Tuning of wavelength of exciplex emission of pyrene and perylene in fluorene matrix

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The exciplex emission of pyrene and perylene has been studied systematically in fluorene matrix. The fluorescent fluorene act as energy donor. The fluorescence spectra of mixed stack crystals of fluorene are recorded on spectrofluorometer by monitoring the excitation wavelength at 363 nm. Addition of 10⁻¹ mol pyrene and 10⁻¹ mol perylene quenches the structured monomeric emission of fluorene and new structureless emission band appear at a wavelength 510 nm. The broad band is attributed to the emission arising from the exciplex formed between pyrene and perylene. The observed emission does not correspond to the pyrene-perylene exciplex emission without fluorene matrix. It is believed that the varying degree of molecular overlapping changes the wavelength of exciplex emission of pyrene and perylene. Systematic variation of concentration of pyrene and perylene in fluorene matrix has given mixed stack crystals of fluorene having molecular overlapping of different degrees. The fluorescence spectra of these mixed crystals of fluorene show exciplex emissions at different wavelengths in the range 485-560 nm. The tuning of exciplex emission wavelength is possible by controlling concentration of pyrene and perylene in fluorene matrix.

Photophysical and electrical processes of molecular organic semiconductors need to be understood for potential applications of these materials in the field of electroluminescence and low cost light emitting materials¹². Tuning of the colours of phosphor material is an attractive topic in fabrication of organic light emitting diodes. Creation of the materials emitting with desired colours can be achieved by mixing homogeneously red, yellow or green emitting materials in a material emitting with a blue or violet colour.

Fluorene is a planar molecule which crystallizes in orthorhombic form with four molecules per unit cell. It is a wide band gap organic semiconducting material and fluoresce in violet sector of the visible spectrum. We found that fluorene solubalise polynuclear aromatic hydrocarbons in molten state from which its mixed crystals can be grown. Use of planer and highly conjugated aromatic hydrocarbons as an impurity in fluorene can give mixed stack luminophors emitting in the green, yellow and orange region of the spectrum. The highly fluorescent pyrene and perylene whose lattice contains four molecules per unit cell favouring formation of excimers, dimers etc. were chosen as guest molecules³⁴. The present work aims at the preparation of mixed crystals of fluorene containing pyrene and perylene impurities. The fluorescence spectra of these polycrystalline luminophors were recorded and discussed with a view to understand the fluorescent behaviour of mixed stack crystals.

Materials and Methods

Fluorene obtained from Merck-Schuchardt (Hohenbyunn) Germany was recrystallized from ethanol with charcoal, and then from ethanol alone. The recrystallized fluorene is fluorescent and exhibits violet fluorescence. The fluorescent grade pyrene and perylene procured from Fluka AG, Buchs SG, (Switzerland) were used without further purification. The purity of all the components were confirmed by comparing the fluorescence spectra with those reported in the literature. The mixed stack crystals of fluorene containing pyrene and perylene were prepared by conventional solid state reaction technique⁵. Appropriate amounts of pyrene, perylene and fluorene were intimately mixed, placed in a silica crucible and heated in close furnace at temperature 217°C for about 5 h. The melt was then cooled and the mixed crystals were crushed to a fine powder.
The fluorescence and fluorescence excitation spectra of pure crystalline components and mixed crystal powders were recorded on PC based Spectro­fluorometer model FP-750, JASCO, Japan.

Results and Discussion

Figure 1 represents fluorescence and excitation spectra of crystalline fluorene. The fluorescence spectrum is structured and has emission bands at 391, 412, and 435 nm of which the band at 412 nm is intense. The excitation spectrum of fluorene monitored at emission wavelength 412 nm is structured with bands at 280, 347, 363 and 385 nm. The excitation band at 363 nm is more intense. Hence, the fluorescence spectra of fluorene and doped fluorene were recorded at the excitation wavelength 363 nm. The fluorescence and excitation spectra exhibit mirror image relationship with a very small Stokes shift of 398.57 cm⁻¹. The small Stokes shift indicates that the fluorene emission is monomeric in nature. The fluorescence spectrum of crystalline fluorene does not match with its solution spectrum at a concentration $10^{-5} \text{ M}$ in methanol. Figure 2 presents the fluorescence spectra of fluorene as a function of concentration in benzene. It is observed that the dilute solution spectra are structureless and as concentration increases, the spectra become more structured. The structured spectrum of concentrated solution matches with the spectrum of crystalline fluorene. The spectral shift from 314 nm to 392 nm observed in Fig. 2 as a function of concentration is due to two phenyl rings becoming more co-planar with concentration.

The crystalline fluorene emitting in violet region is doped by the fluorescent materials emitting towards red of the visible spectrum. Fig. 3 shows the fluorescence spectra of pyrene doped fluorene (a) and perylene doped fluorene (b).

![Fig. 1—Fluorescence and excitation spectra of crystalline fluorene.](image1)

![Fig. 2—Fluorescence spectra of fluorene in benzene as a function of concentration.](image2)

![Fig. 3—Fluorescence spectra of pyrene doped fluorene (a) and perylene doped fluorene (b).](image3)
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Fluorescence spectrum of pyrene doped fluorene is broad and structureless with maximum at 470 nm. The emission bands of fluorene are not observed in the fluorescence spectra of pyrene doped fluorene. From this observation it is concluded that the pyrene quenches the monomeric emission of fluorene and the observed broad emission is a well known pyrene excimer emission. The fluorescence spectrum of perylene doped fluorene is structured and corresponds to the fluorene emission with two additional weak broad bands at 462 and 489 nm. This observation indicated the absence of interaction between fluorene and perylene in mixed crystal. Figure 4 reveals the fluorescence studies on fluorene-pyrene system in solution. These studies have shown similar results when concentration of pyrene is varied. The two component solution systems containing higher concentration of pyrene exhibited excimer emission. In contrast, the solution spectra of fluorene-perylene system show separate intense emission bands of fluorene and weak emission bands of perylene due to different orientations of its isomers in the excited state.

Figure 5 shows fluorescence spectrum of tricomponent fluorene powder containing $10^{-3}$ mol pyrene and $10^{-1}$ mol perylene per mol fluorene. The figure reveals the quenching of fluorescence of fluorene and appearance of a broad intense emission band peaking

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**Fig. 4**—Fluorescence spectra of two component solution system.

a. Fluorene + 0 M Pyrene  
b. Fluorene + $1\times10^{-3}$ M Pyrene  
c. Fluorene + $1\times10^{-1}$ M Pyrene  
d. Fluorene + $1\times10^{-1}$ M Pyrene

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**Fig. 5**—Fluorescence spectra of pyrene doped fluorene (a), fluorene doped by pyrene and perylene (b) and perylene doped pyrene (c).

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**Fig. 6**—Excitation spectra of (1) crystalline fluorene, (2) pyrene doped fluorene and (3) fluorene doped by pyrene and perylene.
at 510 nm. The excimer emission of pyrene is not observed in the spectrum. The absence of excimer band of pyrene suggests that there could be an interaction between perylene and pyrene in fluorene matrix. In the two component systems of pyrene and perylene, pyrene is known to interact with perylene and exhibits an exciplex emission. The fluorescence spectrum of exciplex emission of pyrene-perylene without fluorene matrix is shown in Fig. 5(c). This exciplex emission occurring at 500 nm does not correspond with broad emission band appearing at 510 nm in tricomponent fluorene luminophor. We believe that during formation of mixed crystal, the pyrene and perylene must be oriented in different manner in fluorene matrix as such molecular orientations are probable at lower concentrations of impurity in matrix. The formation of exciplex of pyrene and perylene in fluorene matrix is confirmed from the excitation fluorescence spectra. Figure 6 represents excitation spectra of pure fluorene, pyrene doped fluorene and fluorene doped by pyrene and perylene. The excitation spectrum of pyrene doped fluorene shows broadening of the spectrum compared to that of the structured excitation spectrum of fluorene. The structured excitation bands indicate monomeric emission while structureless bands support the formation of excimer and exciplex in the excited state. The excitation spectrum of pyrene and perylene doped fluorene shows a bathochromic shift and additional broad bands are observed at the wavelengths 426 and 460 nm. The emission spectra monitored at these excitation wavelengths were identical with the structureless emission band of tricomponent fluorene shown in Fig. 5(b). These observations confirm the formation of exciplex between pyrene and perylene in fluorene matrix.

It is possible that the different orientations of pyrene and perylene in fluorene may give exciplex emitting at different wavelengths. With a view to understand these interactions, fluorescence spectra of fluorene containing different amounts of pyrene and perylene were recorded and discussed. Figure 7 shows fluorescence spectra of fluorene containing varying amounts of pyrene and perylene. The composition and optical characteristics of these luminophors are summarized in Table 1. These observations indicate that the interaction of pyrene and perylene must be of different type in fluorene matrix.

Table 1—The composition and optical characteristics of fluorene mixed crystals

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Host: Fluorene</th>
<th>Fluorescence colour</th>
<th>Position of the emission peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Guest-1 (G1)</td>
<td>Guest-2 (G2)</td>
<td>Peak 1</td>
</tr>
<tr>
<td>1</td>
<td>pyrene</td>
<td>perylene</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10⁻³</td>
<td>10⁻³</td>
<td>Green</td>
</tr>
<tr>
<td>3</td>
<td>10⁻²</td>
<td>10⁻³</td>
<td>Yellow</td>
</tr>
<tr>
<td>4</td>
<td>10⁻¹</td>
<td>10⁻³</td>
<td>Orange</td>
</tr>
<tr>
<td>5</td>
<td>10⁻²</td>
<td>10⁻²</td>
<td>Green</td>
</tr>
<tr>
<td>6</td>
<td>10⁻¹</td>
<td>10⁻¹</td>
<td>Yellow</td>
</tr>
<tr>
<td>7</td>
<td>10⁻¹</td>
<td>10⁻³</td>
<td>Orange</td>
</tr>
<tr>
<td>8</td>
<td>10⁻¹</td>
<td>10⁻²</td>
<td>Parrot green</td>
</tr>
<tr>
<td>9</td>
<td>10⁻¹</td>
<td>10⁻¹</td>
<td>Greenish yellow</td>
</tr>
</tbody>
</table>

Concentration of guests is in mole per mole of fluorene.
concentration of perylene broadens and shifts the spectra towards red.

The fluorescence spectra of fluorene containing $10^3$ mole pyrene and varying amounts of perylene are shown in Fig. 7(c). All the emission bands are structureless. The fluorescence emission shifts from 494 nm to 510 nm when concentration of perylene is varied from $10^3$ to $10^1$ mol perylene. Thus, by varying concentration of perylene and pyrene in fluorene matrix, the emission wavelength of exciplex can be tuned from 485 nm to 560 nm. The new exciplex like broad emission bands observed in the range 485-560 nm are due to aggregation of molecules with different degree of overlap. When usual sandwich type overlap occurs, the center of perylene and pyrene molecule overlap as shown in Fig. 8(a) and exciplex emission band as shown in Fig. 5(c) has to appear. However, the fluorescence spectra of fluorene containing different amounts of pyrene and perylene neither corresponds to the excimer band of bare pyrene nor to the exciplex emission of pyrene and perylene without fluorene matrix. Hence, these bands are attributed to the exciplex formed in excited state due to the partial overlap of pyrene and perylene in fluorene matrix. The variation in emission wavelength is due to varying degree of overlap between pyrene and perylene when they are coming in pairs during formation of mixed crystals from the melt in fluorene matrix. When pyrene and perylene containing fluorene crystals were grown from the melt, the pyrene and perylene replaces the fluorene by fitting into the empty lattice sites. This double replacement forms microcrystalline aggregates. The stack sequence is of the type $D G_1 G_2 D G_1 G_2 D \ldots \ldots$ and is

![Fig. 7](image1.png)  
![Fig. 8](image2.png)
known as mixed stacks. In two molecules comprising a pair, the molecular centres are shifted as shown in Fig. 8(b). It is known that the varying degree of overlap shifts the centre to centre distance of two parallel molecules\textsuperscript{12}. The emission spectra of mixed stack microcrystalline powder do not show the emission of individual components.

Fluorescence spectra of three component solution systems have shown the emission bands corresponding to the monomer emission of the perylene. The expected pyrene-perylene exciplex emission is not observed in the solution fluorescence spectra. The two component solution spectra without fluorene have shown separate bands of pyrene and perylene. These studies indicate that the pyrene-perylene exciplex emission is possible only in crystal systems.

The fluorescence of fluorene is modified by doping it with pyrene and perylene. The fluorescence spectrum of perylene doped pyrene shows exciplex emission band peaking only at 500 nm indicating maximum molecular overlap. However, pyrene and perylene are observed to undergo molecular overlap of varying degree when they are coming in pairs during formation of mixed crystals in fluorene matrix. These molecular orientations have given fluorene luminophors emitting with different wavelengths. The blue emitting fluorene is thus made to emit in the wavelength range 485-560 nm. The tuning of emission wavelength is dependent on concentration of pyrene and perylene. The luminophor prepared in this study provide materials suited for use in fluorescent lamps and in electroluminescent devices.

References