CHAPTER 6

CONCLUSION
Fluorescence of naphthalene, fluorene and biphenyl has been investigated by doping them intentionally by highly fluorescent impurities. The fluorescent impurities were selected properly so that they can form excimer, exciplex or charge transfer state in the host compound and emit at longer wavelength side. Some of the impurities act to enhance the fluorescence.

The mixed bicomponent and tricomponent crystals were prepared by using doping technique. The appropriate amounts of host and guests were intimately mixed, crushed and heated to melt. The mixed crystals were grown by cooling the melt in the evacuated chamber. The crystals were crushed to fine powder and their absorption and fluorescence spectra were recorded.

**Naphthalene luminophors:**

Fluorescence spectrum of naphthalene is structured and has mirror image relationship with its absorption and excitation spectra. The emission is arising from single molecule as in solution. Naphthalene serves as a good host in which solid solution of other organic components can be prepared and also acts as an efficient donor in EET processes with anthracene and pyrene. The mixed crystals of anthracene doped naphthalene gives characteristic emission of anthracene guest and intensity
depends upon concentration of guest. The mixed crystal of pyrene doped naphthalene exhibits well known excimer emission of crystalline pyrene. The photophysical behaviour of mixed crystal are explained on the basis of EET processes occurring between naphthalene and guest molecule.

The fluorescence of tricomponent naphthalene containing pyrene and perylene are broad bands occurred in the wavelength range 484-610 nm. The addition of perylene in naphthalene containing pyrene has changed the fluorescence spectra of naphthalene from structured monomeric emission to structureless bands. The emission bands are attributed to as arising due to charge transfer state created below the emitting level of naphthalene. The CT states are believed to be produced due to different interaction of pyrene and perylene with naphthalene. The energy of CT state seems to depend upon the concentration of perylene. Therefore, emission in different wavelength region is observed when concentration of perylene is varied in naphthalene-pyrene system. Such results were not observed when concentration of perylene was varied in naphthalene bicomponent system and in pyrene-perylene bicomponent system. The energetic interaction of perylene to generate CT state is probable only in tricomponent
naphthalene-pyrene-perylene system. The perylene incorporated as impurity acts as wavelength shifter.

**Naphthalene-anthracene-pyrene system:**

Singlet-singlet EET processes between excited naphthalene and ground state anthracene is responsible to give characteristic emission of anthracene moiety. The anthracene impurity in naphthalene quenches the fluorescence of naphthalene and guest fluorescence is sensitized by concentration of anthracene upto $10^{-2}$ mole while above this concentration the rate of sensitization decreases due to concentration quenching. The fluorescence of anthracene doped naphthalene was further enhanced by adding pyrene impurity in anthracene- naphthalene system. The enhancement effect introduced by pyrene is explained on the basis of triplet-triplet annihilation process occurring between anthracene and pyrene triplet to form singlet excited anthracene. The increased rate of anthracene excited singlet enhance fluorescence of doped naphthalene. The blue emitting, highly fluorescent naphthalene luminophors containing anthracene and pyrene impurities would be used as emitting materials for fluorescent lamp.

**Biphenyl luminophors:**

The biphenyl has two phenyl rings joined by C-C linkage, which facilitates orientation of the rings during excitation. The
absorption and excitation spectra of crystalline biphenyl are broad bands due to the random orientation of phenyl rings. Broad absorption band indicates the possibility of formation of exciplex with other component by CT process or by orbital overlapping. The fluorescence spectrum of crystalline biphenyl is structured from which it is concluded that the phenyl rings in the excited state becomes more co-planer and excited biphenyl may undergo EET processes with intentionally added impurities.

From the fluorescent studies of anthracene doped biphenyl and pyrene doped biphenyl, it is observed that the energy absorbed by the biphenyl is delocalized through out the matrix and localized by the anthracene and pyrene. These EET processes result in the monomer fluorescence of anthracene and pyrene respectively. The fluorescence spectra of biphenyl containing higher concentration of pyrene have revealed the exciplex formation between the two components. The probable mechanism is suggested for formation of exciplex and exciplex emission.

**Biphenyl-pyrene-perylene system:**

The addition of perylene has shifted the wavelength of fluorescence beyond 460 nm towards red. The pyrene monomer fluorescence observed at $10^{-3}$ mole concentration is quenched
when $10^{-3}$ mole perylene is added. The new emission bands observed at wavelength 457 nm and 486 nm are due to the molecular emission of $\alpha$ and $\beta$ perylene. When concentration of perylene is increased to $10^{-2}$ mole, the exciplex emission of pyrene-perylene has been observed, however, at higher concentration the dimeric emission of perylene becomes more probable. These emission bands are explained on the basis of probable EET process occurring between the three components. It is observed that at lower concentration of the impurity the monomeric emission of the impurities appears, whereas at higher concentration excimer emission of perylene becomes more probable. When concentration of impurities is medium, the exciplex emission of pyrene-perylene appears in the spectra of doubly doped biphenyl host.

**Biphenyl- anthracene system:**

The fluorescence of biphenyl is completely quenched by anthracene. The fluorescence spectrum of anthracene doped biphenyl is structured. Though the emission bands are identical with that of bare anthracene, a shift in emission by 15 nm is observed towards blue. The observed anthracene like emission is explained on the basis of singlet-singlet EET process occurring from biphenyl to anthracene. The blue shift is due to intermolecular forces of attraction between anthracene in...
biphenyl lattice, which are not as strong as in pure anthracene lattice. The host sensitized fluorescence found to depend on the concentration of anthracene.

**Biphenyl-anthracene-pyrene system:**

The fluorescence of tricomponent biphenyl mixed crystals containing anthracene and pyrene is identical with that of anthracene doped biphenyl. The incorporated pyrene enhances the anthracene like fluorescence of biphenyl when tricomponent biphenyl is excited by the excitation wavelength of biphenyl. The enhancement effect is explained by considering the formation of triplets of anthracene and pyrene by intersystem crossing which is believed to be followed by triplet-triplet annihilation to give anthracene singlets. The increased rate of formation of anthracene singlets enhances the anthracene like fluorescence.

**Fluorene luminophors:**

The fluorene has two phenyl rings joined by methylene bridge which seems to decrease conjugation as compared to biphenyl and naphthalene, and hence, it is weakly fluorescent. Its excitation and absorption spectrum overlaps indicating incapability to form molecular aggregates with itself or with other components. Similarly, in the molecular structure the hydrogen atom of methylene bridge produces a steric hindrance for an incoming molecule during aggregation.
Bicomponent systems:

i) Pyrene-fluorene

ii) Perylene-fluorene

Fluorescence spectra of pyrene doped fluorene and perylene doped fluorene are identical with that of bare fluorene. The absence of fluorescence of pyrene and perylene in the doped spectra indicates that the excited fluorene is not transferring its excitation energy, however, it serves as good matrix in which solid solution of pyrene and perylene could be prepared.

Tricomponent fluorene luminophors:

Pyrene-perylene-fluorene system:

The fluorescence spectra of fluorene containing varying amounts of pyrene and perylene are broad bands and the emission bands are observed in the range 485-520 nm. The well-known excimer as well as monomer emission bands of both the impurities are absent in all the spectra of the fluorene luminophors. The observed broad emission bands are interpreted as arising due to an exciplex formed between pyrene and perylene by lateral π-orbital overlapping in fluorene matrix. Fluorene serves only as a matrix to prepare solid solution of pyrene and perylene. It is believed that the pyrene and perylene are coming in pairs during formation of mixed crystals. Variation in concentration of pyrene and perylene has given the
fluorene luminophors emitting with different wavelength. These different wavelengths are due to the exciplex formed by the orbital overlap of different degree. Such partial degree of overlap is possible when concentration of components is solid solutions are varied. The usual perfect sandwich possible only in perylene doped pyrene has given an exciplex emitting at 500 nm. None of the fluorene luminophors containing pyrene and perylene has given emission at 500 nm. In the partial overlap the center to center distance of two parallel molecule shifts result would give emission wavelength other than 500 nm.

**Fluorescence of doped fluorene:**

**Fluorene-anthracene system:**

Fluorescence of fluorene is sensitized by anthracene impurity. The characteristic emission bands of anthracene are not observed in the spectra of anthracene doped fluorene. The increase in the intensity of fluorene fluorescence is found to depend upon the concentration of anthracene. The fluorescence sensitization is expressed in terms of the relative quantum efficiency of doped fluorene to that of the undoped fluorene. The quantum efficiency is found to be greatly increased at lower concentration of anthracene than at higher concentrations. The sensitization effect is also corelated with the grain size. The doped fluorene exhibiting intense fluorescence found to posses
smaller grain size. However, fluorene luminophors containing very small and very high concentration of anthracene, crystallize in larger grain size. The sensitization effect is explained on the basis of formation of triplets followed by triplet-triplet annihilation which results into first singlet excited fluorene. The work is published in international journal "Materials Chemistry and Physics". The synthesis of blue emitting intense luminophors are economical and could be used as emitting materials for fluorescent lamps.

**Tricomponent fluorene luminophor:**

**Fluorene-anthracene-perylene system:**

Tricomponent fluorene luminophors containing anthracene and perylene have exhibited interesting fluorescence behaviour due to interaction of perylene with anthracene in fluorene matrix. The addition of perylene quenches the fluorescence of fluorene and a new broad band peaking at 510 nm appears toward red. The intensity and energy of this band found to vary with concentration of anthracene and perylene in fluorene matrix. The exciplex formation between the three components is improbable, as structures of fluorene and anthracene are not favouring formation of such species in the excited state. Hence, the observed broad emission band is attributed to as arising due to formation of CTC between
anthracene and perylene. The probable mechanism for CTC formation and emission is suggested.

The behaviour of naphthalene, biphenyl and fluorene hosts were found different. Naphthalene is an efficient donor of excitation energy and has interaction with impurities. Doubly doped naphthalene has given luminophors emitting towards red. Biphenyl host is not only efficient donor of excitation energy but also acted to form the exciplex with impurities incorporated in it. In contrast, fluorene is neither a donor of excitation energy nor its structure favour exciplex emission with impurities. However, it has served as a good matrix in which different orientations of pyrene and perylene have given luminophors emitting towards longer wavelength sides.

In all the luminophors the colour of fluorescence can be tuned by controlling the concentration of intentionally added impurities in the host. These luminophors could be used for fabrication of light emitting devices. Blue light emitting biphenyl and fluorene luminophors having high efficiency can be used for fabrication of fluorescent lamps. So also, the excitation energy transfer processes resulted either in quenching or sensitization of the fluorescence in bicomponent and tricomponent luminophors, are not only scientifically important but also useful in practice. The mechanisms suggested for the
understanding of the origin of fluorescence in doped luminophors are of interest in the field of organic molecular crystal luminescence. The method suggested for synthesis of the luminophor is more economical. The intense and red shifted luminophors of naphthalene, biphenyl and fluorene can meet the new demands for phosphors required in fluorescent lamp industry and for electroluminescent devices.