Chapter 8

FTIR spectra of lead phthalocyanine hydrogen bonded with six dyes
8.1 Introduction:

Lead Phthalocyanine (PbPc) is a one-dimensional conductor having one-dimensional lead chains along one-direction of crystals [1]. Vibration spectra of CT complexes of PbPc as well as uv-visible spectra of these CTCs are studied [2,3]. Here in the present work, hydrogen bonding of PbPc at nitrogen atoms of the ligand with six O-H and N-H containing dyes such as Congo red, Para red, Direct red, Bismark brown, Evans blue and Trypan blue is attempted. It is verified that there is intermolecular hydrogen bonding.

8.2 Experimental Details:

PbPc (lead phthalocyanine) was prepared by refluxing lead monoxide with phthalonitrile in nitrobenzene medium. The blue powder prepared in this manner was mixed with six dyes namely Congo red, Para red, Direct red, Bismark brown, Evans blue and Trypan blue obtained from Aldrich chemical company, USA in pure form. The mixtures were grinded in an agate mortar with a pastle for half an hour for bringing PbPc molecules and dye molecules in molecular contact. The hydrogen bonded complexes prepared were further mixed with 95% spectrograde KBr powder, grinded to form homogeneous mixture and compressed in a die to form circular palates. These round-shaped discs were placed in a dark chamber of spectrophotometer.
The spectra in the range 400-4000 cm\(^{-1}\) were recorded using a GXFTIR single beam spectrophotometer manufactured by Perkin-Elmer Co., USA. It was having a resolution of 0.15 cm\(^{-1}\), a scan range of 15,600-30 cm\(^{-1}\), a scan time of 20 scan sec\(^{-1}\), an OPD velocity of 0.20 cm sec\(^{-1}\) and MIRTGS and FIRTGS detectors. A beam splitter of opt KBr type was used having a range of 7800-370 cm\(^{-1}\). The spectra were recorded in purge mode. Molecular structure of PbPc and six dyes are shown (Figure 1).
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FTIR Spectra Of PbPc With Six Dyes

(1c)

(1d)

(1e)

(1f)

8.3 Results and Discussion:

The FTIR spectra of PbPc-Para red, PbPc-Congo red and PbPc-Direct red are shown (Figure 2). The FTIR spectra of PbPc-Bismark brown, PbPc-Evans blue and PbPc-Trypan blue are also shown (Figure 3). All of the spectra show noise in absorption spectrum above 3600 cm$^{-1}$ in the range of free carrier absorption and noise just above the absorption edge at about 1700 cm$^{-1}$. The previous one due to photoconducting nature of the hydrogen bonded PbPc complexes and the latter due to localization near the band edges. Band edges are not sharp but having band tailing with localization states near the band edges. The mid-IR spectrum below 1700 cm$^{-1}$ is governed by the absorption of dye molecules because of a large proportion (1:4 molecular weight proportion) of dyes used in preparing the hydrogen bonded complexes. Bands below 700 cm$^{-1}$ contain bands due to metal-ligand vibrations of PbPc molecule. These bands are shifted due to hydrogen bonding at nitrogen atoms.
Figure 2 FTIR spectra of PbPc hydrogen bonded with (a) Para red, (b) Congo red and (c) Direct red.
[Figure 3 FTIR spectra of PbPc hydrogen bonded with (a) Bismark brown, (b) Evans blue and (c) Trypan blue]
The absorption edge spectrum above 1700 cm\(^{-1}\) is modified due to exciton-phonon coupling as discussed elsewhere [4]. Threshold energies for the formation of excitons with phonon emission are found as observed in the absorption spectrum of gallium phosphide [5,6]. The intrinsic absorption edge spectrum is studied in details [7]. At a later date, electron-hole liquid was found in GaP [8] due to high exciton density at low temperature. Because of similarity in absorption edge spectra of hydrogen bonded PbPc and crystalline GaP room temperature there is a possibility of electron-hole liquid in the H-bonded PbPc also at low temperatures. The subject of electron-hole liquid is well established [9]. In many semiconductors this phenomenon is observed. In the present cases also the absorption edge spectra reveal phonon-assisted creation of free excitons and electrons-hole pairs and high density of excitons at room temperature.

The absorption edge is analyzed by plotting \((\alpha h\nu)\), \((\alpha h\nu)^{1/2}\), \((\alpha h\nu)^{1/3}\), \((\alpha h\nu)^{2/3}\), \((\alpha h\nu)^{2}\) vs \(h\nu\) and finding the best fit. Here \((\alpha h\nu)\) vs \(h\nu\) is found to the best fit in all cases of PbPc complexes (Figure 4) which reveals allowed indirect transition in two-dimensional (Layered) semiconductor. When exciton-phonon coupling is strong, phonon are emitted limited in number when this coupling is weak, large number of phonons are emitted. The strength of coupling of excitons and phonons is reciprocal to the number of phonon bands in the edge spectrum. The number of phonon bands vs band gap is plotted (Figure 5). This graph indicates that band gap reduces as exciton-phonon coupling increases. This type of
behavior was also found recently in PbPc-emeraldine, PbPc-nigraniline and PbPc-pernigraniline also. Polyanilines were almost symmetric dyes and cannot be highly polarizable like asymmetric dyes chosen in the present work. There are large number of intramolecular vibrations acting as optical phonon modes in asymmetric dyes. These vibrations get decoupled from excitons when exciton-phonon coupling is weak.

![Graph 4a](image1)

![Graph 4b](image2)
Graphs (4c) and (4d) show the relationship between $\alpha h\nu$ and $h\nu$ (eV) for different samples. The graphs indicate the energy bandgap of the PbPc with six dyes.
[Figure 4  Nature of transition in (a)PbPc-Para red,(b)PbPc-Congo red,
(c)PbPc-Direct red,(d)PbPc-Bismark brown,(e)PbPc-Evans blue and
(f)PbPc-Trypan blue]
Usually in direct band gap semiconductors exciton bands are found just below the gap, while in a indirect band gap semiconductors, steps are found in absorption edge [5]. Here in spite of indirect edge, bands are found so most probably these bands are due to lattice absorption and therefore the combination bands of several TO, LO, LA, TA models [5]. Multi phonon processes occur due to anharmonic and nonlinear interactions in soft materials studied in the present work. The phonon energies cannot be found because average energy will be zero due to disordered materials studied in the present work. The materials are disordered and therefore, (αhv) vs hv is straight line rather than α vs hv, the latter being the absorption function for crystalline material. Indirect transition in metal-organic system due to metal-ligand vibrations are established recently [5,10,11].
Here also the best fits were found to be for indirect transition. Phonon bands rather than exciton band in the edge spectrum are more possible because of infrared range of spectra. Also oscillator model of phonons are many time found in the band edges. The phonon bands poke out of the straight line plotted for step function near $E_g$. In this case a linear interpolation to find phonon energy is not valid. Rather there is phonon peak energy, which can be found out from such indentations.

However, it is possible that broad bands in the absorption edges are due to phonon emissions and one or two sharp bands are due to Mott-Wannier excitons. Then there is real infrared analogy of the excitons found in uv-visible range of inorganic compound semiconductors. There can be excitons with energies lying in the infrared range. These excitons can lead to infrared luminescence due to electron-hole pairs across the infrared band gap. Also there is remote possibility of all bands found in the edge spectrum being exciton bands. There can be broadening of exciton band. There can be broadening of exciton bands due to exciton-phonon coupling. Then there is infrared analogy of optical phenomena in soft semiconductors.

In soft semiconductors like organic charge transfer complexes and hydrogen-bonded system, the infrared band gap is due to gap in the phonon dispersion curves between acoustic and optical modes. Electron-polaron and hole-polaron are formed and there can be a polaronic exciton or excitonic bipolaron in
which there is attractive coupling between electron-polaron and hole-polaron which are oppositely charged. \(E_B - 2E_p\), where \(E_B\) is the binding energy of a bipolaron and \(E_p\) is the polaron binding energy acts as a band gap. Band gap is nothing but dissociation energy of a bipolaron into two polarons. The bipolarons are formed due to exciton-phonon coupling. When phonon is emitted due to weak coupling, bound electron-hole pair results.

The present work and work on polyanilines hydrogen bonded with PbPc clearly show that exciton-phonon coupling is strong for green, blue and violet dyes but weak for yellow, brown and red dyes. Thus band gap is smaller for green, blue and violet dyes hydrogen bonded with one-dimensional conductor than for yellow and red dyes similarly attached.

Moreover, PbPc hydrogen bonded with dyes works as two-dimensional conductor. Exciton density is high on one and two dimensional conductors than three-dimensional (isotropic) conductors. In two-dimensional systems, there are no localization effects which appear in one-dimensional conductors. Two-dimensional electron-hole liquids are also known and studied with both theoretical and experimental points of views [12-14].

Band tailing analysis is also carried out by plotting \(\ln \alpha \) vs \(h\nu\) for the absorption edge spectrum because \(\alpha\) is given by,
\[ \alpha = \alpha_0 \exp \left\{ \frac{(\hbar \nu - E_1)}{E_0} \right\} \]

$E_0$ is the width of the band tail and is given by the reciprocal of the slope of $\ln \alpha$ vs $\hbar \nu$ plot. $E_1$ is a focal point and is a characteristic of the material. $E_1$ may include Burstein-Moss shift parameter ($\xi$) for heavily doped semiconductor apart from $E_g$ and $E_p$ (phonon energy). Band tailing analysis with focal point is shown (Figure 6a) and $E_g$ vs $E_0$ is also plotted (Figure 6b). As $E_0$ increases, $E_g$ decreases almost linearly. This is also expected from theoretical arguments [15].
8.4 Conclusions:

The infrared absorption edge spectrum of hydrogen bonded PbPc with six dyes is modified due to exciton-phonon coupling. This spectrum shows several threshold energies for the formation of free excitons or electron-hole pairs with phonon emission. When exciton-phonon coupling is weak several phonons are emitted due to decoupling. The number of phonon bands vs band gap shows a curve which reveals how band gap decreases as exciton-phonon coupling strength increases.
References:

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