Some new aspects of luminescence in perylene doped pyrene

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Pyrene is a crystalline aromatic hydrocarbon and is found photoluminescent. Pure and doped pyrenes exhibit interesting luminescent properties. Electroluminescence in perylene doped pyrene has been studied. The observed emission is explained by considering formation of mixed excimer in the excited state due to interaction between excited perylene molecule and pyrene molecules. The effect of voltage of applied electric field on electroluminescence help to study optical characteristics. At lower concentration of perylene in pyrene the voltage dependence is exponential. However, at higher concentrations the voltage dependence becomes linear. The effect of temperature on emission has been studied. The study of temperature dependence supports the proposed mechanism of formation of mixed excimer.

The increasing demands of highly luminescent phosphors find interest in basic research in the field of organo electroluminescence (EL). Currently organic compounds are widely used in the synthesis of electroluminescent diodes. Several papers have appeared on EL in various aromatic hydrocarbons over a period of two decades. However, it seems that the study of EL of doped pyrene escaped the attention of workers, though its fluorescence has been studied extensively. Moreover, pyrene is known to exhibit certain interesting properties when doped with perylene and as such system provides an interesting field of research regarding effect of perylene addition. The present paper reports the study of EL properties of perylene doped pyrene. Various phosphors of pyrene containing different amounts of perylene were synthesized. Attempts have been made to study voltage dependence and temperature dependence of phosphors.

Materials and Methods
Pyrene and perylene obtained from Fluka A.G. Buchs S.G. (Switzerland) were purified separately by the process of adsorption column chromatography and were heated in a furnace for about two hours. Purity of these compounds was further confirmed by taking paper chromatograms. Mixed phosphors containing $10^{-3}$, $5 \times 10^{-3}$, $10^{-2}$, $5 \times 10^{-2}$ and $10^{-1}$ mol of perylene per mol of pyrene were prepared.

Since pyrene is a wide band gap insulator, an EL cell suitable for the purpose was fabricated. The emmitter was a film of cellophane prepared by dipping it into a hot saturated solution of EL material in benzene, drying it and placing it with melted paraffin wax between a plate of aluminium electrode and thin uniform sheet of mica. The cell was compressed before cooling to exclude air bubbles. The sheet of mica was covered with conducting glass electrode. Electric contacts with electrodes were achieved by using silver paste. The EL cell was excited with an A.C. electric field in the frequency range from 50 Hz to 2.5 RHZ by audio frequency oscillator (Philips, India) whose output was fed into high voltage transformer (0-5000 volts). The EL emission from cell was measured by sensitive spot reflecting galvanometer coupled with IP-21 photomultiplier tube. An attempt was made to study the emission spectrum with the help of monochromatizing unit consisting of diffraction grating.

Results and Discussion
The electroluminescence spectra of pyrene containing different amounts of perylene is shown in Fig. 1. From Fig. 1 it is evident that the EL of doped pyrene consists of one structureless band in 500-520 nm region. The characteristic EL emission of pure pyrene (475 nm) as well as that of the pure perylene (580 nm) are completely absent in the spectra. In addition the intensity of green emission band observed at about 510 nm decreases with increase in concentration of perylene. Careful examination suggests that this band corresponds to the emission arising from other species formed in the excited state. The nature of excited species responsible in the EL emission can be based on the
available information regarding the structure of pyrene and perylene molecules. For the sake of comparison EL spectra of pyrene and perylene are also shown in Fig. 1.

The crystal structure of pyrene and perylene are identical in which the molecules are arranged in coplaner pairs. The pi orbital overlap of adjacent parallel molecules is large and hence these crystals favour excimer formation. In the mixed crystal perylene molecule exactly replaces a pyrene molecule in the lattice. Hence in perylene doped pyrene EL emission is thought to arise from "mixed excimer" as in photoluminescence. Further support for this statement is found in the studies of ultra-violet absorption spectra of pure pyrene and perylene doped pyrene. It is known that formation of aggregates modifies the absorption spectrum and photophysical properties. Remarkable change in the spectral characteristics of pyrene when doped with perylene indicates the possibility of formation of aggregates.

Perylene has strong absorption in the region of pyrene emission. Hence most of the electrical energy absorbed by the pyrene molecule would be trapped by perylene molecule. This transfer of energy may take place primarily by radiative transfer process or alternatively by a resonance phenomenon between allowed electric dipole transitions in pyrene and perylene molecules. The emission is absent for free perylene. Therefore, the excited perylene formed by the above mechanism must interact with adjacent pyrene molecule and form mixed dimer. The mixed dimer in the excited state is referred as mixed excimer. The energy level diagram of the mixed crystal based on all available information on the lowest energy levels of the singlet manifolds is shown in Fig. 2. Further support for this statement is found in the studies of ultra-violet absorption spectra of pure pyrene and perylene doped pyrene. It is known that formation of aggregates modifies the absorption spectrum and photophysical properties. Remarkable change in the spectral characteristics of pyrene when doped with perylene indicates the possibility of formation of aggregates.

Voltage dependence of EL emission

The study of voltage dependence of EL emission is of prime importance in determining the optical characteristics of a given material. The study also helps to establish condition for maximum EL efficiency for the system under consideration. The experimental results for the voltage dependence of EL emission of perylene doped pyrene is shown in Fig. 3. It shows that at higher concentration of perylene the plots are linear, while at lower concentration the plots are exponential. Thus in the range of concentration from \(10^{-3}\) to \(10^{-2}\) mol perylene, the brightness \(B\) increases exponentially with voltage \(V\) and at higher voltages the EL brightness seems to saturate. The \(B-V\) relationship is explained by the equation of Destriau:

\[
B = a \exp \left[ -\frac{b}{V^{0.5}} \right]
\]  

... (1)
where \( a \) and \( b \) are constants. We have attempted to verify the validity of Eq. (1). In Fig. 4 the plots of \( \log B \) versus \( V^{-0.5} \) are linear. This shows that the equation cited above is applicable. At higher concentrations (above \( 10^{-2} \) mol) Eq. (1) fails and EL brightness increases linearly in accordance with the relation

\[
B = \gamma V 
\]

where \( \gamma \) is a constant parameter. From Fig. 3 it is also evident that the EL intensity of phosphors decreases with perylene concentration. This decrease in brightness was attributed to radiative transfer of energy from pyrene to perylene molecule.

**Temperature dependence of EL emission**

In this particular work, the substance in an EL cell was maintained at the desired temperature for several minutes before the field was actually applied. The temperature dependence is shown in Fig. 5. With increase in temperature the output brightness of the system increases, but the wave-length of the emission peak remains unaffected. This observation can be considered to be an evidence for the fact that the observed emission is true EL and not caused by any discharge. The temperature dependence of EL is very complex in powder phosphors. However, attempt has been made to explain the observed results on the basis of increase in number of trapped electrons involved in EL emission with increase in temperature. At temperature below room temperature, the trapped electrons produced in the thin layer during excitation become more unstable. They may dissociate and diffuse away in the process of escaping recombination with holes. This explains the observed low in-
tensity of EL emission at lower temperature. With increase in temperature, the EL intensity ($B$) increases with temperature ($T$) and follows the exponential equation (3)

$$B = B_0 \exp \left[ -\frac{b}{T_0 - T} \right] \quad \ldots (3)$$

where $B_0$, $b$, and $T_0$ are constants. This may be due to the fact that increase in temperature increases the number of trapped electrons which recombine with holes with subsequent enhanced EL emission.

References