2. Experimental

The polynuclear aromatic hydrocarbons were used to prepare bicomponent organic mixed luminophors for fluorescence studies. The experimental work consists of following stages;

1. Purification of basic compounds.
2. Preparation of mixed crystalline luminophors.
3. Recording of fluorescence excitation and fluorescence spectra.
4. Recording of absorption spectra of the materials in solution.
5. Recording of XRD profile.

2.1 Purification of the compounds

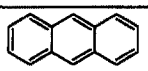
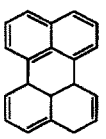
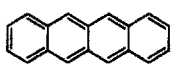
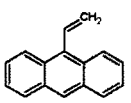
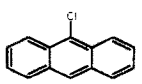
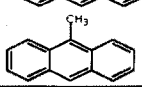
Anthracene selected as host and many other guest components such as perylene, tetracene, 9-vinylanthracene (VA), 9-chloroanthracene (CA) and 9-methylanthracene (MA) were obtained from Merck-Schuhardt. Anthracene was recrystallized from ethanol and the guest components were recrystallized from benzene. Purity of these compounds was further confirmed by taking melting point, paper chromatogram and by production of similar photoluminescence spectra when excited at different wavelengths in UV region [65]. A match between fluorescence spectra of the compound with the corresponding spectra reported in literature has confirmed the purity of fluorescent compound.

2.2 Preparation of crystalline mixed luminophors

The preparation of bicomponent mixed crystals is based on the solid state reaction between anthracene (host) and various guests. Anthracene forms series of solid solutions with these guests. The mixed crystalline powders of anthracene were prepared by conventional solid state reaction technique [34, 66] .Appropriate amounts of host and guests were intimately mixed, placed in silica crucible and heated in closed electric furnace at a temperature just above the melting point of anthracene (215°c) for about 4hr. The melt obtained by this conventional heating method was then cooled to grow mixed crystals. Mixed crystalline powders were also prepared by microwave heating. The contents of silica crucible were heated in microwave oven (BPL-600-T) to obtain melt using 2450 MHz microwave radiations. Small amount of water was used as dielectric. The microwave dielectric uses the ability of dielectric materials to transform electromagnetic energy into heat which propagates through the material and heats it

removing the need to heat the container and then cooling under controlled atmosphere. The process of heating and cooling is repeated 4-5 times to obtain homogeneous mixed crystals. The molten mass obtain in both methods i.e. in conventional and in microwave method were crushed to fine powder [67] and subjected to structural and fluorescence characterization.

Table No.1:-

Sr. No	Name of compound	Molecular Weight (g/mole)	Structural formula	Melting point (^{0}c)		$\lambda_{max\ (nm)}$	
				Expt.	Liter.	Expt.	Liter.
1	Anthracene	178.23		217	217.5	428	430
2	Perylene	252.32		277	277	563	600
3	Tetracene	228.29		357	357	483	-
4	9-Vinylanthracene (VA)	204.27		63	63	413	422
5	9-Chloroanthracene (CA)	212.38		105	105	516	-
6	9-Methylanthracene (MA)	192.26		77	77	419	412

In order to obtain mixed crystals having desired photo physical properties the concentration of host is kept constant and that of guests were varied and expressed in mole per mole of host material. Following bicomponent mixed crystal systems were prepared:

1. anthracene (H) doped by tetracene (G)
2. anthracene (H) doped by 9-vinylanthracene (G)
3. anthracene (H) doped by perylene (G)
4. anthracene (H) doped by 9-chloroanthracene (G)
5. anthracene (H) doped by 9-methylanthracene (G)

where, H - Host and G - Guest.

The compositions of guests present in different mixed crystals of anthracene are shown in Table No. 2.

Table No.2:- Composition of two component luminophors.

System No.1: perylene (G) doped anthracene (H) luminophors.

Sample No.	Wt. of host (H) in gms	Wt. of guest (G) in gms	Concentration of luminophors in mole per mole
1	0.5	0	Pure Anthracene
2	0.5	0.003539	5×10^{-3}
3	0.5	0.007078	1×10^{-2}
4	0.5	0.01415	2×10^{-2}
5	0.5	0.02123	3×10^{-2}
6	0.5	0.03539	5×10^{-2}
7	0.5	0.07078	1×10^{-1}

System No.2: tetracene (G) doped anthracene (H) luminophors.

Sample No.	Wt. of host (H) in gms	Wt. of guest (G) in gms	Concentration of luminophors in mole per mole
1	0.5	0	Pure Anthracene
2	0.5	0.003202	5×10^{-3}
3	0.5	0.006404	1×10^{-2}
4	0.5	0.01921	3×10^{-2}
5	0.5	0.03202	5×10^{-2}
6	0.5	0.06404	1×10^{-1}

System No.3: 9-vinylanthracene (G) doped anthracene (H) luminophors.

Sample No.	Wt. of host (H) in gms	Wt. of guest (G) in gms	Concentration of luminophors in mole per mole
1	0.5	0	Pure Anthracene
2	0.5	0.0005728	$1 X 10^{-3}$
3	0.5	0.002864	$5 X 10^{-3}$
4	0.5	0.005728	$1 x 10^{-2}$
5	0.5	0.01718	$3 X 10^{-2}$
6	0.5	0.02864	$5 X 10^{-2}$

System No.4: 9-chloroanthracene (G) doped anthracene (H) luminophors.

Sample No.	Wt. of host (H) in gms	Wt. of guest (G) in gms	Concentration of luminophors in mole per mole
1	0.5	0	Pure Anthracene
2	0.5	0.0005958	$1 X 10^{-3}$
3	0.5	0.02979	$5 X 10^{-3}$
4	0.5	0.005958	$1 X 10^{-2}$
5	0.5	0.01787	$3 X 10^{-2}$

2.3 Recording of fluorescence spectra

The fluorescence and fluorescence excitation spectra of the pure component and mixed organo-luminophors were recorded on spectrofluorometer. During recording of the fluorescence and fluorescence excitation spectra the parameters like spectral bandwidth (10 nm) data pitch (1 nm) and wavelength scanning speed (250 nm/min) were kept constant while other parameters were changed as per requirement of the experiment. The detailed information regarding its specifications is given below;

Instrument	:	PC based spectrofluorometer
Make	:	JASCO, Japan
Model	:	FP-750
Light source	:	150W xenon lamp with shielded lamphouse
Monochromator	:	Holographic grating with 1200 lines/mm
Wavelength range	:	220 nm to 730 nm
Spectral bandwidth	:	10, 20 nm on both Ex. and Em monochromator
Wavelength accuracy	:	±3 nm
Wavelength threw speed	:	30,000 nm/min
Wavelength scanning speed	:	60,250,1000,4000 nm/min
Response	:	Fast, Medium, Slow, Auto
Sensitivity	:	Signal to noise ratio of Raman band of water is higher than 300:1
Photometric display	:	-999 to +999
Sample chamber	:	Single cell holder (standard)
Detector	:	Silicon photodiode for Ex. monochromator and Photomultiplier tube for Em. monochromator

2.3.1 Optical system of FP-750 Spectrofluorometer

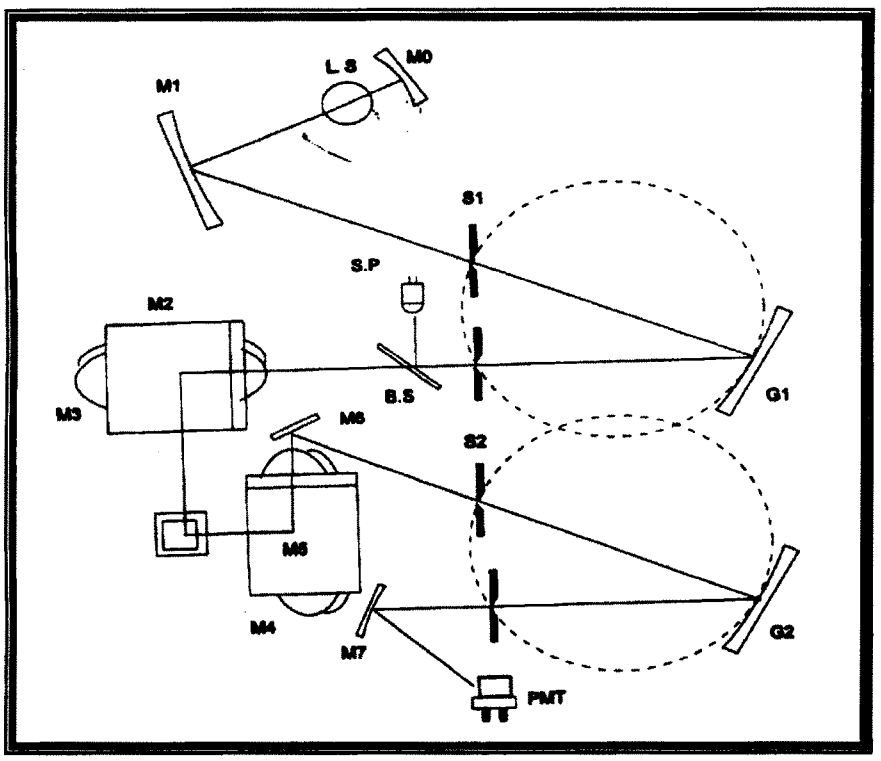
The optical system of the instrument is given in Fig.2.1. The light from the source (Xenon lamp) is focused on to the entrance slit of the excitation monochromator by the ellipsoidal mirror Mo. The light from the slit is dispersed by the diffraction grating G_1 and monochromatic light is taken out by the exit slit. A part of the monochromatic light is led to the monitoring silicon photodiode (SP) by the beam splitter chamber by the plane mirror M_2 and ellipsoidal mirror M_3 where it is focused on the center of the sample cell. The emission from the sample is focused on to the entrance slit of the emission (Em) monochromator by ellipsoidal mirror M_4 and two plane mirrors M_5 and M_6. The light dispersed by the diffraction grating of the emission monochromator going through the exit slit finally led to photometric photomultiplier tube PMT by the spherical mirror, M_7.

The schematic diagram for the FP-750 system is shown in Fig.2.2. The light incident on the monitoring detector (Silicon photodiode) and the emission detector (PMT) is

converted into an electrical signal and then converted into digital signal by the A/D converter and is introduced to the microcomputer. The signal subjected to arithmetic operation by the microcomputer is outputted to the display unit as digital data or spectrum. Both wavelength as well as slit drives is controlled by the microcomputer.

The steps involved during recording of the fluorescence and fluorescence excitation spectra of luminophors are as follows;

1. Visual fluorescence color was observed by exciting the sample at 365nm (Hg line) excitation wavelength.
2. The emission monochromator was set at the approximate wavelength of visually observed color.
3. The excitation monochromator was scanned from 230nm to a wavelength of emission monochromator.
4. The excitation spectrum was recorded and the λ_{ex} was noted.
5. The excitation monochromator was set at λ_{ex} observed in excitation spectrum.
6. The emission monochromator was allowed to scan in the range 300nm to 750nm.
7. The fluorescence emission spectrum was recorded and the λ_{em} was noted.
8. The emission monochromator was then set at the λ_{em} and excitation spectrum monochromator was scanned and thus the excitation spectrum was recorded.
9. Finally the fluorescence spectrum was obtained by setting the excitation monochromator at λ_{ex} obtained in above step. Similarly fluorescence excitation spectrum was obtained by setting λ_{em} observed in the final emission spectrum.



LS : Light source (150W xenon lamp)

M1 : Ellipsoidal mirror

S1 : Excitation entrance/exit slit

G1 : Excitation concave diffraction grating (1200lines/mm)

SP : Silicon photodiode

BS : Beam splitter

M2,M5,M6 : Plane mirror

M3,M4 : Ellipsoidal entrance/exit slit

S2 : Emission entrance/exit slit

G2 : Emission concave diffraction grating (1200lines/mm)

PMT : Photomultiplier tube

MO,M7 : Spherical mirror

Fig. 2.1 Optical system of FP-750.

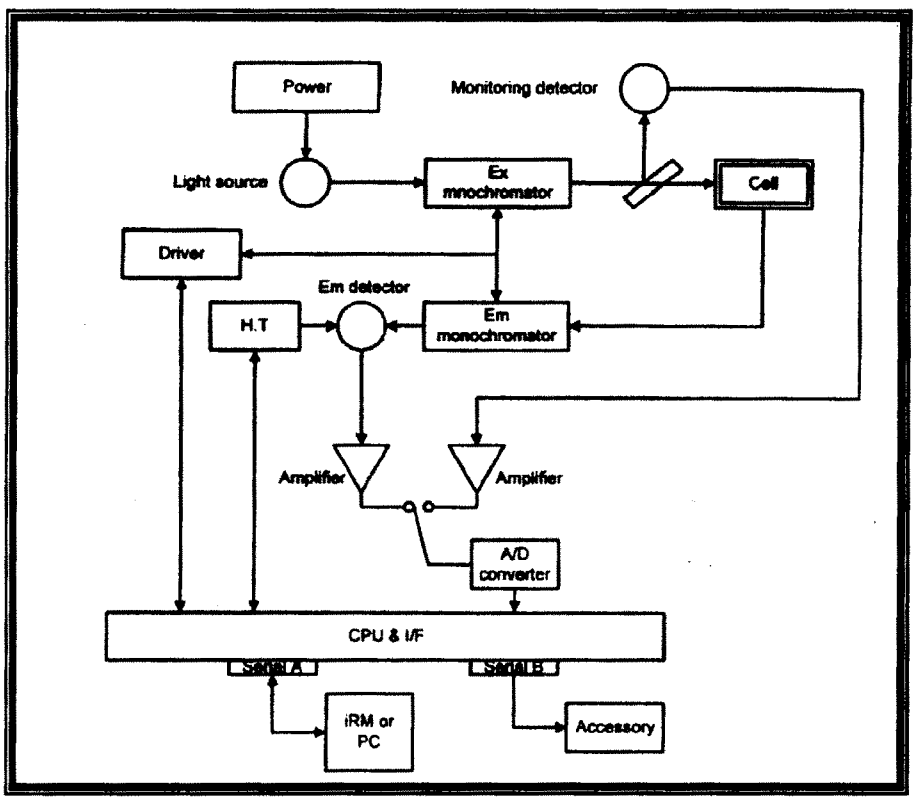


Fig. 2.2 System Diagram.

2.3.2 Calibration of the Spectrofluorometer

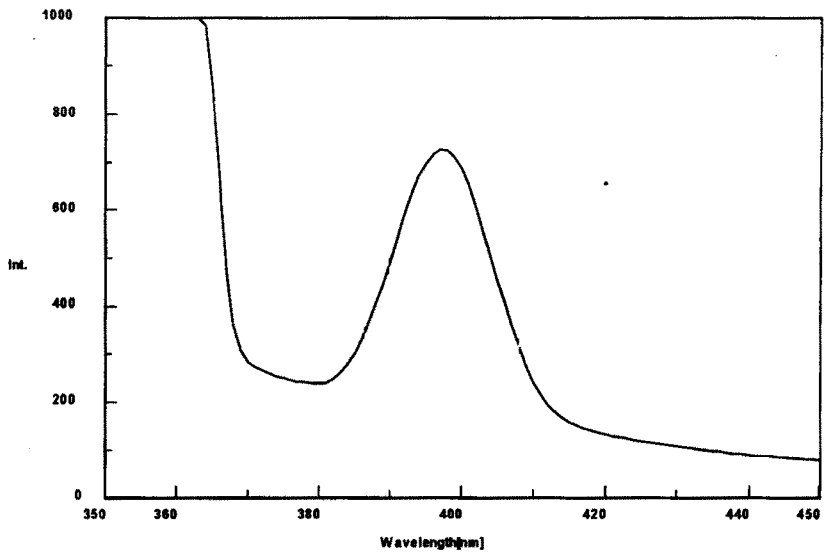
Calibration and sensitivity of the instrument is checked by measuring the Raman spectrum of water. The Quartz distilled water was used for calibration. The detailed procedure given in the Hardware manual of Spectrofluorometer was used. The parameters as given below were set on the parameter screen;

Measurement Mode	:	Em
Excitation wavelength	:	350 nm
Excitation Slit bandwidth	:	10 nm
Emission Slit bandwidth	:	10 nm
Response	:	Fast
Sensitivity	:	High
Start Wavelength	:	350 nm
End Wavelength	:	450 nm
Scanning Speed	:	250 nm / min
Number. of cycles	:	1
Display mode	:	Autoscale

2. Rectangular cell containing distilled water was set in the cell holder.
3. Em shutter at Ex was closed. Autozero was pressed and allowed to execute.
4. Ex and Em shutters are opened and executed by pressing autozero.
5. The spectra was scanned and presented in Fig.2.3.

The Raman spectrum of water given in the manual Fig.2.3 (b) is identical. The maximum peak value at 397 nm is 726 a.u. According to the reports in the manual, if the intensity value is above 300 a.u. the sensitivity is normal and with the best performance of the instrument [68].

(a)



(b)

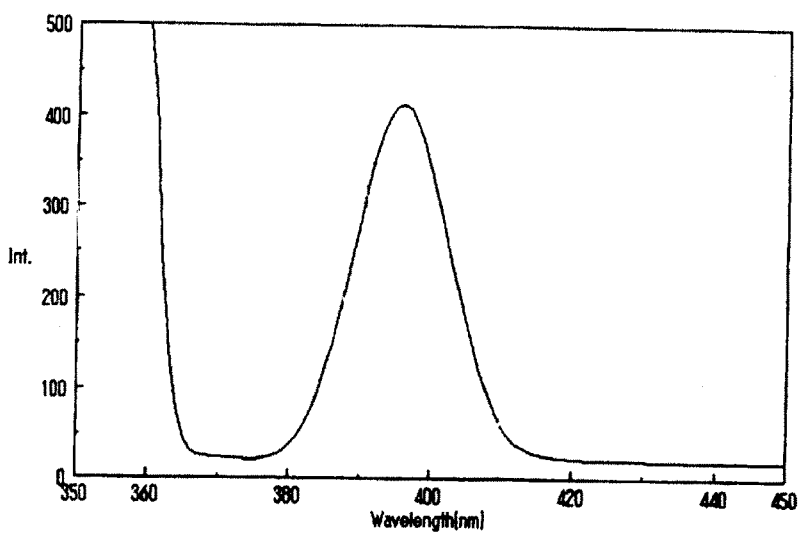


Fig. 2.3 Raman spectrum of water;

(a) Experimental.

(b) From the operational manual supplied by JASCO-JAPAN.

2.4 X-ray diffraction studies of the mixed luminophors

The pure as well as mixed crystals crushed to fine powder were subjected to Powder X-ray diffraction patterns registered at the rate of 0.1 (2θ) min^{-1} by means of Philips diffractometer (Model PW-1710, Holland) with PW 1725 generator using filtered Cu LFF Kα radiation (1.54 A°).

2.4.1 Indexing of the X-ray diffraction peaks

Anthracene belongs to low symmetry monoclinic system. Here molecular packing is governed by atom-atom potential and sandwich pairs of molecules are formed. Its XRD pattern recorded shows many reflections hence lines on the patterns need to be indexed.

As crystal system is monoclinic, indexing is carried out using $\sin^2\theta$ method [69]. The expected values of $\sin^2\theta$ for the various reflections were calculated and compared with the observed values. The expected values of $\sin^2\theta$ were calculated by using following equation of the monoclinic system;

$$\sin^2\theta = \frac{\lambda^2}{4\sin^2\beta}\left|\frac{h^2}{a^2}+\frac{l^2}{c^2}-\frac{2hl\cos\beta}{ac}+\frac{k^2}{b^2}\right|$$

where, h, k, l are the Miller indices.

Table No.3:- Crystallographic data of the anthracene.

Peak No.	Angle 2θ (deg)	Theta θ (deg)	'd_1'value (A°)	'd_2'value (A°)	Relative Intensity (%)	$Sin^2\theta$ (Cal.)	hkl values
1	9.590	4.795	9.2148	9.2378	100	0.0069	-
2	19.280	9.640	4.5999	4.6113	27.2	0.0280	[001]
3	21.165	10.582	4.1943	4.2047	3.3	0.0337	-
4	25.225	12.612	3.5276	3.5364	6.5	0.0476	[100]
5	29.320	14.660	3.0436	3.0512	5.0	0.0640	[101]
6	36.720	18.360	2.4454	2.4515	1.2	0.0992	[010]
7	39.135	19.567	2.2999	2.3056	2.9	0.1121	[011]
8	49.530	24.765	1.8388	1.8434	0.9	0.1754	[102]

The values for lattice constants for anthracene were taken from literature [70] and are shown in Table No.3. The sufficient equivalence between the calculated values permitted the indices of observed lines. The XRD pattern of pure crystal was used as 'fingerprint' to identify the reflections coming from the guest molecules in the mixed crystal systems.

Table No. 4:-Lattice parameters of the Crystal systems.

System No.	Crystal system	a (A^o)	b (A^o)	c (A^o)	β
1	anthracene	8.58	6.02	11.18	125°
2	perylene	11.27	10.82	10.26	100.55°

2.4.2 Determination of Particle size

The maximum intensity band obtained in XRD pattern was broadened by using line broadening analysis. And from the value of full width at half maximum (FWHM) the grain size was calculated using Scherer formula [71].

Absorption measurements of solutions of mixed luminophors were taken on UV-Visible spectrometer (Chemito UV-2100, India).