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## Optical studies of phthalocyanine molecules in PVA film

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### Abstract

Optical absorption and emission spectral studies of various phthalocyanine (Pc) molecules in PVA matrix have been reported for the first time. The recorded spectra are analyzed to get the important spectral parameters, such as optical absorption cross-section ( $\sigma_a$ ), emission cross-section ( $\sigma_e$ ), oscillator strength ( $f$ ), fluorescence bandwidth ( $\Delta\lambda$ ), emission wavelength ( $\lambda$ ), radiative decay time ( $\tau$ ) and optical gain ( $G$ ). Analysis shows that the emission cross-section and optical gain are maximum in the NdHPC<sub>2</sub>-doped PVA matrix. However, a comparison of the calculated emission parameters with that of borate glass matrix show that they are many times smaller in the present matrix. © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Phthalocyanines; PVA film; Optical absorption; Decay time; Optical gain

### 1. Introduction

The phthalocyanines (Pc) are a class of planar aromatic organic compounds that have attracted a great deal of attention for quite some time because of their unique properties, such as semiconductivity, photocunductivity, photochemical reactivity, chemical stability, electrochromism, biorganic and catalytic activity and their application in the field of colour display technology and gas sensors [1–3].

Since the discovery of Pc's in 1907, a great deal of effort has been made to study the optical properties of Pc's and associated compounds. Optical absorption studies of these molecules have been reported in a variety of forms including thin films [4–6], crystals [7], vapors [8,9] and various solvents [10–12]. Studies of these molecules in condensed systems such as glasses and polymers are interesting because of their effectiveness in technological applications. Recently, the authors of the present report have done an extensive analysis on the optical absorption and stimulated emission characteristics of these molecules in amorphous solids including both organic (PMMA) and inorganic (borate glass) [13–15] glasses. The objective of the present analysis is to study the optical absorption and emission spectral properties of vari-

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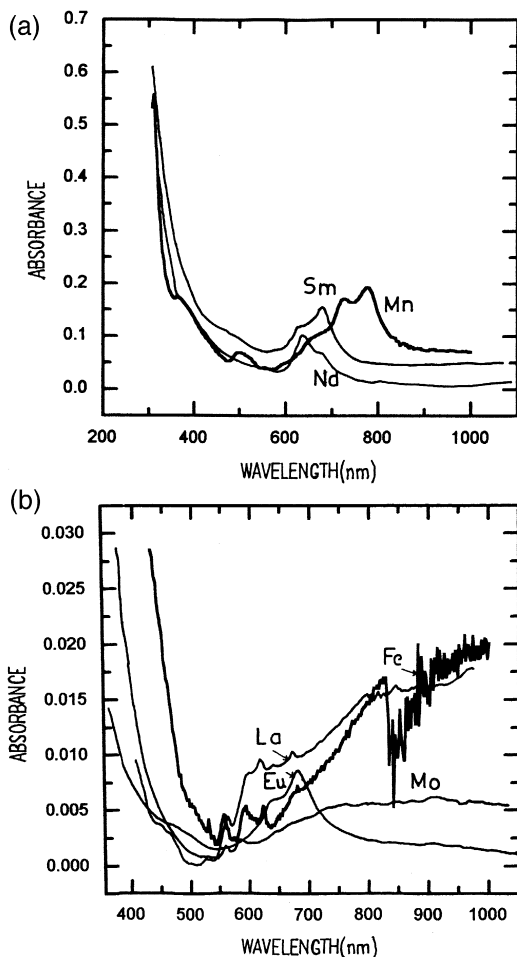


Fig. 1. (a,b) Optical absorption spectra of various Pc impregnated PVA films.

ous Pc-molecules in PVA matrix and compare the data with other reported matrices.

## 2. Experimental

All the metal Pc's used in the present study were synthesized in the laboratory using the conventional procedure [16].  $H_2Pc$  was prepared by direct cyclization in a melt of phthalonitrile and hydroquinone in a sealed, partially evacuated quartz tube. A typical preparation employed 4 g of phthalonitrile and 1 g of hydroquinone thoroughly mixed together. The crude product was washed with hot water, chloroform and acetone several times and subsequently sublimed twice at  $450^\circ\text{C}$  and  $10^{-5}$  Torr.

All the rare earth Pc's were prepared by modification of a known method [17]. They were prepared by heating a mixture of 3 g of 2,3-dicyanobenzene and 1 g of rare earth acetate to  $280^\circ\text{C}$  for 2 h in a nitrogen flushed evacuated glass ampoule until a dark blue mass was obtained. The product was isolated from the mixture by soxhlet extraction with chloroform. The sample so obtained in the powder form was carefully washed with acetic anhydride and acetone to remove traces of persistent impurity. Final purification was done by dissolving the sample in dimethyl formaldehyde (DMF) and passing it through a column of aluminium oxide. It was then eluted using methanol. The solution was evaporated to dryness and the residue was dried at  $100^\circ\text{C}$  for 1 h. All

Table 1  
Calculated optical absorption spectral parameters of various Pc's in PVA film

Sample	Energy (nm)			$C$ ( $10^{-4}$ m/l)	$\varepsilon$ ( $10^4$ )	$\sigma_a$ ( $10^{-17}$ cm $^2$ )	$q^a$ ( $\text{A}^0$ ) $^2$	$f^b$	$\sigma_a$ ( $10^{-20}$ cm $^2$ ) $^c$	$\sigma_a$ ( $10^{-18}$ cm $^2$ ) $^d$
	$B$	$Q_X$	$Q_Y$							
EuHPc $_2$	316	668.7	636.7	1.15	7.3	1.09	2.21	0.342	15.0	0.84
FePc	–	622.2	691.3	1.6	0.34	5.28	0.05	0.008	–	0.26
LaPc	–	621.8	1.68	0.19	2.97	0.02	0.0003	2.51	0.036	–
MnPc	366	776	719	1.77	17.0	0.27	4.73	0.66	–	0.74
MoOPC	–	771	598.3	1.6	0.19	1.29	0.069	1.41	–	0.77
NdHPC $_2$	–	679.7	636.7	0.84	65.0	9.71	15.9	2.72	4.5	0.21
SmHPc $_2$	–	679.7	640.3	1.15	8.6	1.30	1.27	0.019	8.8	0.42

$$^a q = 1/2500 \varepsilon \Delta \lambda / \lambda.$$

$$^b f = 4.32 \times 10^{-9} \int \varepsilon(\nu) d\nu.$$

$^c$  PMMA.

$^d$  Borate glass.

**Table 2**  
Calculated emission spectral parameters of various Pc's in PVA film

Sample	$\lambda$ (nm)	$I$	$\tau$ (ns) <sup>a</sup>	$\Delta\lambda$ (nm)	$\sigma_e$ ( $10^{-16}\text{cm}^2$ ) <sup>b</sup>	$G$ (dB/cm)	$\sigma_e$ ( $10^{-14}\text{cm}^2$ ) <sup>c</sup>	$G$ (dB/cm) <sup>c</sup>
EuHPc <sub>2</sub>	681.8	0.38	7.63	26.3	5.55	–	9.29	41.1
FePc	–	–	329*	–	–	0.02	6.02	–
LaPc	684.7	0.12	659*	22	0.78	2.16	1.25	5.6
MnPc	684.7	0	5.28	26	8.27	–	4.13	–
MoOpC	–	–	247*	–	–	11.7	0.34	–
NdHpC <sub>2</sub>	685.2	0.22	0.87	29.1	44.9	0.95	4.0	17.8
SmHPc <sub>2</sub>	680.8	1.0	13.8	22	3.67	–	4.43	19.4

<sup>a</sup> $\sigma_e = \lambda/8\pi\text{cm}^2\Delta\lambda\tau.$

<sup>b</sup> $\tau = (2.88 \times 10^9 \text{n}^2 \nu^2) (\int \epsilon(\nu) d\nu)^{-1}.$

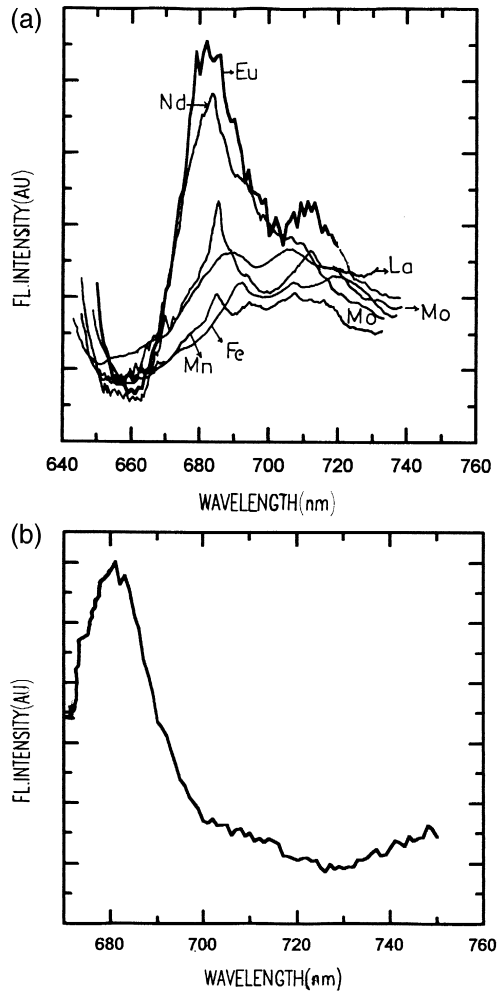
<sup>c</sup>Borate glass.

the purified samples were identified by elemental analysis, UV–VIS and IR spectroscopic techniques.

One gram of PVA was dissolved in 10 ml of DMF by heating it to about 100°C. Weighed Pc samples were added to the above solution and dissolved completely by stirring it at hot condition. The solution was allowed to cure in a vacuum oven at 60°C for 24 h to get films of different samples. All the samples were greenish blue in colour with good optical transparency. The optical absorption measurements of the film was carried out using a UV–VIS spectrophotometer (Hitachi 3410). All the emission spectra were recorded using a SPEX spectrofluorimeter.

**3. Results and discussion**

The measured absorption spectra of the samples are shown in Fig. 1(a,b). Tables 1 and 2 summarize the relevant spectral parameters. All the spectra contain the prominent *B* and *Q* bands with their intensities varying from one to another. All Pc's except LaPc show the characteristic *Q*-band splitting (Davidov's splitting). The splitting is maximum in MoOPc and minimum in EuH(Pc)<sub>2</sub>. A comparison of the splitting with that of other solid matrices viz. borate glass and PMMA shows that the splitting is larger in PVA for all the Pc's except the REPC whereas for the REPC the splitting is larger in glassy matrix. As already noticed in all other matrices, the



**Fig. 2.** (a) Emission spectra of various Pc impregnated PVA films. (b) Emission spectrum of SmPc impregnated PVA film.

larger red shift of MnPc is attributed to the comparatively smaller atomic radius of the Mn atom. Comparison of the  $Q$ -band oscillator strength shows that it is least in the PVA system as compared to borate glass and PMMA matrix. However, in the case of NdH(Pc)<sub>2</sub>, an anomaly exists. The calculated  $Q$ -band absorption cross-sections are 10 times larger than borate glass and 1000 times larger than PMMA matrix.

All the fluorescence spectra (Fig. 2) show a well-resolved band in the 621–779 nm region. The relative fluorescence intensity is found to be maximum in SmH(Pc)<sub>2</sub>. It should also be noted that FePc and MoOPc do not show any fluorescence. Emission cross-section and thereby the optical gain measured are maximum in NdH(Pc)<sub>2</sub>-doped PVA sample. All the measured emission cross-sections are found to be 100 times smaller in the PVA matrix as compared to glassy matrix. Optical gain also shows a considerable reduction in PVA matrix, whereas the excited state lifetime shows a considerable increase.

#### 4. Conclusions

All the phthalocyanine (Pc) molecules show very good absorption in PVA matrix with considerable absorption cross-section enhancement as compared to borate glass and PMMA matrix. Contrary to the borate glass matrix, FePc and MoOPc impregnated PVA medium does not show any fluorescence. In all other cases, the emission cross-section and optical gain measured are very much less as compared to the glassy matrix.

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