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Spectral behavior and laser activity of N,N-bis (3- hydroxypyrimidenyl) 3, 4, 9, 10-perylenebis(dicarboximide) (HPyPBD)

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ABSTRACT

The photophysical properties such as singlet absorption, molar absorptivity, excitation and fluorescence spectra as well as fluorescence quantum yield of HPyPBD have been measured in different solvents. Both electronic absorption and fluorescence spectra are not sensitive to medium polarity, while the fluorescence quantum yield (ϕ_f) is solvent dependent. HPyPBD dye displays molecular aggregation in water. The photochemical quantum yield (ϕ_c) of contact ion pair formation has been determined in carbon tetrachloride upon irradiation with 525 nm lights. Dye solution in DMF gives weak laser emission around 560 nm upon pumping with 337.1 nm nitrogen laser pulses. The excitation energy transfer from 9, 10-diphenylanthracene (DPA) to HPyPBD has been studied to improve the laser emission of HPyPBD. The values of energy transfer rate constant k_{ET} and critical transfer distance (R_o) indicate a Förster type energy transfer mechanism. The geometrical and electronic structures of HPyPBD molecule, in both the ground and excited states, have been elucidated using AMI and ZINO/S semiemperical quantum calculations.

KEYWORDS

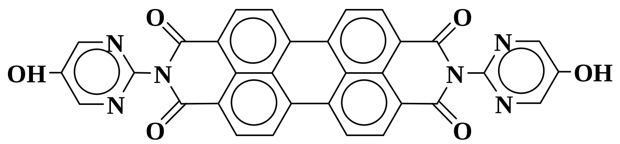
Laser dye;
Energy transfer;
Molecular aggregation.

INTRODUCTION

The dyes derived from 3, 4, 9, 10- perylenetetra carboxylic dianhydride have high molar absorptivity in visible spectrum (10^4 - 10^5 M^{-1} cm^{-1}), high fluorescence quantum yield (0.5 - 1.0)[1-5] and excellent stability to heat and light[6]. These derivatives have been used as building blocks for molecular switches, wires and logic gates[7-9] as well as organic light emitting diodes[10,11] and laser dyes[12-15], light harvesting arrays[16-18], photo reactive thin films[19,20], and in solar, cells[21,22]. Also perylene derivatives were found to include some promising microcrystalline photoconductors for electro-photography and have been incorporated in prototype photovoltaic cells[22]. In this paper, we report the photo physical properties, laser activity and energy transfer of a new perylene derivative namely, N, N-bis (3-hydro xypyrimidenyl) - 3, 4, 9, 10-perylenebis (dicarboximide).

EXPERIMENTAL

N, N-bis(3-hydroxypyrimidenyl)-3,4,9,10-perylenebis (dicarboximide) (HPyPBD) was prepared and purified according to procedure described in detail in[23]. TLC and spectroscopic techniques as well as elemental analysis confirmed the purity of the dye. The



HPyPBD

solvents used in this work were of spectroscopic grade. Sodium dodecyl sulfate (SDS) was used to prepare anionic micelle. Steady state emission spectra were measured with a Shimadzu RF 510 spectrofluoro photometer connected to an ultrathermostate (Julabo F 10) of temperature precision 0.1^{0}C using a rectangular quartz cell of dimension 0.2 × 1 cm to minimize the reabsorption. The emission was monitored at right angle. The electronic absorption spectra were measured using a Shimadzu UV 2100S spectrophotometer. Light intensity was measured by using ferrioxalate actinometry[24]. Fluorescence quantum yields were measured relative to rhodamine 6G as a reference standard for which $\phi_f = 0.96$ ($\lambda_{ex} = 420$ nm) in ethylene glycol[25]. The following relation has applied to calculate the fluorescence quantum yields[26]

$$\phi_f(s) = \phi_f(r)\frac{F_s\{1-\exp(-A_r \ln 10)\}n_s^2}{F_r\{1-\exp(-A_s \ln 10)\}n_r^2} \qquad (1)$$

where F denotes the integral of the corrected fluorescence spectrum, A is the absorbance at the excitation wavelength, and n is the refractive index of the medium. The subscripts s and r refer to sample and reference, respectively. The lasing action of the dye was monitored in a dye laser (GL-302 Dye Laser, PTI) pumped by a nitrogen laser (GL3300) Nitrogen Laser, PTI), the pump laser (λ_{ex} = 337.1 nm) was operated at repetation of 3 Hz with a pulse energy of 1.48 mJ and pulse duration of 800 ps. The narrow band output of the dye laser was measured with a pyroelectric Joule meter (ED 100, Gen-Tec).

The geometrical, electronic structures and dipole moment of both the ground and excited states of HPyPBD have been performed with the help of Argus Lab 4.0 software[27]. AMI Hamiltonian obtained the precise geometry optimization, while the electronic structure and dipole moments were calculated by AMI and ZINDO/s methods. All the calculations were performed using the default parameters.

RESULTS AND DISCUSSION

Electronic and emission spectra of HPyPBD in different solvents

The electronic absorption, emission and excitation spectra of dilute solutions of HPyPBD were measured in different solvents at room temperature. Figures 1, 2 show the absorption, emission and excitation spectra of HPyPBD in chloroform and methanol. The absorption and excitation spectra have three distinctive maxima at 525 nm, 490 nm and 460 nm. They are attributed to the vibronic peaks of the first electronic transition ($S_o \rightarrow S_1$). The Stokes shift is about 180 cm^{-1}. The approximate mirror-image relation between absorption

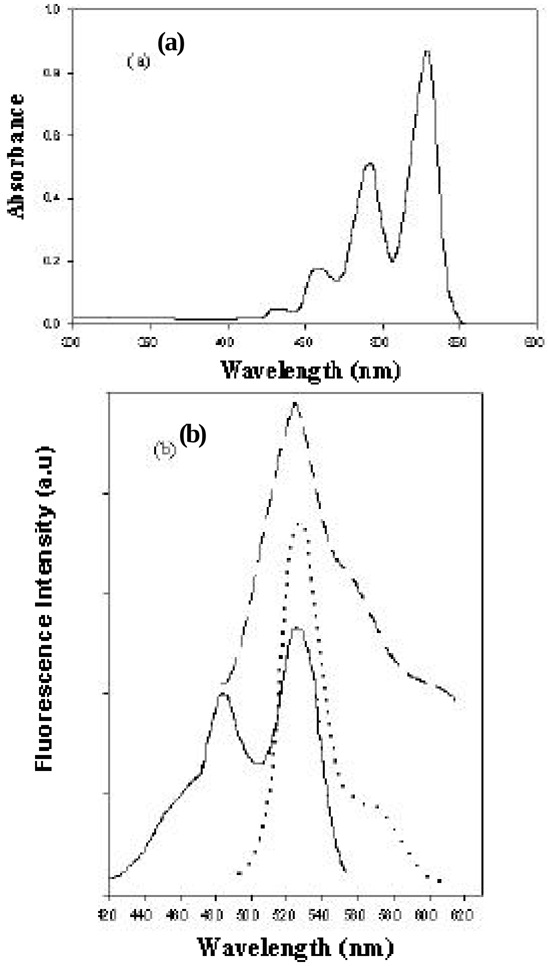


Figure 1: (a) Electronic absorption spectrum of 1.3 × 10^{-5} mol dm^{-3} of HPyPBD in methanol; (b) Emission (…….) and excitation (- -) spectra of 1.3 × 10^{-5} mol dm^{-5} of HPyPBD in methanol and emission spectrum (- - -) of HPyPBD in ethylene glycol. The same excitation spectrum was obtained in ethylene glycol

and fluorescence bands is caused by relatively small differences between the geometry and the solvation of the ground and excited singlet states, which is typical of rigid polycyclic aromatic molecules[26].

The absorption and emission features of HPyPBD are not solvatochromoic which, coupled with high molar absorptivity and relatively high fluorescence quantum yields, suggest that the lowest excited singlet state (S_1) possesses little or no charge transfer and the dipole moment of HPyPBD is essentially the same in both ground (S_0) and excited (S_1) states. The loss of vibrational structure in emission of HPyPBD in polar protic solvents (Figure1-b) was attributed to the formation of hydrogen bond between the heteroatoms of fluorophors and the alcohol, which occurred during the lifetime of excited singlet state. A greater loss of vibrational structure in the emission of HPyPBD was observed in ethylene glycol than in methanol. These results were attributed to a higher probability of specific solvent-fluorophors interaction in ethylene glycol, where the average concentration of hydroxyl groups is higher.

The energy of the lowest excited singlet state (Es) was estimated by averaging the energy of the absorption and emission maxima, respectively as Es = 2.3 eV. TABLE 1 summarizes the photophysical properties of HPyPBD in different solvents. As shown in TABLE 1, fluorescence quantum yield (ϕ_f) decreases with increasing solvent polarity. This could be attributed to increase the non-radiative processes caused by increase of the vibronic coupling between the lowest $^1(\pi\text{-}\pi^*)$ and $^1(n\text{-}\pi^*)$ as well as, in case polar protic solvents, the hydrogen bond formation between solvent and dye molecules which enhances the radiationless internal conversion which competes with fluorescence emission[28,29].

TABLE 1 : Photophysical properties of HPyPBD in different solvents

Solvents	λ_{ab}(nm)			λ_{em}(nm)		ε_{max} M^{-1} cm^{-1}	ϕ_f	τ_f (ns)
	$0\rightarrow0$	$0\rightarrow1$	$0\rightarrow2$	$0\leftarrow0$	$1\leftarrow0$			
Toluene	527	491	460	510	550	70000	0.82	3.9
CCl_4	527	489	455	525	566	76000	0.78	3.8
$CHCl_3$	527	491	457	530	570	85000	0.64	3.1
Acetone	522	483	454	525	563	72000	0.77	3.5
1,4-Dioxan	523	485	454	525	575	71000	0.74	3.3
CH_3CN	522	484	454	525	563	73000	0.58	2.5
Et.Ac	523	486	456	526	564	76000	0.44	2.3
DMF	526	490	458	530	570	72000	0.58	3.3
n-BuOH	527	491	457	530	568	74000	0.54	2.8
n-PrOH	525	487	457	526	570	71000	0.48	2.7
MeOH	524	486	455	526	570	71000	0.29	2.4
EG	525	486	456	526	-	-	0.18	-

Et.Ac = Ethyl acetate ; EG = Ethylene glycol

In highly concentrated sulfuric acid (Analar 96 %) the dye gives absorption spectrum in visible region in the range 400-700 nm with absorption maximum at 552 nm and emission maximum at 660 nm (λ_{ex} = 550 nm) as shown in figure 3. The red shift in both absorption and emission spectra would be due to simple protonation at the basic centers (carbonyl centers and pyrimidenyl moiety).

The transition dipole moment (μ_{12}) from ground to excited state was calculated in chloroform and dimethylformamide using the relation[30]

$$\mu_{12}^2 = \frac{f}{4.72\times10^{-7}\times E_{max}} \qquad (2)$$

Where E_{max} is the energy of maximum absorption in cm^{-1} and f is the oscillator strength which is given by the relation[31]

$$f = 4.32\times10^{-9}\int \varepsilon(\bar{\upsilon})d\bar{\upsilon} \qquad (3)$$

The integral is the experimental molar absorbtivity, the values of μ_{12} for HPyPBD were found to be 9.80 and 10.20 Debye in chloroform and dimethylformamide,

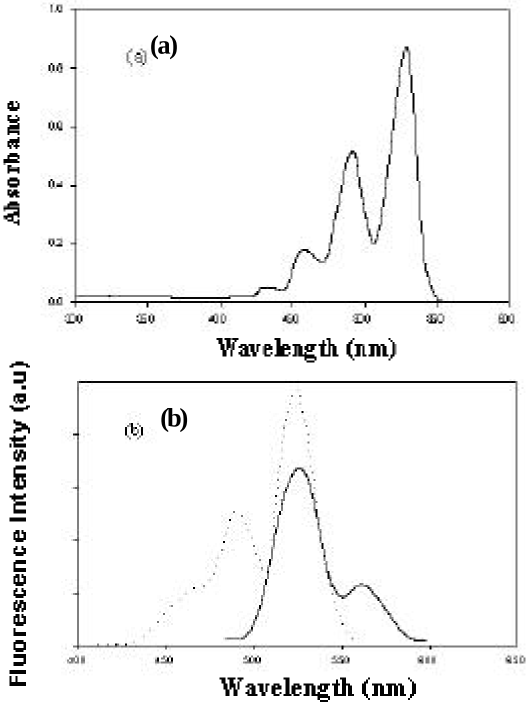


Figure 2 : (a) Electronic absorption spectrum of 1.05× 10^{-5} mol dm^{-3} of HPyPBD in chloroform; (b) Emission and excitation spectra of 1.05 × 10^{-5} mol dm^{-3} of HPyPBD in chloroform

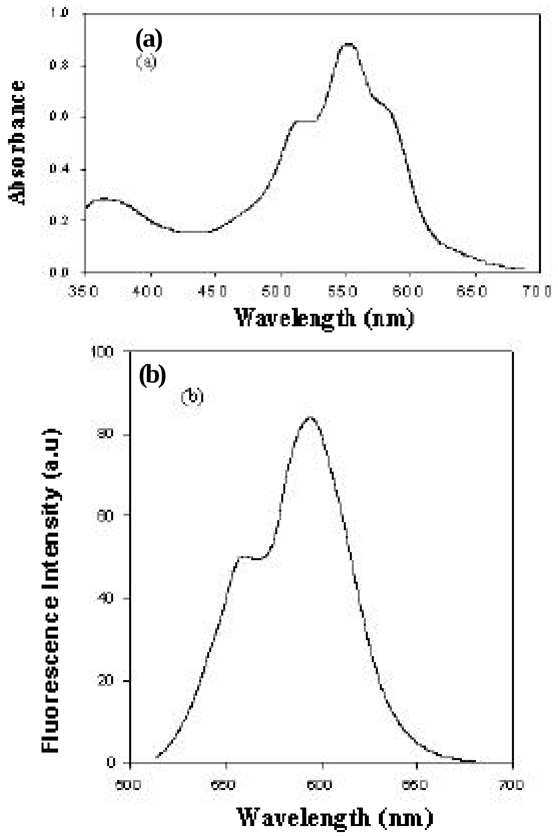


Figure 3: (a) Electronic absorption spectrum of 2×10^{-5} mol dm^{-3} of HPyPBD in H_2SO_4 (Analar 96%); (b) Emission spectrum of 2×10^{-5} mol dm^{-3} in H_2SO_4

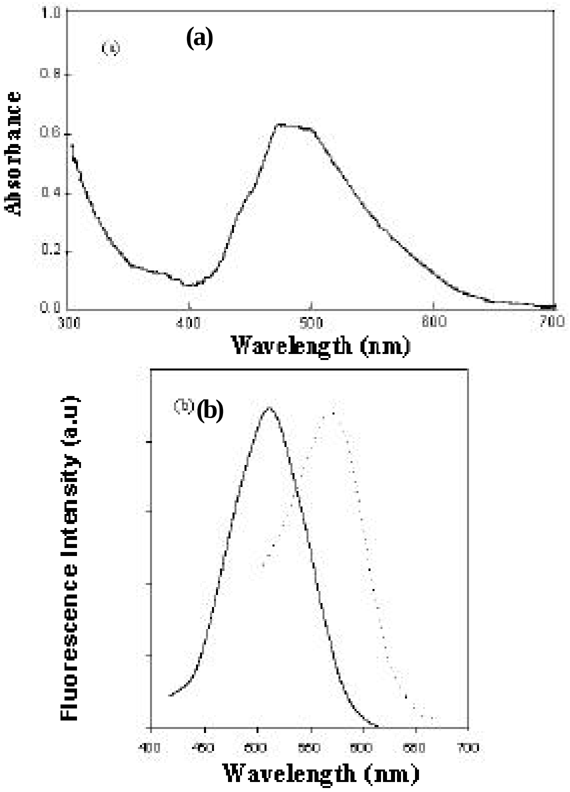


Figure 4 : (a) Electronic absorption spectrum of 2.8×10^{-5} mol dm^{-3} of HPyPBD in water containing 5 % by volume ethanol; (b) Emission (……) and excitation (-) spectra of 2.8×10^{-5} mol dm^{-3} of HPyPBD in water containing 5 % by volume ethanol

respectively.

The radiative lifetime τ_o (ns) was calculated from the modified Strickler-Berg equation[31].

$$\frac{1}{\tau_f^o} = 3\times10^{-9} n^2 \bar{\upsilon}_m^2 \int \varepsilon(\bar{\upsilon}) d\bar{\upsilon} \qquad (4)$$

Where n is the refractive index is the energy of the absorption maximum (cm^{-1}), the $\bar{\upsilon}_m^2$ integration is the area under the absorption curve. By knowing the values of fluorescence quantum yield (ϕ_f) in different solvents, the fluorescence lifetime (τ_f) in ns was calculated from the relation $\tau_f = \tau_o \times \phi_f$. The values of τ_f for HPyPBD are also listed in TABLE 1.

Molecular aggregation of HPyPBD in water

The electronic absorption, excitation and emission spectra of 2.8×10^{-5} mol dm^{-3} in water containing 5 % by volume ethanol or DMF have been measured at room temperature. As shown in figure 4, the absorption spectrum is broad with maximum at 476 nm and the molar absorptivity was reduced (ε = 21000 M^{-1} cm^{-1}) compared to that in organic solvents. The emission band was red shifted (λ_{em} max = 570 nm) and is broadened. The excitation spectrum compares with the absorption spectrum obtained at room temperature indicating that the red shift in emission spectrum is due to the excitation of the ground state molecular aggregates with fluorescence quantum yield of 0.035.

The drastic changes in the absorption and fluorescence properties of HPyPBD dye in water that are associated with dimerization can be interpreted in terms of molecular exciton theory for plane-parallel dimers in the strong (π-π*) interaction limit. Accordingly, interaction between the transition dipole moments of the two units in the dimer causes a splitting of the S_1 excited state of the monomer in two states, one at a higher energy (transition dipoles in phase) and the other at a lower energy (out of phase) relative to that of monomer.

The blue shift in the absorption spectrum of the dimer (Figure 4- a) indicates that the transition dipoles of the two dye molecules in the dimer were oriented strictly parallel to each other and perpendicular to in-

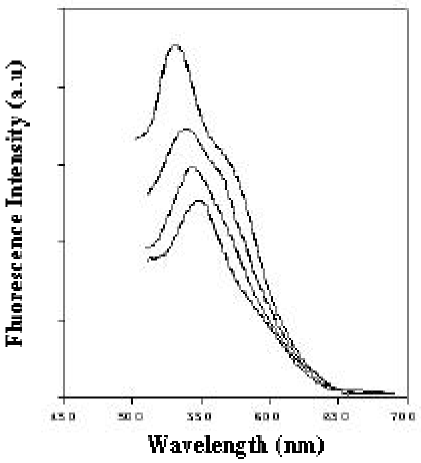


Figure 5 : Emission spectra of 2.8×10^{-5} mol dm^{-3} of HPyPBD in SDS micelle solution (λ_{ex} = 480 nm). The concentrations of surfactant at increasing emission intensity are: 0.0, 2×10^{-3}, 4×10^{-3}, 6×10^{-3} and 8×10^{-3} mol dm^{-3}

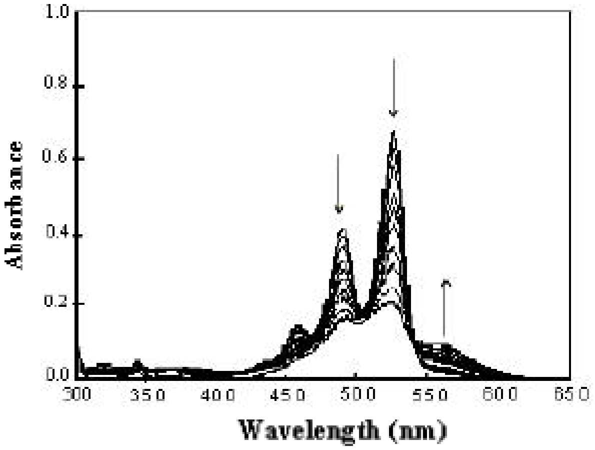


Figure 6 : Effect of irradiation on the electronic absorption spectrum of 1×10^{-5} mol dm^{-3} of HPyPBD in CCl_4 (λ_{irr} = 525 nm). The irradiation times at decreasing absorbance are 0.0, 5, 10, 20, 30, 40, 60, 80, 90, and 120 min

termolecular axis. The mechanism by which the fluorescence of HPyPBD dye is quenched upon dimerization most likely involves either enhancement in the rate of intersystem crossing (isc) owing to a shifting of relative energies of the excited singlet and triplet states or enhancement in the rate of internal conversion to the ground state owing to the exciton (dipole-dipole) interaction[32-34] as well as hydrogen bonding with water molecules.

The dissociating effect of organic solvents such as EtOH, DMF and CH_3CN on dimer of HPyPBD dye was observed. By increasing the ratio of organic solvent in water content, the absorption and emission are shifted to the monomer features. The mechanism of dissociation by organic solvents is not well understood but it probably involves specific dye-solvent interaction rather than being a bulk solvent effect[35]. It seems that the high dielectric constant of water molecules decreases the electrostatic repulsion between dye molecules and then enhances the molecular aggregation. The dissociating effect of EtOH and DMF on the dimer of HPyPBD dye was generally observed in other dye systems as well[36-41].

The emission spectrum of 2.8×10^{-5} mol dm^{-3} HPyPBD has also been measured in anionic (SDS) miceller media as shown in figure 5. The emission intensity increases as the concentration of surfactant increases. An abrupt increase in the fluorescence intensity is observed at surfactant concentration of 8×10^{-4} mol dm^{-3} that is the critical micelle concentration (CMC) of SDS[42]. There is also a blue shift in the emission maximum of HPyPBD in SDS at CMC, λ_{em} (max) = 532 nm compared with that in water λ_{em} = 560 nm. This is due to the role of anionic SDS micelle aggregates in causing physical separation between HPyPBD molecules and prohibiting molecular aggregation during the lifetime of singlet excited state.

Study of contact ion pairs

A compound formed when a positive cation and a negative ion interact with each other by Coulomb attraction and get close together, but with both charges still separated, is called a contact ion pair. Since the charge separation is complete, a large dipole moment can be expected. The formation of a contact ion pair usually occurs by electron transfer from excited donor molecule to the acceptor. In order for such a compound to be formed, a low ionization potential of the donor and high electron affinity of the acceptor are necessary. A direct observation of a contact ion pair $HPyPBD^+ Cl^-$ in CCl_4 solvent was studied by UV/VIS absorption technique. Photo irradiation of 1×10^{-5} mol dm^{-3} of HPyPBD by 525 nm light ($I_o = 4\times10^{-6}$ Ein/min) in CCl_4 (E_A = 2.12 eV) causes a decrease in absorbance and a new absorption peak appears at 570 nm with isosbestic point at 541 nm (Figure 6).

The photochemical quantum yield (φ_c) of ion pair formation was calculated using a method described elsewhere[43] and was found to be $\phi_c = 0.018$. The formation of the ion pair is a one-photon process as represented by the following SCHEME:

$\mathrm{HPYPBD} \rightarrow {}^{1}(\mathrm{HPyPBD})^{*}$ absorption of light (1)
${}^{1}(\mathrm{HPyPBD})^{*} \rightarrow \mathrm{HPyPBD} + h\nu$ fluorescence (2)
${}^{1}(\mathrm{HPyPBD})^{*} + \mathrm{CCl_4} \rightarrow [\mathrm{HPyPBD}^{\cdot+}.....\mathrm{CCl_4}]^{*}$ exciplex (3)
$[\mathrm{HPyPBD}^{+}\delta \ldots {}^{-}\delta\mathrm{CCl_4}] \rightarrow [\mathrm{HPyPBD}^{\cdot+} \ldots {}^{\cdot-}\mathrm{Cl} \ldots \mathrm{CCl_3}]$ (4)
$[\mathrm{HPyPBD}^{\cdot+} \ldots {}^{\cdot-}\mathrm{Cl} \ldots \mathrm{CCl_3}] \rightarrow$ photoproduct formed in solvent cage (5)

We propose that the electron transfer from the excited singlet state of HPyPBD to CCl_4 in the transient excited charge transfer complex is the main primary photochemical process, which initiates a chemical reaction. It leads to the radical cation, a chloride ion and a trichloromethyl radical in solvent cage. The photoionization of some aromatic and aliphatic amines in chloromethane solvents has been reported earlier[44,45].

Laser activity and excitation energy transfer

A 2×10^{-4} mol dm^{-3} solution of HPyPBD in DMF gives weak laser emission in the lasing range (540-580 nm) with emission maximum at 560 nm. The weak laser emission of HPyPBD dye can be attributed to strong overlap between its emission and electronic absorption spectra, low molar absorptivity at pumping wavelength (337.1 nm) as well as low solubility in DMF. The maximum gain coefficient (α) was calculated as 0.87 cm^{-1} at maximum laser emission by measuring the intensity I_L of laser emission from the entire cell length L and the intensity $I_L/_2$ from the cell half-length. One can calculate the laser gain (α) from the following relation[46].

$$\alpha = \frac{2}{L}\ln\left[\frac{I_L}{I_{L/2}} - 1\right] \quad (5)$$

The cross section of stimulated laser dye emission σ_e was calculated at laser emission maximum (560 nm) according to the equation[47]

$$\sigma_e = \frac{\lambda_e^4 E(\lambda)\phi_f}{8\pi c n^2 \tau_f} \quad (6)$$

where λ_e is the emission wavelength, n is the refractive index of the dye solution, c is the velocity of light, τ_f is the fluorescence lifetime, and $E(\lambda)$ is the normalized fluorescence line-shape function at certain wavelength where:

$$\int E(\lambda)d\lambda = \phi_f \quad (7)$$

(λ) was obtained from the fluorescence spectra of dilute solutions to minimize reabsorption. For HPyPBD dye value of $\sigma_e = 7.62 \times 10^{-17}$ cm^2 was obtained at 560 nm. The photochemical stability of laser dye was determined as the half-life energy ($E_{1/2}$) that is the amount of total absorbed pump energy until the dye laser energy has dropped to 50% of its initial value; the value of $E_{1/2}$ was calculated as 2970 JL^{-1}[48].

HPyPBD dye acts as energy acceptor from laser dyes that have a good molar absorptivity at 337 nm such as 9,10- diphenylanthracene (DPA). An equimolar mixture (2×10^{-4} mol dm^{-3}) of HPyPBD and DPA in DMF gives laser emission in the same spectral region of HPyPBD (energy acceptor) with maximum gain coefficient α= 1.4 cm^{-1} upon pumping with nitrogen laser, indicating an energy transfer from excited donor DPA* to ground state acceptor (HPyPBD). Energy transfer is expected to occur because of the remarkable overlap between DPA emission and HPyPBD absorption spectra, thus most of excitation energy absorbed by donor (DPA) molecules is transferred to acceptor (HPyPBD) as a useful pump power making excitation transfer efficient.

The output energy of maximum laser emission (λ_{em} = 560 nm) of HPyPBD in DMF as solvent in the presence of different concentrations of DPA is shown in figure 7. For increase in the concentration of the donor, self-absorption is responsible for screening the tunable laser action. Thus the maximum output energy decreases with increasing the concentration of DPA in dye mixture. In addition to the above energy transfer dye laser (ETDL) study, fluorescence quenching characteristics have also been studied to determine the rate constant of energy transfer and assert the nature of energy trans-

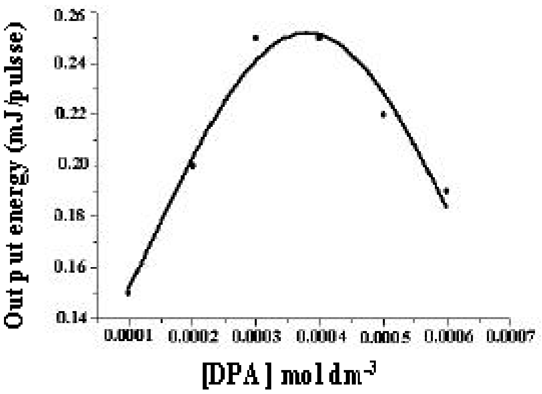


Figure 7 : Plot of laser output energy at λ= 560 nm of 2×10^{-4} mol dm^{-3} of HPyPBD in DMF versus the concentrations of DPA

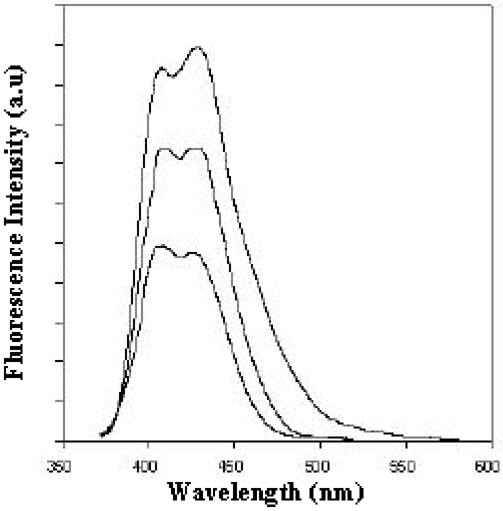


Figure 8: Fluorescence quenching of 1 × 10^{-5} mol dm^{-3} of DPA by HPyPBD in DMF (λ_{ex} = 337 nm). The concentrations of HPyPBD at decreasing emission intensity are 0.0, 4 × 10^{-5} and 1.2 × 10^{-4} mol dm^{-3}

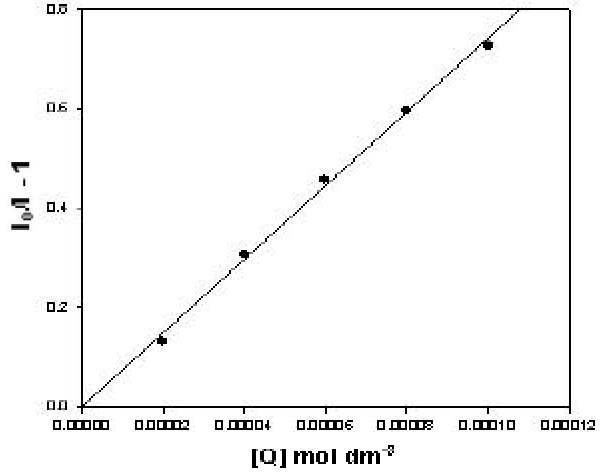


Figure 9 : Stern-volmer plot of fluorescence quenching of 1×10^{-5} mol dm^{-3} of DPA by HPyPBD in DMF

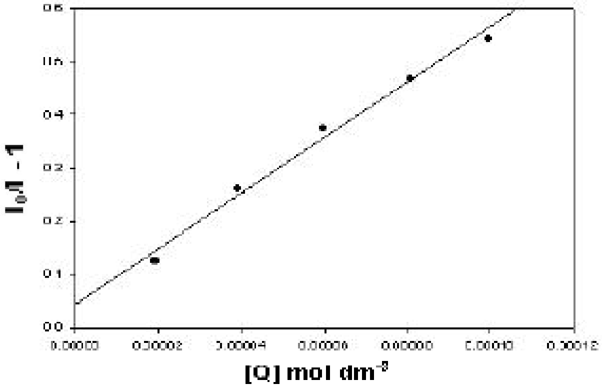


Figure 10: Dependence of ln(I_0/I) on quencher concentration according to Perrin model for 1 × 10^{-5} mol dm^{-3} DPA with quencher HPyPBD in DMF

fer involved in the DPA/HPyPBD system. Figure 8 shows the decrease in fluorescence intensity of 1×10^{-5} mol dm^{-3} of DPA in DMF as the concentration of HPyPBD increases. The rate constant of energy transfer (k_{ET} in M^{-1} s^{-1}) can be calculated by applying the Stern-Volmer relation[49] (Figure 9)

$$\frac{I_o}{I} = 1 + k_{ET}\tau_f[Q] \tag{8}$$

where I_o and I are the fluorescence intensities in the absence and presence of the acceptor with concentration[Q], τ_f is the fluorescence lifetime of donor in the absence of the acceptor. Taking τ_f of DPA as 6.8 ns[48] in DMF, the rate constant of energy transfer has been calculated as 1.8×10^{12} $M^{-1}s^{-1}$. This value is much higher than the diffusion rate constant in DMF (1.5×10^{10} $M^{-1}s^{-1}$) at room temperature, indicating a diffusionless energy transfer mechanism.

From the overlap between the emission spectrum of donor and absorption spectrum of acceptor, the critical transfer distance of DPA/HPyPBD pair can be calculated by

$$R_o^6 = \frac{1.25\times10^{-25}\phi_f}{n^4}\int\frac{F_D(\bar{\upsilon})\varepsilon_A(\bar{\upsilon})d\bar{\upsilon}}{\bar{\upsilon}^4} \tag{9}$$

where R_o is the Förster critical transfer distance at which 50 % of the excitation energy is transferred to the acceptor. R_o then defines the spatial relationship of the donor and acceptor at which the probability of donor de-excitation by energy transfer equals the probability of de-excitation by other processes that occur in the absence of acceptor, (ϕ_f) is the fluorescence quantum yield of donor, n is the refractive index of the medium and the integral is the overlap integral for fluorescence spectrum of donor normalized to unity (F_D) and absorption spectrum (ε_A). The critical transfer distance R_o was calculated as R_o = 32 Å. This value is higher than that for collision energy transfer mechanism in which R_o is less than 10 Å[50]. The high value of the critical transfer distance and energy transfer rate constant indicate that the underlying mechanism of energy transfer within DPA/HPyPBD system is a resonance energy transfer due to the long range (dipole-dipole) interaction between excited donor and ground state acceptor.

The fluorescence quenching of DPA (donor) by HPyPBD (acceptor) at various concentrations fulfill the Perrin's relationship[51-53] which is given in the following equation

$$\ln[I_0/I] = VN[Q] \tag{10}$$

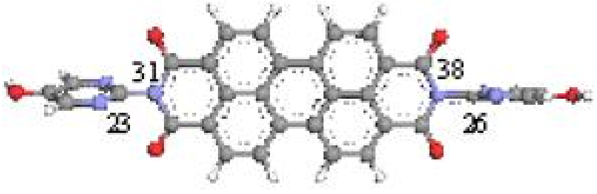


Figure 11: The optimized molecular structure of HPyPBD

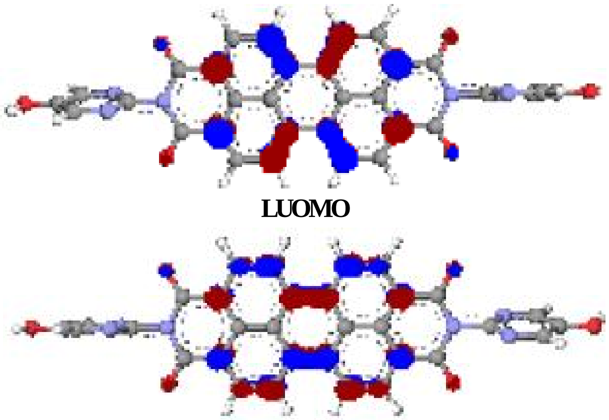


Figure 12: HOMO-LUOMO molecular orbital representation

where V is the volume of active sphere of quenching in cubic centimeters and N is Avogadro's number. From the plot shown in Fig. 10, the value of V was found to be 9.6×10^4 Å^3. The radius of active sphere can be calculated assuming its spherical shape in a simple way $R= (3V/4\pi)^{1/3}$ and was calculated as 60Å.

Theoretical calculations

Semiempirical quantum chemical calculations using AM1 method were performed to study the molecular and electronic structures of the (HPyPBD) dye under investigation. Optimization of bond lengths, bond angles and dihedral angles in the ground state produces a stable structure with a minimum energy (heat of formation is 30.95 k cal mol^{-1}), as shown in figure 11.

The calculations show that the hydroxyl pyrimidine rings are out of plane with respect to perylene moiety. The distortion from planarity takes place by rotation of both pyrimidine rings around C_{23}-N_{31} and C_{26}-N_{38} bonds by 82°. Also, both the attached pyrimidine rings are twisted from each other's due to rotation around the plane containing the bonds C_{23}-N_{31} and C_{26}-N_{38} by 17^{O}.

The calculated bond lengths of C_{23}-N_{31} and C_{26}-N_{38} are quite longer (1.448 Å) compared to the bond lengths within the rings (1.339 Å for C-N and 1.38-1.42 Å for C-C bonds) indicating a single bond character, which is in agreement with the expected ones. This is probably due to the balanced electronic interaction of the pyrimidine groups. This is confirmed by calculating both the HOMO level (at -4.96 eV) and LUMO level (at -2.41 eV), Figure 12, which indicates a little modification in the electronic density over the whole skeleton of the perylenebis (dicarboximide) moiety. The calculations were also extended using INDO1/S to investigate the nature of this electronic transition and calculate its energy. The calculations show that the lowest energy corresponding to the HOMO-LUMO transition equals to 2.55 eV.

In addition, the oscillator strength of this transition was calculated as 1.38 indicating ($\pi \rightarrow \pi^*$) transition. The energy of the last electronic transition corresponds to a wavelength of 486 nm, which is in a close agreement with the experimental observations of $0 \rightarrow 1$ transition at (about 490 nm). Furthermore, the dipole moment of both ground and excited states was calculated as 0.58 and 0.63 Debye, respectively. The small change in dipole moment upon excitation indicates again the little change in the electronic distribution upon excitation.

CONCLUSION

In conclusion, it was found that HPyPBD dye is highly photostable in polar solvents with solvent dependent fluorescence quantum yield. HPyPBD dye gives laser emission in the range 540-580 nm and acts as a good energy acceptor from DPA laser dye. Also, the dye displays ground state molecular aggregation in water, and forms contact ion pair in carbon tetrachloride upon irradiation at 525 nm lights. The dipole moment is essentially the same in both ground (S_0) and excited (S_1) state.

REFERENCES

[1] H.Langhals; Chem.Ber., **118**, 4674 **(1985)**.
[2] W.E.Ford; J.Photochem., **34**, 43 **(1986)**.
[3] W.E.Ford, P.V.Kamat, J.Phys.Chem., **91**, 6373 **(1987)**.
[4] E.M.Ebeid, H.Langhals, S.A.El-Daly; J.Phys. Chem., **92**, 4565 **(1988)**.
[5] V.J.Sapagovas, V.Gaidelis, V.Kovalevskji, A. Undzenas; Dyes and Pigments, **71(3)**, 178 **(2006)**.

[6] L.Feller, H.Langhals, K.Polborn; Liebigs Ann., 1229 **(1995)**.

[7] R.T.Hayes, M.R.Wasielewski, D.Gosztola; J.Am. Chem.Soc., **123**, 2440 **(2001)**.

[8] W.B.Davis, W.A.Svec, M.A.Ratner, M.R. Wasielewski; Nature, **396**, 60 **(1998)**.

[9] A.S.Lukas, P.J.Bushard, M.R.Wasielewski; J.Am. Chem.Soc., **123**, 123 **(2001)**.

[10] M.A.Angadi, D.Gosztola, M.R.Wasielewski; Mater. Sci.Eng., **B63**, 191 **(1999)**.

[11] P.Ranke, I.Bleyl, J.Simmerer, D.Haarer, A.Bacher, H.W.Schmidt; Appl.Phys.Lett., **71**, 1332 **(1997)**.

[12] H.G.Lomannsroben, H.Langhals; Appl.Phys., **B48**, 449 **(1989)**.

[13] M.Sadrai, L.Hadel, R.R.Sauter, S.Husain, K.Krogh-Jespersen, J.D.Westdrook, G.R.Bird; J.Phys.Chem., **96**, 7988 **(1992)**.

[14] S.A.El-Daly, T.A.Fayed; J.Photochem. and Photobiol.A:Chem., **137**, 15 **(2000)**.

[15] S.A.El-Daly; Spectrochimica Acta, Part A, **55**, 143 **(1998)**.

[16] R.S.Loewe, K.Tomizaki, W.T.Youngblood, Z.Bo, J.S.Lindsey; J.Mater.Chem., **12**, 3438 **(2002)**.

[17] K.Tomizaki, R.S.Loewe, C.Kirmaier, J.K.Schwartz, J.L.Retsek, D.F.Bocian, D.Holten, J.S.Lindsey; J.Org.Chem., **67**, 6519 **(2002)**.

[18] P.Wu, L.Gong, H.Ye, X.Liu, L.C.Zeng, X.Guo, S.L. Lu, M.J.Yang; J.Mater.Sci., **39**, 5837 **(2004)**.

[19] M.J.Fuller, M.R.Wasielewski; J.Phys.Chem., **B105**, 7216 **(2001)**.

[20] M.J.Fuller, C.J.Walsh, Y.Zhao. M.R.Wasielewski; J.Chem.Mater., **14**, 952 **(2002)**.

[21] M.J.Yang, S.L.Lu, Y.Li ; J.Mater.Sci.Lett., **22**, 814 **(2003)**.

[22] P.Panayotatos, D.Parikh, A.Piechowski, S.Husain; Solar Cells, **18**, 71 **(1986)**.

[23] V.J.Sapagovas, V.Kadziauskas, A.Undzenas, V.Gaidelis; Dyes and Pigments, **71**, 178 **(2006)**.

[24] S.L.Murov; Handbook of Photochemistry, Marcel Dekker, New York, **(1973)**.

[25] Harriman; J.Chem.Soc.Faraday Trans., **1(76)**, 1978 **(1980)**.

[26] J.B.Birks; Photophysics of Aromatic Molecules, Wiley-Interscience, London, **(1970)**.

[27] M.A.Thompson, G.K.Schenter; J.Phys.Chem., **99**, 6374 **(1995)**.

[28] S.C.Shim, M.S.Kim, K.T.Lee, B.M.Jeong and B.H. Lee; J.Photochem. and Photobiol, A: Chem., **65**, 121 **(1992)**.

[29] T.D.Z.Atvars, C.A.Bortolato, D.Dibbern Brunelli; J.Photochem and Photobiol.A: Chem., **68**, 41 **(1992)**.

[30] B.J.Coe, J.A.Asselberghs, I.Clays, K.Olberechts, G.Persoon, A.Hupp, J.T.Johnson, R.C.Coles, S.J.Hursthouse, K.Nakatain; Adv.Funct.Mater., **12**, 110 **(2002)**.

[31] J.B.Birks; Photophysics of Aromatics Molecules, Wiley, New York, **(1969)**.

[32] M.Kasha, H.R.Rawis, M.A.El-Bayoumi; Pur.Appl.Chem., **11**, 371 **(1965)**.

[33] R.S.Becker; Theory and Interpretation of Fluorescence and Phosphorescence, Wiley, Interscience, Ney York, **(1969)**.

[34] F.G.Patterson, H.W.Lee, W.L.Wilson, M.D.Fayer; Chem.Phys., **84**, 51 **(1984)**.

[35] T.G.Dewey, P.S.Wilson, D.H.Turner; J.Am. Chem.Soc., **100**, 4550 **(1978)**.

[36] E.Rabinowitch, L.F.Epstein; J.Am.Chem.Soc., **63**, 69 **(1941)**.

[37] W.West, S.Pearce; J.Phys.Chem., **69**, 1894 **(1965)**.

[38] R.W.Chambers, T.Kajiwara, D.R.Kearns, J.Phys. Chem., **78**, 380 **(1974)**.

[39] D.G.Doff, C.H.Giles in F. Franks (ed.), Water a Comprehensive Treatise, Plenum, New York, **4**, **(1975)**.

[40] A.H.Herz; Adv.Colloid Interface Sci., **8**, 237 **(1977)**.

[41] V.Vitagliano, E.Wyn-Jones, J.Gormally; Aggregation Processes in Solution, Elsevier, Amsterdam, **(1983)**.

[42] C.A.Bunton; Prog.Solid State Chem., **8**, 239 **(1973)**.

[43] E.M.Ebeid, R.M.Issa, M.M.Ghoneim, S.A.El-Daly; J.Chem.Soc.Faraday Trans., **1(82)**, 909 **(1986)**.

[44] A.J.Bord, A.Ledwith, H.J.Shine; Adv.Phys.Org. Chem., **21**, 155 **(1976)**.

[45] H.Shimamori, J.F.Robek; Photochemistry and Photophysics, CRC Press, New York, London, **6**, **(1992)**.

[46] J.C.de Valle, M.Kasha, J.Catalan; J.Phys.Chem., **A101**, 3260 **(1997)**.

[47] M.Rink, H.Gusten, H.Ache; Phys.Chem., **90**, 2661 **(1986)**.

[48] V.S.Antonov, K.L.Hohla; App.Phys., **B32**, 9 **(1983)**.

[49] F.E.Critchfield, J.A.Gebson, J.L.Hall; J.Am.Chem. Soc., **57**, 1991 **(1953)**.

[50] A.Gilbert, J.Baggett; Essential of Molecular Photochemistry, Blackwell, Oxford London, **(1991)**.

[51] F.Perrin; C. R.Acad.Sci.Paris, **178**, 1978 **(1924)**.

[52] S.R.Bigham, J.L.Coffer; J.Phys.Chem., **96**, 10581 **(1992)**.

[53] M.Marian, P.Hardlovic; J.Photochem and Photobiol, A: Chem., **127**, 45 **(1999)**.