Effect of polar dopants on structure of emission spectrum of crystalline anthracene powders

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The effect of polar dopants on the spectral properties of crystalline anthracene is studied as a function of concentration by steady state fluorescence spectroscopy. The dopant is a fluorescent 9-vinylanthracene. The incorporation of the dopant not only quenches the fluorescence but also changes the structure of emission of anthracene. The higher dopant concentration induces significant enhancement in the intensity of low energy (0 ← 1) vibronic band at the expense of high energy (0 ← 0) band and wavelength of maximum emissions is shifted from 427 nm to 446 nm. The characteristic monomer and excimer emission of dopant are not observed even at higher concentration in the fluorescence spectra of doped anthracene. This observation rules out the possibility of excitation energy transfer from anthracene to dopant molecule. The shift in structure of emission of anthracene has been attributed to the local electric field generated by the polar dopant which is acting across the anthracene molecule and induces the changes both in the molecular vibrational levels and in transition dipoles. This effect is similar to solid state solvation effect and favors transition to the higher vibrational level of the ground state.

Keywords: Fluorescence, Emission spectra, Anthracene, Polar dopants, Spectral shifts, Oscillatory transitions

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The presence of impurities in the fluorescent host material always results in quenching of fluorescence of host either by excitation energy or by charge transfer and appearance of red shifted impurity fluorescence or exciplex fluorescence due to charge transfer complex formation. The incorporation of impurity in aromatic compounds is often done by doping. Thus, doping the light emitting material with appropriate dopants can tune the emission color or enhance the emission efficiency and stability compared to undoped material. The doping experiments involve growing crystals from melt to which a known amount of dopant has been added. Blue emitting crystalline anthracene is known to be the best host and can solubilize many dopants such as tetracene, pentacene, carbazole, perylene, etc. The conditions required for efficient excitation energy transfer from anthracene to dopant are satisfied because first excited singlet of anthracene are at higher level than the corresponding state of dopants and also the emission spectrum of anthracene has large integral overlap region with absorption spectra of these dopants. The red shifted emission in doped anthracene makes it a potential candidate for application in electroluminescent diodes and also as a scintillator.

Emission spectra of many organic molecular solids in liquid solution depend on the local electric fields generated by the surrounding polar molecules. This “solvation effect” is the result of intermolecular solute – solvent interaction forces such as dipole-dipole or dipole induced dipole that tend to stretch molecular bonds and shift charge distribution on molecules altering the energy difference between ground and excited state of solutes. It is also reported that solvation effect is also present in molecular solids where closely packed polar molecule can generate local electric fields. It is expected that in nonpolar planar anthracene doped by polar molecules such as monosubstituted crystalline anthracene, the spectral changes may be produced due to alteration of its electronic structures by neighboring polar molecules. In view of this fact, vinyl anthracene (VA) was selected as dopant in the present studies. Host anthracene and dopant have compatible size and shapes and that the anthracene excited singlet is of higher energy.

We report herein, the preparation and fluorescence studies of polycrystalline powders of doped anthracene. The spectral behavior of anthracene doped by polar molecules has been compared with that of anthracene containing nonpolar planar dopants. Attempts have been made to discuss the results of spectral shifts on the basis of solid state solvation effect of polar dopant molecules.

Experimental

Anthracene and VA, MA and CA obtained from Merck-Schuchardt were recrystallised from ethanol.
and purified further by sublimation. The purity was then confirmed by production of similar photoluminescence spectra when excited at different wavelength in UV region\textsuperscript{15}. Anthracene forms a series of solid solutions with VA. The mixed crystalline powders were prepared by conventional solid state reaction technique\textsuperscript{2}. Appropriate amounts of anthracene and VA dopant were intimately mixed, placed in silica crucible and heated in a closed electric furnace at a temperature just above the melting point of anthracene (215°C) for about 4 hr. Anthracene doped by CA and anthracene doped by MA were also prepared under similar experimental conditions. The molten mass obtained was cooled under controlled atmosphere, crushed to a fine powder and then subjected to fluorescence studies.

The fluorescence and fluorescence excitation spectra of the polycrystalline doped anthracene powders were recorded on PC based spectrofluorometer (Jasco, Japan, model FP-750). A fine powder of the sample was placed on the sample holder and pressed under quartz cover plate. The sample holder was then mounted on a special front surface attachment provided with the instrument. The frontal geometry makes an angle of 45° between excitation radiation and sample surface during fluorescence measurements.

Results and discussion

The excitation and fluorescence spectra of crystalline anthracene presented in Fig. 1 exhibit mirror image relationship and are largely Stoke shifted. The observed Stoke shift is because of intermolecular forces of attraction between neighboring anthracene molecule in its herringbone structure proposed by Desiraju & Gavezzotti\textsuperscript{16}. The structured fluorescence of anthracene shows two clearly resolved peaks with a shoulder on the low energy side. The location of the band maxima for three components of \( L_0 \) transition of anthracene are assigned as 0→0; 0→1 and 0→2. The first band corresponding to 0→0 transition is more intense and wavelength of maximum emission band corresponding to this transition is 427 nm. This band is stoke shifted from 0→0 vibronic band in excitation spectrum by 997 cm\(^{-1}\). The fluorescence spectrum of anthracene doped by VA is also shown in Fig. 1 (spectrum c). The careful comparison of this spectrum with the spectrum of bare anthracene reveals that the incorporation of VA does not change the spectral region of anthracene, although the vibronic band intensities are seen to be changed. The high energy band corresponding to 0→0 transition is quenched and the nearby 0→1 is enhanced. These vibronic changes induced in excited anthracene molecule by VA exhibits a shift in \( \lambda_{em} \) from 427 nm to 446 nm. The fluorescence of VA expected to occur in the region 400-500 nm is not observed\textsuperscript{17}. This conclusion is further supported by the fact that the excitation spectrum of VA is widely separated from the fluorescence spectrum of the crystalline anthracene (Fig 2). Hence, it is believed that the observed changes in spectrum of anthracene in terms of vibronic band intensity in anthracene are because of polar VA dopant.

The evolution of fluorescence features of anthracene was studied as a function of concentration of VA. Figure 3 shows the fluorescence spectra with

![Fig. 1](image1.png)  
**Fig. 1**—(a) Normalized excitation; (b) fluorescence spectra of pure anthracene; (c) anthracene doped by 3 × 10\(^{-2}\) mole VA.

![Fig. 2](image2.png)  
**Fig. 2**—Spectral separation between the fluorescence of anthracene (1) and excitation of VA (2).
varying concentration of VA as the impurity in anthracene host at room temperature. It is evident from the figure that no energy shifts are observed for any of the three peaks when concentration is increased. It is seen that as concentration of VA increases the intensity of both vibronic bands decreases. The rate of decrease in intensity of 0←0 band is more and hence, at and above 1×10^2 mole dopant concentration its intensity actually becomes lower than that of 0←1 band. The higher amount of VA creates sufficient electric field which induces dipolar changes in the band intensity. The spectral shape of anthracene containing high dopant concentration (3×10^2 mole per mole) seems to be reversed when compared to the spectrum of undoped anthracene (Fig. 1). The ratio of fluorescence intensity of the bands (F_{0←1} to F_{0←0}) determined at different dopant concentrations are given in Table 1. The ratio increases with the dopant concentration, reaches a maximum at about 3×10^2 mole of VA per mole anthracene and saturates at higher concentration. The broad, structureless excimer fluorescence of bare VA shown in Fig. 3 (spectrum 7) is not seen even at higher dopant concentration. This observation rules out the possibility of induced excitation by excitation energy transfer (EET) from the excited anthracene to VA molecule.

Planar dopants such as tetracene, perylene, etc., partially quench the fluorescence and red shifted fluorescence characteristic of dopant appears in the emission spectrum of doped anthracene. However, in the present studies, polar VA dopant quenches intensity of one band and simultaneously induces the enhancement in the intensity of the other band.

The band intensities are related with oscillatory transition strength (f) which is proportional to the integrated area of the fluorescence peak of the band. The estimated values are listed in Table 1. The dependence of the relative oscillatory strength of the transition bands of anthracene as function of VA concentration are illustrated in Fig. 4. The negative slope of the line obtained for 0←0 transition indicates decreased probability of this transition while positive slope of 0←1 transition shows increased probability of the transition due to dopant concentration. The FWHM of 0←0 bands seems to decrease while that of 0←1 band remains nearly constant at ≈12 nm. The spectral band width at half maximum less than 15 nm indicates saturated color emission. The typical molecular organic light emitting diodes (LEDs) have FWHM of between 60 and 100 nm and for some polymers and phosphorescent molecule it has shown to be as narrow as 26 nm (ref. 19). The values of full width at half maximum (FWHM) of both vibronic bands from Fig. 3 are given in Table 1. These results reveal that the FWHM of 0←0 emission band

<table>
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<tr>
<th>Conc.(mole of VA per mole anthracene)</th>
<th>Emission band intensity (au) for transitions at</th>
<th>FWHM (nm)</th>
<th>Rel. oscill. strength f (au)</th>
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<tr>
<td></td>
<td>427 nm</td>
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Fig. 3—Fluorescence spectra of anthracene doped by VA. [1, pure anthracene; 2, 1×10^{-3} mole; 3, 5×10^{-3} mole; 4, 1×10^{-2} mole; 5, 3×10^{-2} mole; 6, 5×10^{-2} mole of VA per mole anthracene; 7, crystalline VA.]
decreases while that of 0←1 remains nearly constant with dopant concentration. The observed decrease in band broadening suggests the closer packing of polar VA molecules with anthracene in the doped lattice. The doped anthracene system exhibits vibronic emission lines of very narrow band width. The lower dopant concentration does not induce significant changes in the relative oscillatory strength of 0←0 and 0←1 transition and the values are not much different. However, at higher dopant concentration, oscillatory strength of 0←1 band is about 5 to 10 times greater than that of 0←0 band. These results indicate that the increase in relative oscillatory strength of the vibrational states of excited manifold of anthracene is because of the presence of the VA only which interacts with excited anthracene and altering its electronic configuration.

The polar dopant effect on change in structure of anthracene emission is further confirmed by similar studies performed on the MA doped anthracene and CA doped anthracene. The spectral results illustrated in the Fig. 4, indicate the quenching of 0←0 band and sensitization of 0←1 band.

Anthracene doped with tetracene is a classic system where very efficient transfer of singlet energy occurs. The blue anthracene fluorescence is quenched and characteristic green fluorescence of tetracene in this system appears because of anthracene exciton (excited electron- hole pair) trapped at physical defect created by tetracene in doped lattice. However, every doping does not induce traps. In the present study, characteristic fluorescence of VA is not observed upon optical excitation of doped anthracene as in tetracene doped anthracene system. The quenching in doped anthracene containing small amounts of VA is because of random migration of excitation energy (exciton) through the lattice and will remain with the foreign VA molecule until dissipated non-radiatively. However, the dopant does not quench the anthracene fluorescence appreciably; rather it sensitizes low energy vibronic band as compared to high energy band.

Compared to tetracene or other similar type of dopants (perylene, pentacene), VA is polar and thought to act in a different manner. The solid state solvation effect reported in literature indicates that the closely packed polar solute in the organic molecular solids induces appreciable red spectral shift in the emission spectrum by local electric field. The solid state solvation (SSS) luminescence is explained on the basis of energy structures both for excitons and for conduction level. The excited anthracene molecule is expected to be more polarizable as electron in the excited state occupies a more extended orbital than the electron in the ground state. The presence of larger amounts of VA in the anthracene lattice generates strong local electric field which acts across the excited anthracene molecule and induces changes both in the molecular vibrational energy levels and in transition dipoles leading to Stark effect. These effects results in increase in overlap of $S_0$ ground state wave function with $S_1$ vibronic levels thereby favoring the transition to higher vibration levels.

The observed relative oscillatory strength of $S_1$ (0←1) is more than that of $S_1$ (0←0) even for lower concentration of VA and becomes more than ten times for higher concentration. Therefore, with increase in VA concentration the transitions to the higher vibrational levels are expected to increase faster than that of lower vibrational levels of $S_1$ states. Hence vibration band intensity of (0←0) are enhanced by VA and the vibration band intensity gets reversed.

In contrast to earlier reports of quenching of anthracene fluorescence and appearance of guest fluorescence in mixed crystals, the present study reports quenching of high energy vibronic emission band and sensitization of low energy band by polar VA dopant. The presence of VA in sufficient concentration can shift the wavelength of maximum emission of anthracene to longer wavelength side which is necessary to produce emitter required for organic light emitting devices.
It is considered that local electric field generated by polar dopant interacts with excited anthracene and alters the electronic configuration because of induced dipole-dipole interaction resulting in spectral shift. This Stark effect mechanism is also of significance to those working in the field of fluorescence spectroscopy of mixed organic molecular crystal systems. The effect is confirmed by testing other polar dopants in anthracene.

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References