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Optical properties of phthalocyanine molecules in cyano acrylate polymer matrix

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Abstract

Optical absorption and emission spectral studies of various phthalocyanine molecules, viz., LaPc, NdPc, SmPc, EuPc, CuPc and ZnPc in a polymer matrix of cyano acrylate are reported for the first time. All the absorption spectra show an intense B band (Soret) in the UV region followed by a weaker Q band in the visible region. The positions of the Q and B bands are found to have dependence on the metallic substitution. Values of the important spectral parameters, viz., molar extinction coefficient (ϵ), oscillator strength (f), radiative transition rate and decay time of the excited singlet state are also presented and compared with other solid matrices. The recorded fluorescence spectrum shows two broad emission bands in the case of NdPc, whereas for ZnPc only a very weak band is observed. The absence of emission bands for the other metallated phthalocyanines is attributed to increased spin orbit interaction and intersystem crossing. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Organic semiconductors play a very important role in modern high technology applications, viz., optical imaging, optical switching, data storage, photodynamic therapy, dynamic

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holography, frequency mixing, harmonic generation and optical communication [1–4]. Among the organic semiconductors, phthalocyanines (Pc-s) are of special importance because of their inexpensiveness, thermal and environmental stability, non-toxicity as well as its excellent optical and electronic properties. A combination of these features makes them an important class of photo-electronic materials for applications in various optoelectronic devices.

Ever 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. Because of the very good optical absorption of these molecules in the UV-VIS region, there is considerable interest in the optical characterization of phthalocyanines in a variety of matrices. All these materials have very good absorption in the UV (300–400 nm, B band region) and VIS (600–700nm, Q band region) region. Values of the various optical parameters, viz., optical absorption coefficient, emission coefficient and decay time of these molecules are comparable with those of common laser dyes. All these optical parameters related to linear optical properties together with the four level electronic band structures of these molecules favor them as suitable candidates for applications in optical amplifiers. Absorption spectral studies of free as well as metallated Pc-s have been reported in vapor phase [5,6], various solvents [7–10], thin films [11–14], crystals [15], and thermoplastic media [16]. Studies on the optical properties of phthalocyanines in solid matrices have barely been done except for some reports on thermoplastic media, viz., Styron, Tyril 767, and plexiglass [16]. Recently we have done an extensive investigation on the physical and optical properties of various rare earth and metal phthalocyanine doped borate glass matrices [17–19].

Solid hosts for lasing dyes are attractive alternatives to liquid dye lasers. The requirement of large volumes of organic solvents has limited the use of these lasers in some technical applications. As a result over the last decade there has been a renewed interest in the use of solid matrices containing lasing dyes, and significant advances have been made towards the development of practical tunable solid-state dye lasers [20]. Obvious technical advantages of using solid hosts for lasing dyes include compactness, manageability, lack of toxicity and flammability, and suppression of flow fluctuations, solvent evaporation, etc. Although both inorganic glasses and organic polymeric materials have been successfully used as host matrices for lasing dyes, polymers offer a number of advantages from both the technical and the economical point of view, including high optical homogeneity, better chemical compatibility with organic dyes, and control over medium polarity and viscosity in a way similar to a conventional solvent. In addition, relevant properties of these materials, such as free volume, molecular weight, and viscoelasticity can also be modified in a controlled way [21], providing desirable flexibility in the search for improved host material for lasing dyes.

Although dozens of polymers and their formations have been studied as active laser media, only a few polymers have been studied as host media for lasing dye, up to the present time. Of these polymers, polymethyl methacrylate (PMMA) is the most frequently used and most rewardingly studied, because it shows the best optical transparency in the visible and the relatively best laser-damage threshold. However, in polymer matrices both the lasing efficiency and photostability can be improved up to a certain point by controlled cross-linking of polymeric chains with a suitable difunctional monomer. Costela and co-workers [22–24] have conducted an elaborate study on the photophysical aspects of various laser dyes

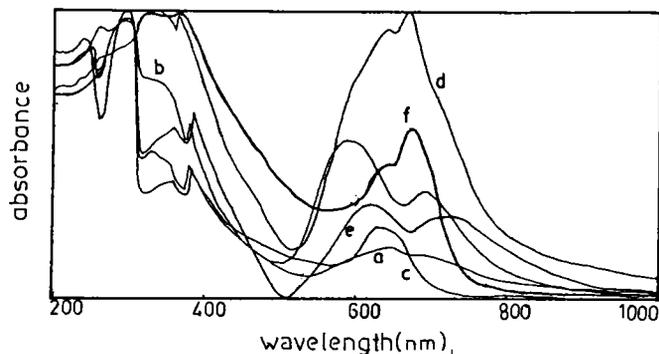


Fig. 1. Optical absorption spectrum of the polymer samples: a-LaPc, b-ZnPc, c-NdPc, d-EuPc, e-CuPc, f-SmPc.

such as Coumarine, Rh-6G, etc. with the aim of developing a powerful optical gain medium. However, to our knowledge, there is no report on the optical characterization of phthalocyanine molecules in PMMA matrices. The objective of this work was to study the optical absorption and emission spectra of metallated phthalocyanines in a polycyano acrylate matrix and to derive the important optical parameters, viz., molar extinction coefficient (ϵ), absorption cross-section (σ_a), oscillator strength (f), radiative transition rate (K_R), and radiative decay time of the excited singlet state (τ).

2. Experimental

Samples of polycyano acrylate doped with phthalocyanines molecules are obtained by mixing appropriate quantities of Pc-s with the monomer cyano acrylate. Films of 0.3 mm thick were obtained by casting the monomer solution in between two glass plates and allowing it to polymerize. All the samples were greenish blue in color with good optical transparency. To simplify the optical measurements, all the samples were doped with 4×10^{-4} m/l of the Pc molecules. Absorption spectra of the samples were recorded using a spectrophotometer (Hitachi U2000) in the wavelength range 200-1100 nm. Emission spectra were recorded using a SPEX spectrofluorimeter with a wavelength resolution of ± 0.2 nm. All the measurements were taken at room temperature.

3. Results and discussion

Fig. 1 shows the absorption spectra of various Pc doped polymer matrices. The observed transitions, their spectral assignments and calculated optical constants are summarized in Table 1. All the absorption spectra show an intense B band in the UV region followed by a comparatively weaker Q band. The molar extinction coefficient of the B band is found to be maximum in the SmPc doped sample. It should be noted that values of the molar extinction coefficient of both the Q and B bands in the present polymer matrix is comparatively smaller

Table 1
Band assignments and calculated optical constants of phthalocyanine molecules in cyano acrylate polymer matrix

Pc-s	Wavelengths (nm)			Molar extinction coefficient (10^4) (mol/cm^2) ⁻¹			Oscillator strength (f)			Absorption cross-section σ_a (10^{-18} cm^2)	Radiative decay rate ($\text{K}_R \text{ s}^{-1}$) (10^{10})
	B	Q _x	Q _y	B	Q _x	Q _y	f _B	f _x	f _y		
LaPc	302	685	642	12.5	1.8	2.2	3.7	0.27	0.38	2.51	4.3
NdPc	301	654		12.5	3.0		3.6	0.27		4.5	0.95
EuPc	351	681	654	10.8	10.8	10		1.06	1.35	15.0	3.1
SmPc	340	682	636	13.0	7.7	6.0	1.8	0.48	0.5	8.8	5.2
ZnPc	306	700	600	12.5	4.5	6.9	3.4	0.49	1.03	10.4	1.6
CuPc	295	727	624	10.0	2.7	3.4	2.7	0.37	0.42	5.0	1.8

than that of other reported solid matrices, viz., borate glasses [17–19] and thermoplastic media [16]. However the oscillator strength values of the Q bands in both the acrylate and borate glass matrices are comparable except in the case of SmPc and LaPc. Absorption cross sections of both the Q and B bands are found to be 10 times smaller than those of the borate matrix.

Both energy and oscillator strength of the Q band depend on the central metal ion and they can be used as a simple measure of the degree of interaction between the metal ion and the phthalocyanine π system. In the present systems the relative magnitudes of the oscillator strengths, as noted here, appear to be a complex function of atomic number, ionic radius, planarity and electronegativity effects. Fig. 2 shows the relationship between Q band energies and oscillator strengths of various Pc doped polymer matrices studied. From Fig. 2(a) and (b), it can be inferred that there is a strong interaction between metal ion and Pc π

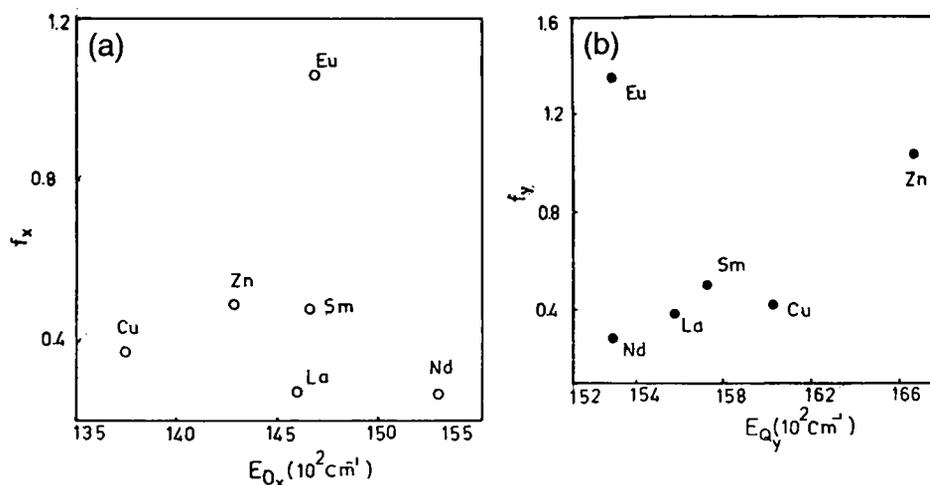


Fig. 2. (a) Variation of Q_x band energy with oscillator strength. (b) Variation of Q_y band energy with oscillator strength.

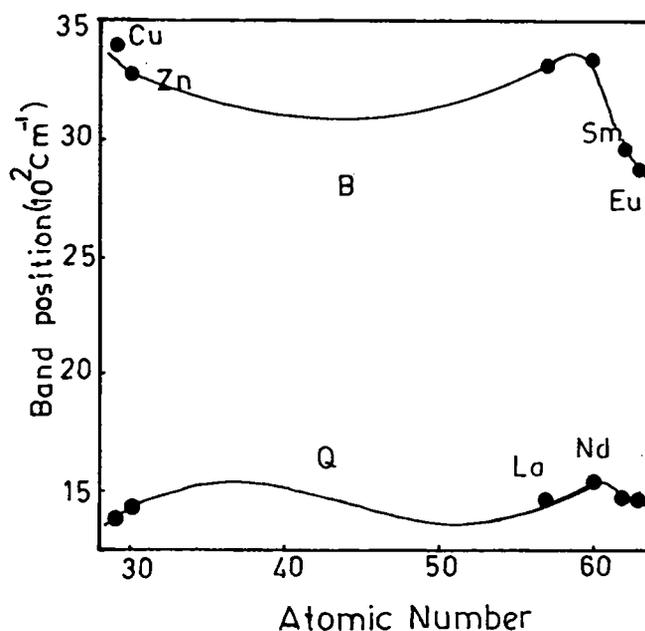


Fig. 3. Atomic number vs. band position.

system for EuPc, while the interaction is quite weak for NdPc. Further, the extent of interaction is controlled by a combination of several features, including the size of the metal ion, the geometry of Pc-s, and electrostatic and inductive effects [25]. Hence, Fig. 2 does not provide a satisfactory evidence for comparison of the relative efficiency with which the orbitals of the metal ion interact with the Pc- π system.

The introduction of metal into the Pc molecule has a variable effect on the intensity and spacing but on the whole does not alter the general type. If the positions of the Q and B bands of each of the Pc in the present system are plotted against the atomic number of the metal as shown in Fig. 3, the values fall on a smooth curve, the displacement reaching a maximum with NdPc (At No. 60). In view of the fact that the tendency to form planar 4-coordinate compounds reaches its maximum with NdPc, it is possible that the magnitude of the shift in the absorption spectrum can be correlated with the strength of the coordinate links of the central metal ion.

The extent of Q band splitting (Davidov's splitting) of various Pc-s in the present polymer matrix is graphically shown in Fig. 4. The graph does not show any linear relationship of the Davidov's splitting with the atomic number of the central metal ion. It can be seen that Davidov's splitting in the present system is maximum for ZnPc whereas it is least in EuPc. A comparison of the Davidov's splitting in the present polymer matrix with that of the borate glass matrix shows that the splitting in polymer matrix is comparatively larger than that of glassy matrix [17–19]. According to Davidov's theory the amount of splitting is a measure of the interaction energy between molecules having different site symmetries. The bands split into as many components as there are non-translationally equivalent molecules present

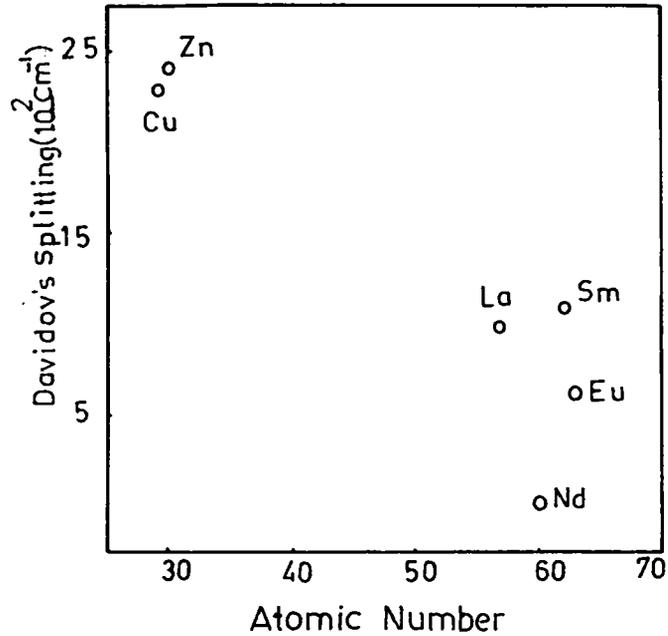


Fig. 4. Atomic number vs. Davidov's splitting.

in the unit cell. Also there exists a correlation between the tendency of the central metal ion to form out of plane bonding and the magnitude of the Davidov's splitting [19].

The fluorescence spectra recorded show two broad bands at 681nm and 650nm for NdPc (Fig. 5a), whereas for ZnPc only a weak emission band is observed at 680 nm (Fig. 5b). The remaining Pc doped samples does not show any fluorescence. This is due to the increase in

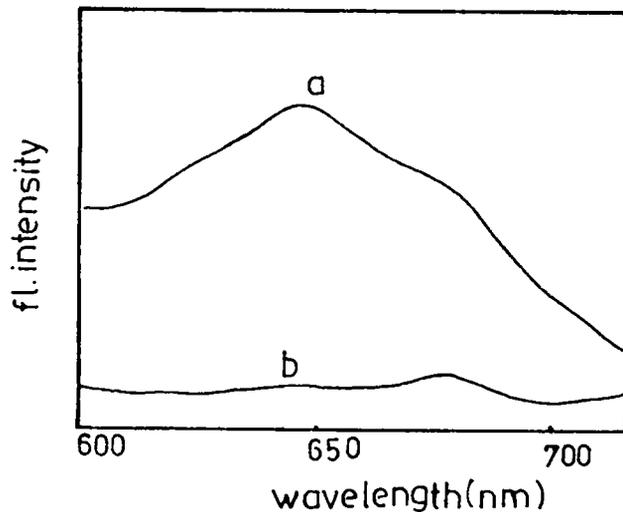


Fig. 5. Emission spectrum of the Pc doped polymer samples: (a) NdPc, (b) ZnPc.

the atomic number of the metal ions, which leads to a strong overlapping of the orbital of the pyrrole ring and the metal ions. It should also be mentioned that the effects of increased electronegativity and, in particular, the ionic radius corresponding to an increase in atomic number of the central metal atom are found to quench the fluorescence, which is consistent with standard theories [25]. The oscillating electrons create an orbital magnetic moment, which couples with the spin of the electrons [26]. When the ionic radius of the central metal atom increases, there should be a greater overlap between the pyrrole nitrogen orbitals and those of the metal ion. This would tend to perturb the charge cloud even more with a consequent increase in the spin-orbit interaction. The effect of increased spin-orbit interaction is to considerably reduce the fluorescence intensity by converting them into a non-radiative part (through intersystem crossing). This accounts for the absence of fluorescence emission in the case of EuPc, LaPc and SmPc doped samples. The significance of the difference in the ionic radii of the various metal ions is closely related to the bonding and spin-orbital considerations of the metallated phthalocyanines. In the case of phthalocyanines, there would be a fairly uniform distribution of electron density in the vicinity of the pyrrole nitrogens. With the ionic radius, the bond distance between the metal ion and the four-pyrrole nitrogens could be shortened, enhancing the coupling mechanism. Thus, the pyrrole ring system in the Pc molecule would be moved closer towards the center of the ring system. The lack of emission in the CuPc sample can be accounted as arising out of the high electronegativity (19) of Cu^{2+} ion. Because of the increased electronegativity, an internal degradation mechanism could exhibit, which would allow drain off of excitation energy in a radiationless manner. Atomic number also has a negative effect on the emission properties of Pc molecules, but the extent of this is smaller than that arising out of the increase in electronegativity and ionic radius.

4. Conclusions

The preparation and optical characterization of phthalocyanine doped cyano acrylate polymer matrix is reported for the first time. The recorded absorption spectra show very good absorption in the UV-VIS-NIR region. Compared to glassy and other plastic media, the absorption spectra of the phthalocyanine molecules in cyano acrylate matrix is characterized by a low value of molar extinction coefficient and absorption cross sections. The lack of fluorescence emission in the case of EuPc, LaPc and SmPc is attributed to increased ionic radius of the central metal atom, which in turn enhances the spin-orbit coupling and intersystem crossing. However, for CuPc, the high electronegativity value seems to suppress fluorescence.

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