

Optical properties of porphyrins in borate glassy matrix

G.A. Kumar^a, Vinoy Thomas^b, Gin Jose^b, N.V. Unnikrishnan^{b,*}, V.P.N. Nampoory^c

^a *Optical Materials Group, Centro de Investigaciones en Optica, A.P. I-948, 37000 Leon, Gto, Mexico*

^b *School of Pure and Applied Physics, Mahatama Gandhi University, Kottayam 686560, Kerala, India*

^c *International School of Photonics, Cochin University of Science and Technology, Kochi 682022, Kerala, India*

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Abstract

Optical properties of free and substituted porphyrins (PP) doped borate glass matrix are reported for the first time. Absorption spectral measurements of H₂TPP, CdTPP, MgTPP and ZnTPP doped borate glass matrix have been made in the 200–1100 nm region and the spectra obtained are analyzed to obtain the optical bandgap (E_g) and other important spectral parameters viz. oscillator strength (f), molar extinction coefficient (ϵ), electric dipole strength (q^2), absorption cross-section (σ_a) and molecular concentration (N). Intense fluorescence was observed in the region 668–685 nm for CdTPP, ZnTPP and MgTPP doped matrices, whereas no such fluorescence was observed in H₂TPP doped matrix. Fluorescence intensity was observed to be almost similar in all the metallated porphyrine matrices. Fluorescence bandwidth ($\Delta\lambda$), decay time (τ), stimulated emission cross-section (σ) and optical gain (G) of the principal fluorescence transitions corresponding to the Q-band excitation were also evaluated and discussed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Porphyrins (PP) are a class of molecules that are derived from the basic skeleton of carbon and nitrogen atoms. The skeleton consists of four pyrrole rings linked by methylene bridge [1]. The ring system may be substituted at any of the meso-positions. The central region may be occupied by hydrogen atom or any metal atom. A compound of the first type is called the free base porphyrin; the second type, the metal salts. Chlorophyll, the green color pigment is basically a porphyrin-like species where the central position is occupied by Mg atom.

There are several reports on the optical studies of free as well as metallated porphyrine molecules in various solvents and vapor phase [2–5] while investigations of these systems in solid matrices especially in inorganic glassy matrices have received little attention. The present work has been undertaken because of the following reasons: (i) the metalloporphyrine systems are particularly useful as photosensitizers and it is an inherent necessity for such systems to absorb strongly in the visible region and possess a relatively long excited state lifetime; (ii) the formation of triplet state can be reduced to a considerable extent in solid phase as compared to solution or vapour phase; (iii) the potential for these

systems in realizing intense fluorescence and optical amplification is enhanced by the above mentioned factors; (iv) the present systems studied possess such properties and may have significant applications in energy storage devices. The aim of the present work is, in general, to elucidate the optical absorption and emission spectral properties of H₂TPP, CdTPP, ZnTPP and MgTPP molecules in borate glassy matrix and to investigate the effect of the metal ions on these properties. A quantitative analysis of the spectral and radiative properties of the investigated samples have also been reported and discussed.

2. Experimental

All the glass samples were prepared by the well-known rapid quenching technique [3]. Reagent grade boric acid (H₃BO₃) and doubly sublimed PP have been used as the starting materials for the preparation of the glass samples. The weighed quantities of the starting materials for 18 gm of glass are mixed homogeneously using an agate mortar. The batch was then placed in a silica crucible and heated in an electric muffle furnace. A slow heating was initially maintained until the temperature reaches 80 °C and decomposition of H₃BO₃ to B₂O₃ is complete. The temperature was then rapidly increased to 120 °C so as to obtain a greenish melt. The melt was retained for about 10 min and then

* Corresponding author.

E-mail address: spapforum@vsnl.com (N.V. Unnikrishnan).

rapidly quenched by placing in between two well-polished preheated brass plates so as to obtain glass discs of about 3 mm thickness and with a diameter of about 2 cm. The glass discs thus obtained were annealed at a temperature of about 60 °C and subsequently polished with water free lubricants. All the samples are highly transparent and appear to be of good optical quality.

The amorphous nature of the glass samples was confirmed by X-ray diffraction spectra recorded on a Shimadzu X-ray diffractometer with Ni filtered Cu K α radiation. The absorption spectra were recorded in the UV–VIS NIR region with a Hitachi U-2000 spectrophotometer. All the fluorescence and lifetime measurements were done at room temperature using a SPEX spectrofluorometer. The fluorometer has a wavelength resolution of ± 0.2 nm and time resolution in the pico second time domain.

3. Results and discussion

The porphyrin employed in the present work is 5, 10, 15, 20-tetraphenyl porohyryn whose structure is given in Fig. 1 where M = H₂, Cd, Mg and Zn. Fig. 2 shows the absorption spectra of H₂TPP, CdTPP, MgTPP and ZnTPP doped borate glassy matrices. All the absorption spectra show an intense band in the 440–447 nm region and a comparatively weaker but sharper transition in the 665 nm region. In general, these two bands correspond to the usual $\pi \rightarrow \pi^*$ transition. Specifically, the band in the 440–447 nm is the usual Soret band and is arising out of the $a_{1u}(\pi) \rightarrow e_g(\pi^*)$ transition. The band appearing in the visible region at 665 nm is the well known Q-band arising out of the transition $a_{2u}(\pi) \rightarrow e_g(\pi^*)$. It may be noted that in many solvent media and in vapor phase this band appears as a doublet [2]. However, in the present systems no such splitting was observed.

The electronic spectra and states of free base porphyrin are fairly well described in terms of a simple four-orbital model [4]. Transitions occur between the two highest filled molecular orbital $a_{1u}(\pi)$ and $a_{2u}(\pi)$ and two lowest empty orbitals $e_g(\pi^*)$. With molecular symmetry D_{4h} the orbital $e_g(\pi^*)$ are strictly degenerate whereas the first two orbitals

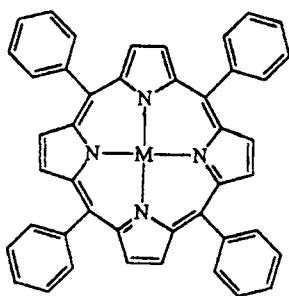


Fig. 1. Basic porphyrin structure used in this work. Here, M= H₂, Cd, Zn, Mg.

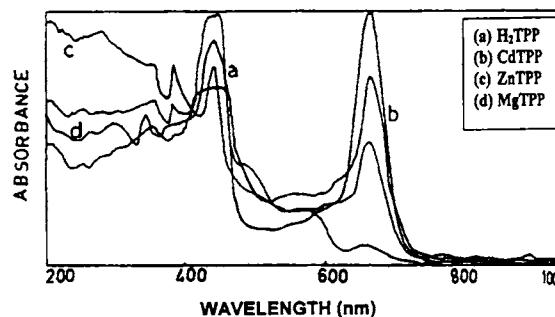


Fig. 2. Absorption spectrum: (a) H₂TPP; (b) CdTPP; (c) ZnTPP and (d) MgTPP doped borate glass.

are non-degenerate. In this case, the electronic configuration of the ground singlet state $^1A_{1g}$ will be $(a_{1u})^2(a_{2u})^2$. Accordingly, the excited configuration will be $(a_{1u}e_g)$ or $(a_{2u}e_g)$. Strong configuration interaction [2] between these two excited configuration in the singlet state forms two combinations: symmetric and antisymmetric. To the first configuration, these correspond the intense absorption band (Soret band) lying in the boundary of the visible and UV spectral regions. To the second configuration, these correspond the much less intense Q band lying in the visible spectral region. However, the picture is greatly complicated as we pass to a metal complex with a vacant d-electron shell. Basically, in the absorption spectrum of such a metalloporphyrin (as in CdTPP, ZnTPP, MgTPP), bands may be observed as a result of (i) dd transition between d orbitals of the metal; (ii) charge transfer (CT) transition ($d-\pi$ or $\pi-d$ transition) in addition to the usual $\pi-\pi^*$ transition. As a result, dd levels and CT states are located near the low lying $\pi-\pi^*$ levels. Usually the dd and CT bands are of very low intensity and are masked by the $\pi-\pi^*$ absorption. Also, being low intensity they are not always distinguishable from impurity absorption when they are beyond these bands. Besides, if these bands lie in the IR region, matrix absorption also prevents them from being recorded. A schematic representation of orbitals and possible transitions between them in metal complex is shown in Fig. 3.

The observed band transition wavelength (λ), oscillator strength (f), band width ($\Delta\lambda$), electric dipole strength (q^2), molar extinction coefficient (ϵ) and absorption cross-section (σ_a) of H₂TPP, CdTPP, ZnTPP and MgTPP molecules in the present glassy matrices are summarized in Table 1. In evaluating these optical parameters standard mathematical expressions [6,7] have been used. From these results it can be noted that in going from free to metallated porphyrin the B band molar extinction coefficient decreases considerably. The band width is observed to be minimum in ZnTPP (12.12 nm) whereas maximum (66.6 nm) is observed in CdTPP. Oscillator strength of the B band are comparable (0.05) in H₂TPP and CdTPP whereas it is the least (0.007) in ZnTPP. A similar behavior was observed in the case of electric dipole strength also. Absorption cross-section

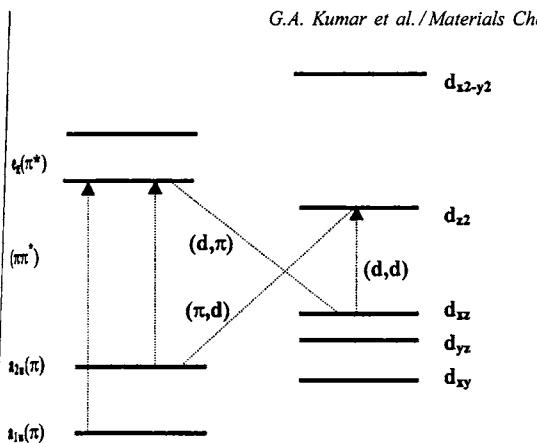


Fig. 3. Schematic representation of orbitals and possible transitions in the porphyrin metal complex.

observed to be maximum in H₂TPP ($4.9 \times 10^{-18} \text{ cm}^2$) whereas it is minimum in MgTPP ($2.8 \times 10^{-18} \text{ cm}^2$) and comparable to ZnTPP ($3 \times 10^{-18} \text{ cm}^2$). Contrary to the case of the B band, the molar extinction coefficient of the Q band is found to be maximum in CdTPP whereas the least was observed in ZnTPP. Other optical parameters viz. oscillator strength, electric dipole strength and absorption cross-section are also observed to be maximum in CdTPP. The central metal atom is thus found to considerably affect the optical properties of porphyrin molecules and this arises as a result of the interaction between the d-orbitals of the metal and the surrounding porphyrin chain. The extent to which metal d-orbitals interact with the porphyrin affects both the intensity and position of Q and B bands. As the extent of interaction increases there is a decrease in both energy and oscillator strength [1]. From the results summarized in Table 1, it is seen that ZnTPP possesses higher metal–porphyrin interaction compared to CdTPP and MgTPP. The extent of interaction is controlled by several factors, including the size of the metal ion, the geometry of the metalloporphyrin and electrostatic and inductive effects.

The optical bandgap (E_g) of the glass can be evaluated from their absorption spectra using the spectral dependence of absorption coefficient (α) upon energy ($h\nu$) and is of the

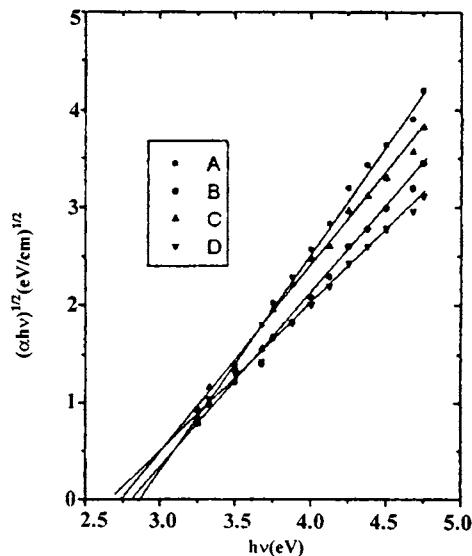


Fig. 4. Plot of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ for various porphyrin doped borate glasses.

form

$$\alpha h\nu = A\{h\nu - E_g\}^n \quad (1)$$

where $h\nu$ is the photon energy, E_g the optical bandgap and n a parameter depending on both the type of transition (direct or indirect) and the profile of the electron density in the valance band and conduction band. Here A is a constant which includes the sample thickness.

The dependence of $(\alpha h\nu)^{1/2}$ on the photon energy $h\nu$ is plotted for different n values. The best fit was obtained for $n = 2$. This is the characteristic behavior of indirect transitions in non-crystalline materials. Fig. 4 shows the functional dependence of $(\alpha h\nu)^{1/2}$ on $h\nu$ for all the samples studied. The extrapolation of the absorption curve $(\alpha h\nu)^{1/2}$ versus $h\nu$ to the value $(\alpha h\nu)^{1/2} = 0$ yields the value of E_g . The magnitudes of E_g obtained are 2.88, 2.84, 2.75 and 2.71 eV, respectively, for H₂TPP, CdTPP, ZnTPP and MgTPP. The nearly steady value of E_g in the present matrix suggests that, optical bandgap of porphyrin molecules in borate matrix is unaffected by the nature of the central metal atom of

Table 1
Calculated spectral parameters of various porphyrin molecules in borate glass matrix

TPP's	Band	λ (nm)	$\Delta\lambda$ (nm)	ϵ^*	f	q^2 (\AA^2)	$\sigma \times 10^{18} \text{ cm}^2$	N (10^{17} mol/cm^3)
H ₂ TPP	B	446	51.48	4813	0.05	0.22	4.9	9.8
	Q	665	42.4	2273	0.006	0.05	2.3	
CdTPP	B	447	66.6	3280	0.05	0.195	3.9	8.3
	Q	665	48.5	6153	0.029	0.179	7.4	
ZnTPP	B	441	12.12	2640	0.007	0.02	3.0	8.8
	Q	667	24.24	305	0.0007	0.0044	0.03	
MgTPP	B	445	35.6	1736	0.028	0.18	2.8	8.6
	Q	665	16.8	606	0.009	0.03	1.6	

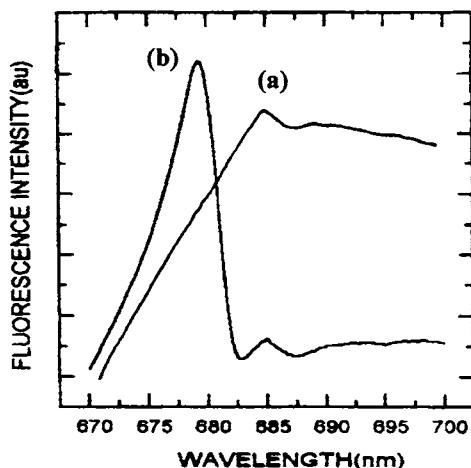


Fig. 5. Emission spectrum of CdTPP: (a) $\lambda_{EX} = 440$ nm; (b) $\lambda_{EX} = 665$ nm.

the porphyrin ring. In fact, this result clearly substantiates our early observations [7,8] on certain other metallated phthalocyanins in borate glass matrices. Actually, it is a consequence of the bonding and antibonding nature of the p orbital of B^{3+} and s orbital of O^{2-} of B_2O_3 . The optical bandgap is closely related to the energy gap between valance band and conduction band. In glasses the latter is strongly influenced by the anions [9,10]. The s and p orbitals of B^{3+} and s orbitals of O^{2-} interact with each other to form bonding and antibonding states which contribute to the valance band and conduction band, respectively. Since in the present case, the amount of B_2O_3 is always fixed the bonding and anti-bonding states remain the same and hence will not affect the optical bandgap.

Figs. 5–7 show the fluorescence spectra of CdTPP, ZnTPP and MgTPP doped borate glass matrices under ex-

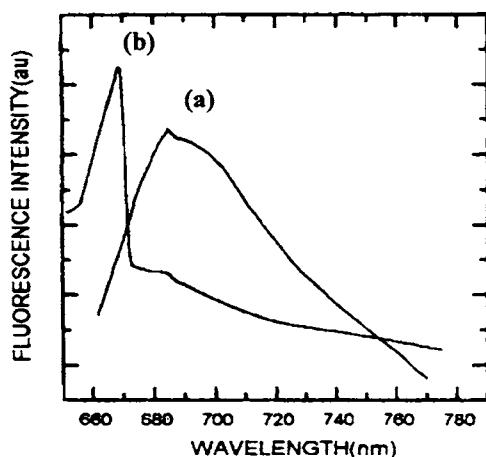


Fig. 6. Emission spectrum of ZnTPP: (a) $\lambda_{EX} = 445$ nm; (b) $\lambda_{EX} = 665$ nm.

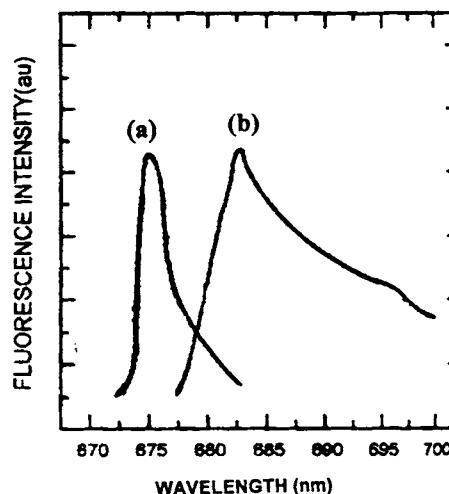


Fig. 7. Emission spectrum of MgTPP: (a) $\lambda_{EX} = 445$ nm; (b) $\lambda_{EX} = 665$ nm.

citation at two wavelengths, viz. 440 nm (corresponding to B band) and 665 nm (corresponding to Q band). All the relevant spectral data viz. emission wavelength (λ), fluorescence bandwidth ($\Delta\lambda$), fluorescence intensity, decay time (τ), stimulated emission cross-section (σ) and optical gain (G) are summarized in Table 2. In evaluating some of these optical parameters standard mathematical expressions [11] have been used. Results show that for CdTPP, ZnTPP and MgTPP fluorescence appears in the 685 nm region corresponding to the B band excitation (440 nm), whereas for the Q-band excitation, CdTPP and ZnTPP yielded fluorescence in the 679 and 669 nm regions, respectively. However, H_2 TPP does not show any such fluorescence. According to Kasha [12] transitions involving emission in condensed organic molecules always take place from the lowest excited electronic level independently of the order of levels to which molecules were excited upon absorption of light. Fluorescence intensity is observed to be almost equal in both the cases. The absence of fluorescence in the case of H_2 TPP can be accounted as a result of strong electronegativity and a larger ionic radius of the central ion [13]. For H_2 electronegativity as well as ionic radius are found to be large. Because of these factors there is larger overlap between the pyrrole nitrogen orbitals and those of the hydrogen ions. This would tend to perturb the charge cloud even more with a consequent increase in the spin-orbit perturbation. Emission cross-section and thereby the optical gain are found to be larger in CdTPP doped matrix. Since both these lie within the range of a good optical material, the present porphyrin doped borate glass matrix can be effectively considered as an efficient solid state active medium capable of optical amplification in the 669–684 nm region.

In an attempt to study the relaxation processes measurements were made of the fluorescence decay of the emission components corresponding to the B- and Q-band excitations.

Table 2
Optical spectral parameters of metallated porphyrins in borate glass matrix

	Band	λ_{EX}	λ_{Em}	$\Delta\lambda$ (nm)	$\sigma \times 10^{18} \text{ cm}^2$	G (dB/cm)
H ₂ TPP	B	440	685	40.4	18.6	70.5
	Q	665	684	8.4	5.5	19.8
CdTPP	B	445	685	41.3	17.7	62.5
	Q	665	669	8.2	3.5	13.3
MgTPP	B	445	685	30.2	15.2	58.3
	Q	665	670	8.1	4.2	12.8

Table 3
Kinetic parameters of metallated porphyrins in borate glass matrix

	Band	k_F (10^7 s^{-1})	τ_F (ns)	ϕ_F	k_{SC} (10^8 s^{-1})
H ₂ TPP	B	5.0	2.4	0.12	3.6
	Q	2.4	7.6	0.18	1.08
CdTPP	B	2.1	6.2	0.13	1.4
	Q	1.08	5.5	0.06	1.7
MgTPP	B	1.18	4.4	0.14	0.72
	Q	6.7	1.8	0.12	1.07

The decay curves are distinctly exponential in nature suggesting that the individual species have the same type of local environment. Our approach is simply to accept the exponential behavior and to fit the resultant plot of $\ln I$ versus time with the equation

$$\ln I = \ln I_0 - \alpha t \quad (2)$$

Here the linear coefficient α remains relatively large, hence we can extract the value of the lifetime $\tau = 1/\alpha$ with a reasonable degree of confidence. Interestingly, the rate constant for fluorescence (k_F) calculated using the Strickler–Berg formula [11] has the same order of magnitude for all the metalloporphyrins except for the numerical factors (Table 3). On neglecting the internal conversion from the excited singlet state to the ground state for the compounds, the observed increment in ϕ_F and τ_F can be attributed to the decreased intersystem crossing. Based on this assumption, values for the rate constant for intersystem crossing (k_{SC}) have also been calculated. The result is as expected, because the collision processes among the porphyrine molecules is restricted to some extent in the glass host unlike in solutions where an enhanced intersystem crossing [14] due to greater freedom of motion of the molecules.

4. Conclusions

Absorption and emission studies of porphyrin doped borate glasses have been reported for the first time. As in different solvent and vapor phase, the recorded optical absorption spectra show well defined Q and B bands. Measured optical parameters viz. molar extinction coefficient,

oscillator strength, electric dipole strengths and absorption cross-section show some variations depending on the nature of the central metal atom whereas the optical bandgap is almost unaffected by the central metal atom substitution. Except H₂TPP, CdTPP, MgTPP and ZnTPP show intense fluorescence in the 669–684 nm region. The absence of fluorescence in H₂TPP doped matrix is attributed to the effect of strong electronegativity and larger ionic radius of the hydrogen atom. For MgTPP, CdTPP and ZnTPP, stimulated emission cross-section and optical gain values lie within the range of a good fluorescent material. Hence, it is concluded that the metalloporphyrins in glassy matrix seem to act as promising candidates in realising high optical gain.

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