reasonably efficient blue EL devices

There have been fewer studies on the injection EL of other organics, although some emission (with low intensity and/or low η) has been reported from tetracene[21,23-25], naphthalene[26], pyrene[27], octaethylporphin[28] and *p*-terphenyl[29] Organic EL arising from other mechanisms has also been reported (see, for example, refs. 20 and 30–33) but seems to have caused less interest for possible device applications.

Most previous work on anthracene EL utilized single crystals. As it is difficult to make these very thin, several hundred volts must typically be applied to obtain high enough currents for bright EL, each photon carries only about 3 eV, so[3] the *power* efficiency of these devices is about a factor of 100 lower than the η values. The current density will obviously rise rapidly, for a given applied voltage, as the thickness of the anthracene is reduced; it is thus natural to look for ways of fabricating very thin anthracene layers without sacrificing electrical integrity or introducing too high a concentration of traps Thin crystals (4–100 μm)[4,5] have been used to reduce the required voltage to around 100 V, but even this is too high for most device applications We have therefore studied anthracene layers made by the Langmuir–Blodgett (LB) technique[34,35] and by vacuum deposition, and we report here on the latter. In addition to the interest in such systems as small-area reasonably efficient blue luminescers, these techniques (since they do not utilize

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conventional single crystals) could conceivably permit the fabrication of large-area doped EL panels for illumination applications.

Some studies of EL in anthracene thin films have been reported[16,36,37], but in most cases the current densities achieved appear to have been too low to give EL of significant brightness. We know of no comparable studies on films of other organics. In the present paper, we discuss the preparation, and the structural and electrical properties, of approximately 0.6 μm anthracene films through which large steady state current densities could be passed; these films gave EL visible in normal room lighting (even through a 15 nm gold electrode) at applied voltages of only about 30 V and up. In thinner films, EL visible in a darkened room could be obtained at only about 12 V. This is apparently the first time that clearly visible EL has been reported for an organic material at voltages significantly less than 100 V. Moreover, while we had little difficulty injecting holes into our films from gold electrodes, we discuss how our results could probably be greatly improved by replacement of our poor electron-injecting contacts. We also give an experimental evaluation of various other potential hole-injecting materials. Furthermore, far better EL behaviour could probably be achieved using recently reported methods of obtaining large-area thin single crystals of organics. We discuss in some detail the prospects for practical high efficiency EL devices based on films of anthracene or other organics; in view of our results, and of the potential improvements, we conclude that the prospects are promising.

2. EXPERIMENTAL DETAILS

The entire electrode/anthracene/electrode sandwich structure was made by thermal evaporation in a vacuum of approximately 2×10^{-6} Torr. The vacuum equipment and the source of the anthracene have been briefly described elsewhere[38]. The usual bottom electrode, 50 nm of aluminium, was deposited onto a cleaned glass substrate at room temperature, and was then exposed to air to permit oxide formation in the hope of forming a tunnel injecting cathode[4,6]. The substrate temperature T_s during anthracene deposition could be varied over a wide range[38]; most of our electrical and EL measurements used films deposited at $T_s = -60\,^{\circ}C$ (see Section 3.1). Nominal anthracene deposition rates were varied from roughly 0.3 to 5 nm s^{-1}, and the thickness from about 0.2 μm to about 3 μm, most samples being approximately 0.6 μm. The top electrode, usually 15 nm of gold, was deposited without breaking the vacuum, usually as a matrix of 3 mm circles; T_s was $-50\,^{\circ}C$, to minimize anthracene re-evaporation. EL was observed through the partially transparent gold electrode, which (unless otherwise stated) was biased positively. For η estimation, the reproducibility was improved by sealing a watch glass over the cell in a nitrogen atmosphere, using a UV-cured adhesive. Relative film thicknesses were monitored by capacitance and stylus techniques (using a rather broad stylus to reduce scratching). Samples were generally stored (for less than a month) and tested under dry nitrogen, although some early experiments were done in air. After a number of months, anthracene recrystallization effects were often observed, leading to structural and electrical changes; the implications of this will be discussed in Section 4. A more detailed experimental description may be obtained by writing to the authors.

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3 RESULTS

3 1 Structure and electrical properties of the films the critical optimization effect

Scanning electron micrographs of the polycrystalline anthracene films have been reported previously[39] for a wide range of substrate temperatures T_s. A completely unexpected and very sharp minimum in the topographic disorder was observed[39] for T_s values within a very narrow range near -60 °C. This has since been shown[40] to be an example of an extraordinarily general and sharp optimization of many properties (the "critical optimization effect") which occurs in a wide range of vacuum-deposited materials (both organics and inorganics) for $T_s/T_b \approx 0.33$, where T_b is the normal boiling point of the evaporant. Optical and electron diffraction singularities[41] in phthalocyanine (Pc) films deposited at their critical temperature T_0 suggest that the various optimization effects are due to singularities in size and orientation of the crystallites at T_0, while the orientations above T_0 are different from those below it. T_0 in anthracene also corresponds[38] to the T_s region at which the structural disorder of the films falls rapidly from "low T_s" to "high T_s" levels Moreover, anthracene films formed exactly at T_0 appear[38] to contain an unusual crystal phase. The critical optimization effect has been explained[40] on the basis of re-evaporation of small *disordered* areas of the films during the deposition process, and the deposition rate dependence of T_0 in Pc[42] provides recent support for this mechanism

Our electrical measurements on anthracene disclosed several further singularities for $T_s = T_0$ Figure 1 shows the capacitance of typical films as a function of T_s; since other conditions were constant, all these films received approximately the same quantity of impinging anthracene There is a substantial fall of capacitance as T_s falls below T_0 (~ -60 °C), and there may be a peak at or near T_0. There is also much more scatter below T_0 than above it The a c conductance data given below strongly suggest that the main capacitance change is not associated with differences in the electrode–sample contacts, although the small *peak* may well be connected with such effects The main capacitance change therefore appears to be evidence for either (i) the theoretical suggestion[40] that re-evaporation of small disordered areas of the film becomes possible at T_0, leading to slightly thinner films above T_0, or (ii) the more ordered and less open crystalline structure which is suspected to be formed at and above T_0 To distinguish between these possibilities would require either accurate measurement of the film thicknesses, which is difficult for the more disordered films, or direct quantity-of-material measurements[41].

A more striking singularity was observed in the a c resistance R_p For all values of T_s, R_p varied as ω^{-2} (Fig 2) over a significant range of frequency ω, while the effective parallel capacitance C_p was independent of ω Such behaviour often indicates a contact or interfacial resistance R_i between the electrode and the sample, if the sample is represented by a pure capacitance C_s in parallel with a high resistance R_s, then for a substantial frequency range C_p is equal to C_s, and the parallel resistance R_p is independent of R_s and given by[35]

$$R_p = (\omega^2 C_s^2 R_i)^{-1} \tag{1}$$

In Fig. 3, R_p is plotted as the dimensionless variable $\omega C_p R_p$ (*i e* the inverse of the loss tangent, $\tan\delta$) against T_s for fixed ω The striking peak implies a sharply minimized

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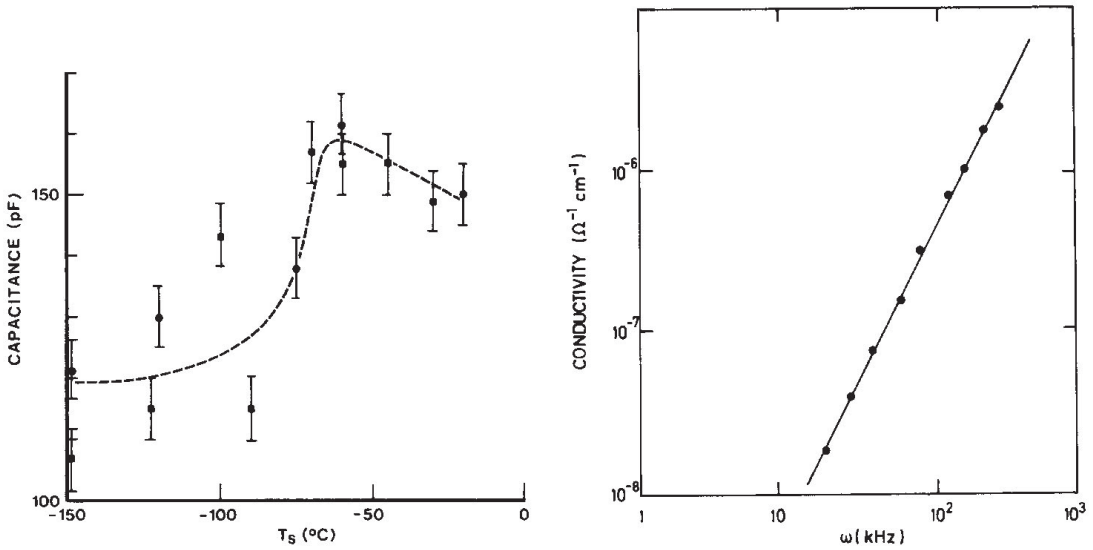


Fig 1 Capacitance of Al/anthracene/Au cells as a function of the substrate temperature T_s used during anthracene deposition (●, ■, two sets of depositions made at different deposition rates) The anthracene impingement rate and deposition time were approximately the same for all the films The error bars represent the variability from cell to cell on a given film, this is probably due primarily to slight variations in area

Fig 2 Variation with frequency of the a c conductivity of a typical freshly prepared anthracene film deposited onto a substrate held at −20 °C

value of R_1 near T_0 (possibly associated with the optimum film smoothness), and this may also account for the small peak in Fig. 1. The slight difference between the singularity temperature in Fig. 3 and that observed in other measurements may not be entirely real: because of the variation of C_p with T_s (Fig. 1), R_1^{-1} would peak at significantly higher T_s (in the region of −70 °C) than $\omega C_p R_p$; also the a.c. conductivity films were made in a different vacuum system from the rest, which could have led to small systematic errors in temperature measurement.

The large concentration of traps in our films (which is usual for evaporated polycrystalline organics) led to large polarization effects: after each application of successively higher voltages to a given film, a very large surge in current was followed by a decay which often lasted several hours and sometimes ended at an apparent steady state current. After subsequent storage for hours or days without an applied field, the samples recovered to nearly their original condition. The unusual nature of films formed at T_0 shows up clearly in the form of this current decay, as illustrated for representative 0.6 μm films in Fig. 4. The current through the −60 °C sample comes fairly rapidly (and nearly exponentially) to a steady state level; the other samples decay (non-exponentially) over much longer periods and do not come to a steady state. The most obvious explanation for this is a difference in the nature and/or concentration of traps for T_0 films, although differences in electrode contact could also play a role. This behaviour makes it difficult to compare the steady state conduction of T_0 and non-T_0 films. Currents flowing soon after application of a given voltage show no clear evidence of major optimization for T_0 films, unlike many inorganics, which show[40] striking electrical optimization at their values of T_0. This is no doubt partly because of the quite large scatter in our data for different films, and perhaps partly because the conduction of organic films (being limited by molecular-

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scale traps) is less sensitive than that of inorganics to factors such as crystallite size. However, since the currents in the non-T_0 films in Fig. 4 are still falling rapidly after 5–6 h, it may well be that their eventual steady state would be significantly smaller than that of the T_0 samples

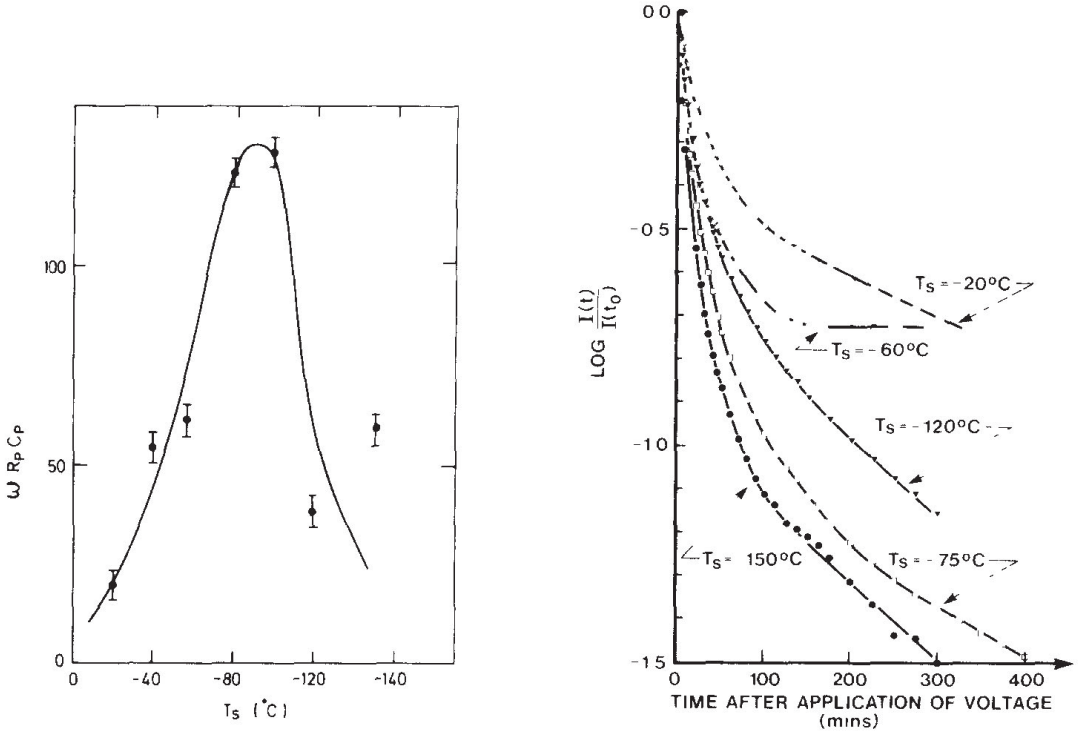


Fig 3 The factor $\omega R_p C_p$ as a function of T_s, the substrate temperature during anthracene deposition (R_p and C_p are the effective parallel a c resistance and capacitance respectively, measured at frequency ω and room temperature)

Fig 4 Decay of observed currents with time after application of a given voltage, for representative values of T_s, the substrate temperature during anthracene deposition (applied voltage, 60 V, except 50 V for T_s = −75 C, nominal film thickness, about 0 6 μm, deposition rate, 0 3 nm s^{-1}) In each case, the currents are normalized to the value at an early stage in the decay (t_0 = 2 5 min)

3.2 Current–voltage behaviour

Figure 5 shows plots of current density J against applied voltage V for typical T_0 samples of three thicknesses. These particular measurements were on fairly early samples and were performed in air, however, measurements on 0.6 μm samples under dry nitrogen give very similar steady state currents. In 0.6 μm samples under dry nitrogen or reasonably dry air, the maximum voltage which could be applied for long periods without serious breakdown was generally about 50–70 V (about 10^6 V cm^{-1}). As voltages just below this were first applied, some self-healing breakdown was typically observed (in the form of a number of minute sparks), leading to a very slight fall in the electrode area and hence in the capacitance Above 50–70 V, the loss of capacitance became progressively more significant. Thinner samples often showed much lower breakdown strength, presumably because of weak spots

One of the most significant aspects of Fig. 5 is that the currents involved are rather large at fairly modest voltage levels. Moreover, Fig. 5 by no means represents the highest currents ever seen; one approximately 0.5 μm sample, for example,

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exhibited a current density of 25 mA cm^{-2} in air at 70 V after 5 min decay, and gave a nearly-steady state value of 7 mA cm^{-2}. Furthermore, the large surge in current, which always occurred when the voltage was increased, indicates that the electrodes are capable of injecting very large current densities into the anthracene; in fact, initial current densities up to about 0.3 A cm^{-2} were seen, and pulse measurements gave similar values.

The power law J–V plots (which were always observed for steady state currents or for currents measured at fixed times after voltage application) are clearly very consistent with space charge limitation (SCL): plots of $\log J$ against V^n, to test for barrier-limited conduction processes (with values of n such as 0.5), are generally not such good straight lines. As expected, the currents are well below the trap-free Child's law limit. The thickness dependence of the current is substantially less marked than the normal SCL proportionality to $L(V/L^2)^n$, and the slopes of the $(\log J)/(\log V)$ plots are apparently thickness dependent. A smaller than expected thickness dependence has been observed previously[43], and has been attributed to traps with spatially non-uniform density; spatial variation of the other trap parameters could account for the slope variations. That the source of the charge carriers is injection from one or both electrodes, rather than field-dependent bulk charge generation processes, is confirmed by the very low currents observed with some electrodes, such as unoxidized aluminium on both sides of the sample.

An interesting and slightly puzzling example of the $J \propto V^n$ conduction occurred when the current was allowed to reach or approach a steady state at a fairly

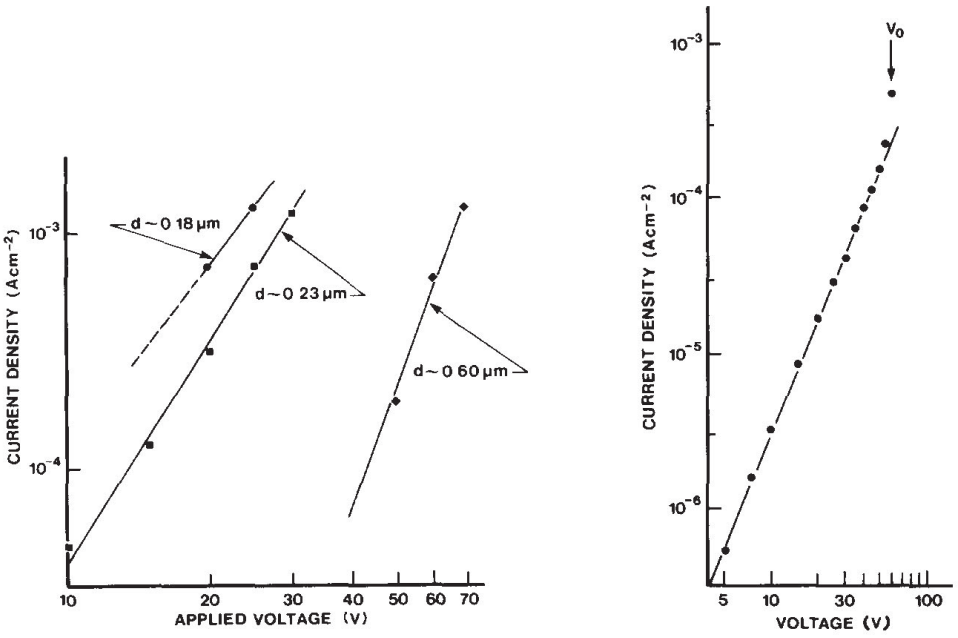


Fig 5 Plot of $\log J$ *vs* $\log V$ for typical $T_s = -60\,^{\circ}C$ samples (deposition rate, 3 nm s^{-1}). The absolute values of thickness are approximate; the relative values (determined by capacitance) are probably accurate to within about 5% These early measurements were done in air, but the steady state nitrogen-atmosphere currents are similar. The slopes of the plots are approximately 2 5, 3 1 and 5 4, reading from left to right

Fig 6 Typical $\log J$ *vs.* $\log V$ plot obtained at lower voltages after long-time application of a higher voltage V_0 (arrowed) (nominal film thickness, about 0.6 μm). The slope of the plot is approximately 2 4.

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high voltage V_0: the (nearly stable) currents obtained at lower voltages (Fig. 6) then followed a very clear power law over a wide range starting a little below V_0. While this can hardly be anything but additional evidence of SCL, there is no obvious reason why the partial trap filling caused by high voltage conditioning would lead to a field configuration likely to give such a simple power law at lower voltages.

The above experiments used our conventional polarity (*i.e.* gold positive), as expected, reversing the polarity gave currents typically several orders of magnitude smaller Early experiments (in air) showed that replacing the normally negative Al/Al_2O_3 bottom electrode with gold did not make a major difference to the currents, and that EL (Section 3 3) was still sometimes emitted from the films. Nor did placing the cells in dry nitrogen make a dramatic difference to the EL at a given current Since it is unlikely that gold would inject electrons strongly when negatively biased, we interpret the above data to imply a rather efficient injection of holes by our gold electrodes. Such injection has often been observed from evaporated gold into tetracene (refs 21, 23–25, 44 and 45, for example), but is much less common[9, 15] with anthracene; in fact, gold evaporated onto anthracene crystals has been found several times[3, 7] to be unacceptable, because good contact occurred only in small areas. Our observation of SCL behaviour does not rule out the possibility that some areas of the gold were injecting well and others not at all, so long as the size of the areas was at least comparable with the film thickness However, the large current densities observed on first applying voltages tempt us to suppose that the gold is in fact a good contact, the difference from earlier work probably being due to the successive vacuum deposition of the anthracene and the gold, without the vacuum being broken. In any event, with the gold injecting holes strongly, efficient injection of electrons by the Al/Al_2O_3 would have given a double-injection situation in which much stronger EL and higher currents would have been observed than with a gold bottom electrode. We thus conclude that our Al/Al_2O_3 electrodes injected electrons inefficiently and (since there was not a very good correlation between current and EL from sample to sample) somewhat irreproducibly Others[4, 6] have observed copious electron injection from such an electrode into anthracene crystals (at least in the absence of oxygen[6]); our problems were probably caused by the well-known dependence of the oxide's properties on its preparation conditions. Very brief attempts to supplement the oxide by an approximately 2 5 nm highly insulating LB fatty acid film were not successful; a thinner anthracene layer might work better in these circumstances, so that more voltage would be available across the thin insulator to field-assist the required tunnelling. Magnesium was also tried as the lower electrode, but its behaviour was similar to that of aluminium.

Other electrodes were briefly investigated, mainly in air and primarily to assess different potential hole injectors (especially lower melting materials, which could conceivably make more uniform contact to the anthracene). The first- and second-named metals are respectively the ones deposited before and after the anthracene. In–In, In–Au and Ag–Ag cells were completely short circuit, and short-circuit clearing procedures (which were often necessary before starting measurements on our normal cells) were ineffective. Bi–Bi gave somewhat higher currents than normal cells at low voltages, but there was difficulty making contact; large currents could not be observed, possibly because of electrode resistance. Te–Te cells were also difficult to contact, but gave similar or slightly larger currents than normal cells; no

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EL (Section 3.3) was seen. Ni–Ni gave rather lower currents than usual, with very little EL. "CuO,I" (see ref. 4)–Au gave very large currents at low voltages, although breakdown was also much more pronounced than usual; as an example, a current density of 10^{-1} A cm^{-2} was observed after 4 h of equilibration time at an applied voltage of 30 V. These cells showed little rectification, and surprisingly the larger current was observed with the CuO,I negative; little, if any, EL was observed, and we cannot rule out the possibility that some or all of the current was due to complexing between residual iodine and the bulk of the anthracene.

3.3. Electroluminescence

As mentioned above, many cells when subjected to about 30 V or more (about 0.5 MV cm^{-1}) exhibited strong blue EL, which decayed with time slightly faster than the currents. This EL, although viewed through the 15 nm gold electrode, was visible under normal room illumination; in some of the thinnest samples (about 0.18 μm), EL was visible in a darkened room at voltages as low as 12 V. This appears to be the first time that strong clearly visible EL has been seen from an organic material at voltages significantly below 100 V. The time decay of the EL and of the currents could be drastically slowed by using a.c. rather than d.c. voltages. The strongest EL could then be observed for continuous periods of more than 10 min, while lower initial current densities gave EL decays extending over hours.

The EL wavelength dependence is shown in Fig. 7. As commonly observed in anthracene, this was identical with the *photo*luminescence spectrum of the samples; it represents emission from the first excited singlet state of individual anthracene molecules, apparently resulting[3] from recombination of some of the primary injected current carriers (holes; Section 3.2) with the smaller number of injected electrons. While recombination is very often simply assumed to be the mechanism of anthracene EL, one should consider alternative mechanisms[20,30–33]. It is fairly clear that field-dependent (rather than current-dependent) mechanisms are not operative

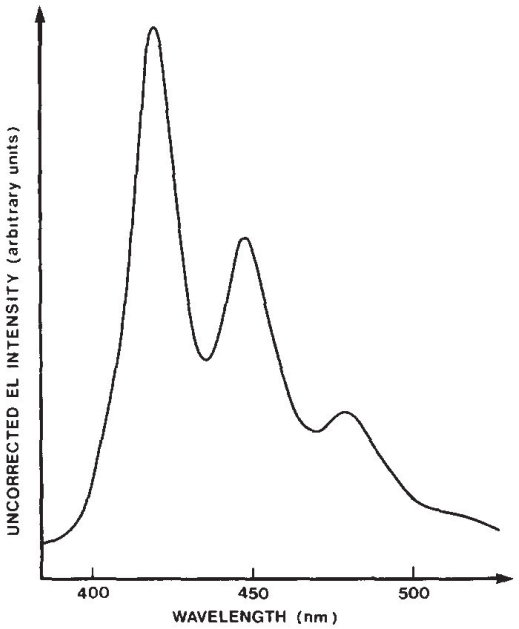


Fig 7 Uncorrected wavelength dependence of the EL intensity

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in our case. for example, reversing the voltage polarity in our normal cells always drastically reduced EL along with the current, and some electrode combinations (*e.g* Al–Al) gave no EL, as well as very little current Acceleration–collision mechanisms resulting from a single sign of injected charge are more difficult to rule out, but seem unlikely in view of the dependence of EL on the cathode material, with gold as anode: gold cathodes seemed to give less EL than Al/Al_2O_3, and insertion of a 2.5 nm LB film between the Al_2O_3 and the anthracene seemed to prevent luminescence, moreover, other electrode combinations (Section 3.2) gave currents comparable with those in the usual cells, but exhibited little or no EL. Finally, "EL" can be observed[33] because of photoluminescence resulting from light produced by nitrogen glow discharge in organic films, and a similar mechanism involving breakdown at weak spots in our films could also be imagined. Again, however, the lack of EL with certain electrode combinations, or with reversed voltage polarity in normal cells, argues against such a mechanism; moreover, there did not appear to be a good correlation between films and voltages showing significant breakdown (Section 3.2) and those showing strong EL, nor did visible breakdown events have an obviously similar time dependence to that of the EL.

In view of the apparently poor electron injection with our particular electrodes (Section 3.2), one would not expect the EL to be produced with high efficiency, and this was in fact the case External quantum efficiencies of up to 0.03%–0.06% were measured, and the best power efficiency was approximately 0.003%.

4 THE PROSPECTS FOR FUTURE THIN FILM ANTHRACENE ELECTROLUMINESCENT DEVICES

We have demonstrated the feasibility of producing large current densities and strong blue EL in an organic material at much lower applied voltages than previously, by using thin films; we now discuss how this kind of approach can probably be drastically improved for anthracene and other organics. The main problems at present are (i) inefficiency of electron injection, which limits the current (space charge overlap can greatly increase trap-limited SCL currents) and leads to low efficiency of photon production, (ii) the substantial trap density, which limits the current and causes polarization, probably irreproducibility, and possibly non-radiative carrier recombination, (iii) the low breakdown strength of most films thinner than about 0 4 μm, and (iv) film recrystallization after a number of months.

Problem (i) probably relates to the oxide's notorious dependence on fabrication conditions, since Al/Al_2O_3 electrodes have previously given good electron injection for single-crystal anthracene EL[4 6], a systematic investigation would probably solve the problem Some alternatives for electron injection are (a) other ultrathin insulators for tunnel injection (*e.g.* SiO_2 [2], or LB films, perhaps thinner[34,35] than conventional 2.5 nm monolayers), (b) alkali metals[3 9,10,14,15], probably in the form of very thin films to keep metal–organic reactions within bounds, or as a dried solution of the metal–organic complex[5,7,13], (c) the less corrosive alkaline earth metals (previously used with tetracene[44] and anthracene[46]), or (d) a p–n junction[47]. Gold electrodes appeared to be acceptable as hole injectors, but other materials (Section 1) could be better. One electrode must be reasonably transparent. Conducting aluminium films, for example, can be made approximately 50%

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transparent, while some hole injectors (*e.g.* CuO,I)[4] are much more so; Nesa glass can inject holes copiously[5] if used with a good electron injector.

To solve problems (ii) and (iii), a structurally more ordered film is needed. Trap problems could be reduced substantially by annealing our films and by using a.c. voltages, and breakdown problems might be improved if electron injection were accomplished via a better insulator on the negative electrode. However, somewhat different film fabrication techniques probably hold out the best hope for drastically improved results. For example, small-area single-crystal films could be made on single-crystal substrates by conventional vacuum epitaxial methods, or for large areas on other substrates by techniques based on solution casting or on graphoepitaxy[48]. Such films might also be reproducibly fabricable thinner than our typical 0.6 μm, further reducing the driving voltages and increasing the engineering efficiency; excessively thin layers, however, would reduce η, if only because of exciton quenching[49] at the metal interfaces (the singlet exciton diffusion length in anthracene crystals is about 40 nm [49]).

Problem (iv), which can be quantitatively explained as vapour-pressure-driven "ripening" of larger crystallites at the expense of smaller ones, could also well be removed by improved film structures, as above. Alternatively, organic materials with lower vapour pressures (and maybe with less tendency to photochemical degradation, see below) could be used. We have obtained[50] EL in other vacuum-deposited organic films, and particularly promising results were obtained with perylene and 1,12-benzperylene.

What other problems might prevent good device performance? Photochemical stability is a concern with anthracene[51], but very promising stability over hundreds of hours of operation has been observed[22] in single-crystal anthracene EL cells, even with alkali metal electrodes, and 9,10-substituted anthracenes have shown reasonable stability in the much worse situation of electrochemiluminescence in liquids[52]. The possible "trapping" of luminescence by repeated internal reflections within a very smooth film structure suggests that one of the surfaces of the film (or of a similar-index material in contact with the transparent electrode) should not be overly smooth. Finally, the very high concentrations of charge carriers and excitons in a functioning thin film EL device could cause non-radiative exciton–exciton and carrier–exciton annihilations: carrier–triplet quenching has been reported in comparatively thick crystal flakes of anthracene[14,53] and in tetracene[21,25]. Rough calculations for a thin film EL device, based on available interaction cross sections for anthracene, indicate no obvious "show-stopping" problems, although singlet–triplet annihilation may not be entirely negligible.

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