Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: R. Nowak , A. Miniewicz , M. Samoc & J. Sworakowski (1981): Steady-State Electroluminescence in Perylene-Doped Anthracene Crystals, Molecular Crystals and Liquid Crystals, 72:4, 113-118

To link to this article: http://dx.doi.org/10.1080/01406568108084046

Mol. Cryst. Liq. Cryst. Vol. 72 (Letters), pp. 113-118
0140-6566/81/7204-0113$06.50/0

Printed in the United States of America

STEADY-STATE ELECTROLUMINESCENCE IN PERYLENE-DOPED ANTHRACENE CRYSTALS

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(Submitted for Publication September 2, 1981)

The steady-state electroluminescence in perylene-doped anthracene crystals is reported. Overlapping components due to both host and guest emission are present in the spectrum, their magnitudes depending on temperature and dopant concentration. Possible energy transfer mechanisms which may explain the electroluminescence behaviour are proposed. The system is found to behave similarly to tetracene- and pentacene-doped anthracene crystals.

The electroluminescence in anthracene has been extensively studied since the first literature reports [1-3], and was attributed to the radiative recombination of injected carriers. The spectral distribution and intensity of the electroluminescence can be modified by doping anthracene with molecules forming carrier and/or exciton traps. In doped crystals, however, the electroluminescence is more difficult to observe because of the diminution of the concentration of free carriers due to enhanced trapping, hence only a few papers have been published to date[4-7] dealing with this phenomenon. The aim of this note is to report on the measurements of steady-state electroluminescence in perylene-doped anthracene crystals.

The doped crystals (12-150 ppm) were grown from the melt using the Bridgman technique. Plane-parallel platelets cleaved from the crystal boules

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were provided with cathodes of sodium-potassium alloy and anodes of silver paste. Measurements of the electroluminescence were carried out over the temperature range 190-300 K. The spectra were recorded using an SPM-2 monochromator followed by an FEU-79 photomultiplier.

Similarly to the case of undoped anthracene the electroluminescence in perylene-doped anthracene commences at a distinct threshold voltage. The log-log current-voltage dependences exhibit straight-line sections described by dependences of the type $I \propto V^m$, with m=3-7 depending on the voltage region and perylene concentration. The double-injection current exhibits a typical temperature-activated behaviour in the range 220-280 K, with the activation energy amounting to approximately 0.25-0.30 eV. This energy cannot be directly considered as a trap depth but is related to the position of the quasi-Fermi level[8]. It may be inferred that in doped crystals impurity trapping levels effectively pin down the position of the quasi-Fermi level for minority carriers (holes) and therefore the activation energy value should be close to the dominant trap energy (cf.Ref.6). It is probably the case in measurements described here: the depth of the hole trap in perylene-doped anthracene crystals was reported to be 0.32-039 eV[9].

The electroluminescence intensity was found to increase linearly with the current, the efficiency of the process being, however, much smaller than in pure anthracene, most probably due to the enhanced trapping. Typical electroluminescence spectra are shown in Fig.1. To a first approximation, the spectra may be considered as a simple superposition of the components due to the emission from the host and guest molecules. Having substracted the anthracene component (see Fig.1), we have obtained spectra being in a good agreement with fluorescence spectra of perylene in solution reported in the literature [10-12]. The shape of the electroluminescence spectrum changes with temperature (Fig.1a,b,c). The appearance of the short-wavelength band of anthracene at low temperatures may be unambigously ascribed to a displacement of the anthracene reabsorption edge. The absence of the excimer emission band at ca. 610 nm [11,12] proves that formation of perylene sandwich pairs in the host lattice is insignificant-at least at concentrations used in our experiments. As can be seen

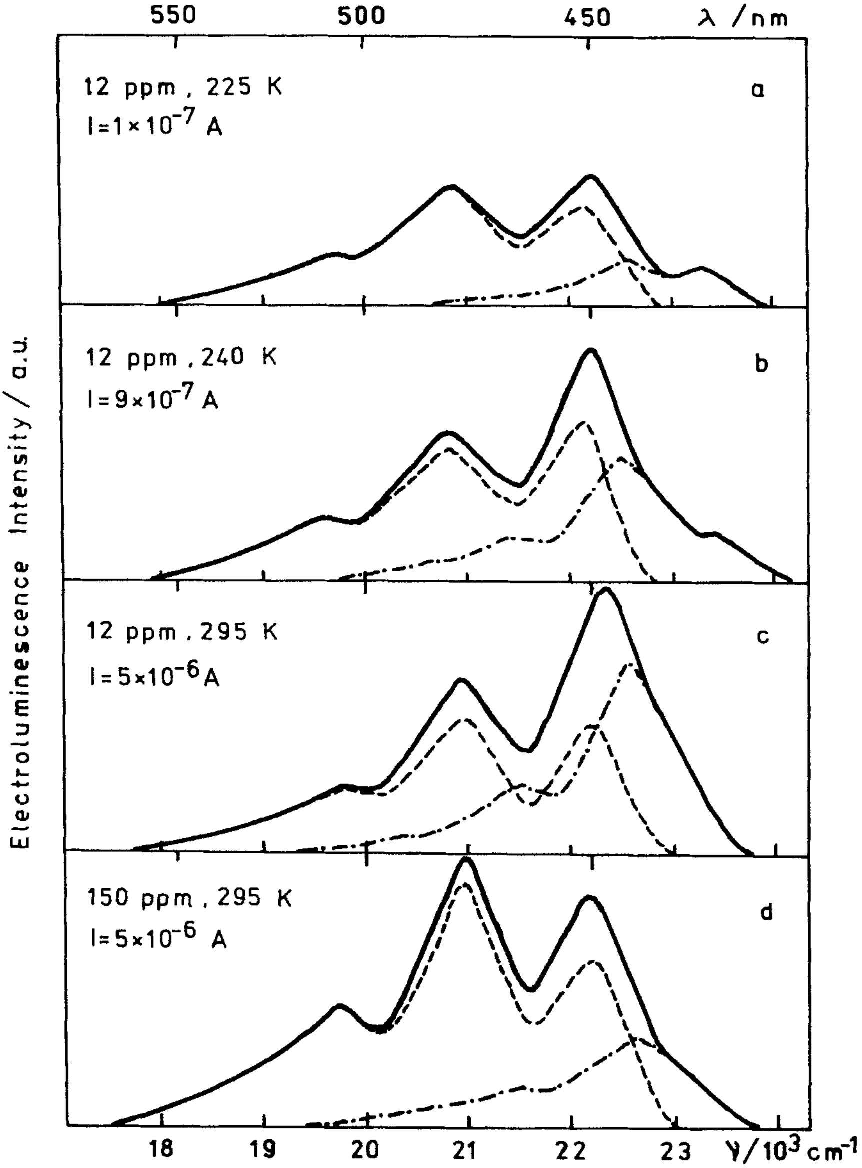

FIGURE 1 Electroluminescence spectra of perylene-doped anthracene crystals —— , undoped anthracene .-.- and perylene spectrum obtained after substration ---- .

from Fig.2, the perylene contribution in the spectrum increases with the dopant concentration, and for the concentration of 150 ppm the room temperature emission consists principally of perylene bands.

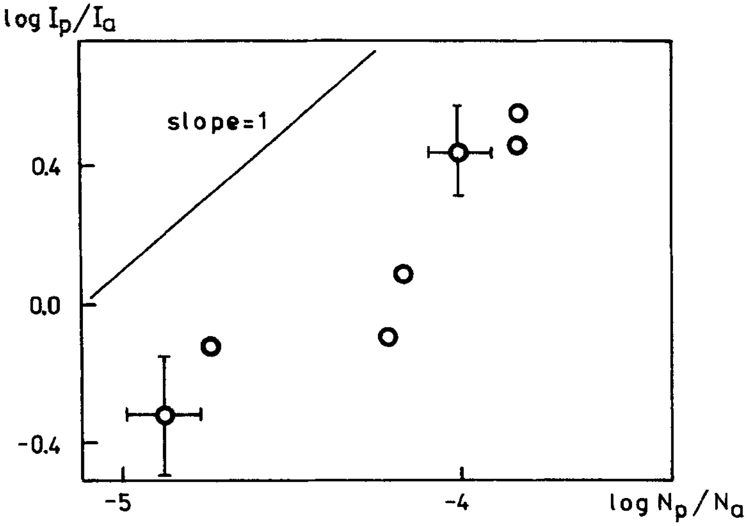

FIGURE 2 The concentration dependence of the ratio of perylene to anthracene integral emission intensities

An efficient energy transfer from the host to the dopant may take place via either of the following mechanisms. Most probably, electrons recombine with holes trapped at perylene traps producing perylene excitons which may subsequently decay to the ground state by the guest fluorescence. This process can be very efficient since the perylene singlet and triplet are lower in energy than the corresponding anthracene levels. Alternatively, anthracene excitons may be produced first, and the energy transfer may proceed by a random walk of excitons as it takes place in photoluminescence of doped anthracene crystals [13]. In this case one should expect a linear dependence of the guest-to-host luminescence intensity ratio on the concentration of the guest molecules[14]. Finally one can in principle consider an optical energy transfer by the reabsorption of the light emitted by the host.The latter process is, however, of no importance for dopant concentrations used in experiments reported here.

The comparison of the electroluminescence of perylene-doped anthracene crystals with that observed for tetracene and pentacene-doped anthracene[4-6] suggest that the energy transfer to the guest molecules may primarily occur by recombination at dopant traps producing singlet and/or triplet excitons of the dopant. Triplet annihilation would, of course, further contribute to the production of guest and host fluorescence. The alternative explanation, i.e. that of the energy transfer taking place by a random walk of host excitons is essentially identical with the process described to account for photoluminescence behaviour of perylene-doped anthracene crystals[13]. Unfortunately, the results reported in this note do not allow us to distinguish between the two possible mechanisms and further studies would be necessary to clarify this point.

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