

IR SPECTROSCOPIC STUDIES OF H₂Pc, CuPc AND ZnPc

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ABSTRACT

The phthalocyanine molecules are unique with respect to structural, electrical and optical properties. Due to their intense colour, and high thermal and chemical stability, phthalocyanines were firstly employed as green and blue colorants in photographic, printing, plastic and textile industries. A metal free phthalocyanine molecule H₂Pc and metal phthalocyanine such as CuPc, ZnPc contains four chelate six member rings. The coordination and covalent coordination of the central metal atoms explain the unusual stability of these atoms in the phthalocyanine molecule. We have studied the IR spectroscopy to see the structural differences between different phthalocyanines used in this paper. In H₂Pc, ZnPc and CuPc there is little difference in optical and structural properties however the solar cells made of these materials give different performances, which suggests that the physical properties have great effect on the devices performance determination.

Keywords: H₂Pc, CuPc, ZnPc, Structural Properties, Photovoltaic Cells.

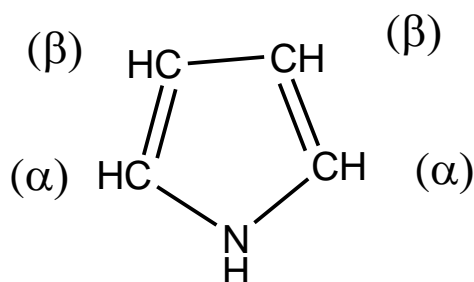
Introduction

The word 'phthalocyanine' is derived from the Greek terms for naphtha (rock oil) and cyanine (dark blue). Naphtha was mentioned in ancient Greek literature. Professor Reginald P. Linstead of the Imperial College of Science and Technology first used the term "phthalocyanine" in 1933 [1].

The phthalocyanine class of compounds consists of various metal derivatives such as copper phthalocyanine (CuPc), zinc phthalocyanine (ZnPc). The two hydrogen atoms in the center of the molecule are replaced by metals, from every group of the Periodic Table to form the group of compounds known as the metal phthalocyanines. Phthalocyanines were first discovered in 1907 when Braun and Tcherniac from South Metropolitan Gas Company in London, treated "o-cyanobenzamide" at high temperatures [2]. Phthalocyanines are not only a new class of organic compounds but also they constitute a new class of colouring matter or chromogen. Moderate cost of manufacture, good stability and tinctorial properties, in a region of the visible spectrum which had been lacking in chromogens with good colour properties, stability, and manufacturing cost, have led the phthalocyanines to become the object of intensive world-wide investigations, particularly with respect to applications in the field of colour.

Phthalocyanine (Pc) molecules are macro-cycle complexes related to porphyrins [3, 4]. The phthalocyanines are macrocyclic compounds containing four pyrrole units (see Fig.1). They are a member of one of three series of macrocyclic compounds containing four pyrrole units:

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pyrrole (I)

Fig.1: Structure of Pyrrole

The pyrrole nuclei in the porphin series are joined together in the α -carbon position by four methine (CH=) groups. The pyrrole nuclei in the porphyrine series are linked in the α -carbon position by four aza (N=) groups. Porphin itself occurs in nature and has been synthesized. Porphyrine has not been found in nature and has not been synthesized. Two important classes of porphins, containing substituents on the β -carbons of porphin are chlorophyll and hemin. Phthalocyanine itself may be considered to be an extremely weak dibasic acid. The metal derivatives of phthalocyanine are therefore salts. In copper phthalocyanine, for example, the copper atom supplies one electron to each of two isoindole nitrogen atoms; each of these isoindole nitrogen atoms in turn supplies an electron to the copper atom, forming a covalent bond.

On the basis of elemental analysis, molecular mass determination, and the method of oxidative degradation, Linstead *et al.* proposed that phthalocyanines are symmetrical macrocycles containing four isoindole units [5]. The molecular structures of these compounds were determined first by Robertson *et al.* during 1935-1937 [6]. In contrast to the porphyrin macrocycles, phthalocyanines contain four additional linearly annulated benzene rings with either a metal atom (metal phthalocyanine, MePc, $C_{32}H_{16}N_8Me$) or two hydrogen atoms in the center (Metal-free Pc, H_2Pc , $C_{32}H_{16}N_8H_2$).

Sample Preparations for IR Studies

Infra-red spectrum is an important record which gives sufficient information about the structure of a material. IR spectrum consists of a large number of absorption peaks from which lots of information can be derived about the structure of the organic compound. The absorption of IR radiation causes various bands of the molecule corresponding to various vibrations related to stretching and banding in the molecules. Sample preparation includes the fine grinding of some amount of the sample with a specially purified salt (usually potassium bromide) to remove scattering effects from large crystals. This powder mixture is then pressed in a mechanical press to form a translucent pellet through which the beam of the spectrometer can pass. For this purpose our phthalocyanine samples were mixed in suitable amount with highly purified and dehydrated powder of KBr and pellets were formed. These pellets were used for the IR spectroscopic studies of the materials. Pellets of pure KBr were used as reference.

Infra-red (IR) spectroscopic studies

The phthalocyanine molecules may be unique with respect to structural, electrical and optical properties. Due to their intense colour, and high thermal and chemical stability, phthalocyanines were firstly employed as green and blue colorants in photographic, printing, plastic and textile industries [7]. Their intriguing optical and electrical properties [8, 9] also enable them to be used in photoconductors, field-effect transistors, optical limiting materials, optical storage media and photovoltaic cells for energy conversion [10].

Metal free phthalocyanine (H_2Pc) exhibits a characteristic IR absorption band at 1000-1020 cm^{-1} . IR spectroscopy has been used as an effective method to check the purity of the samples. All metal-containing pigments possess frequencies common to each other and to those of the metal-free Pc. However, shifts of frequencies are observed peculiar for each metal atom and especially conspicuous around 900 and 1500 cm^{-1} (111,111 and 66,666 Å).

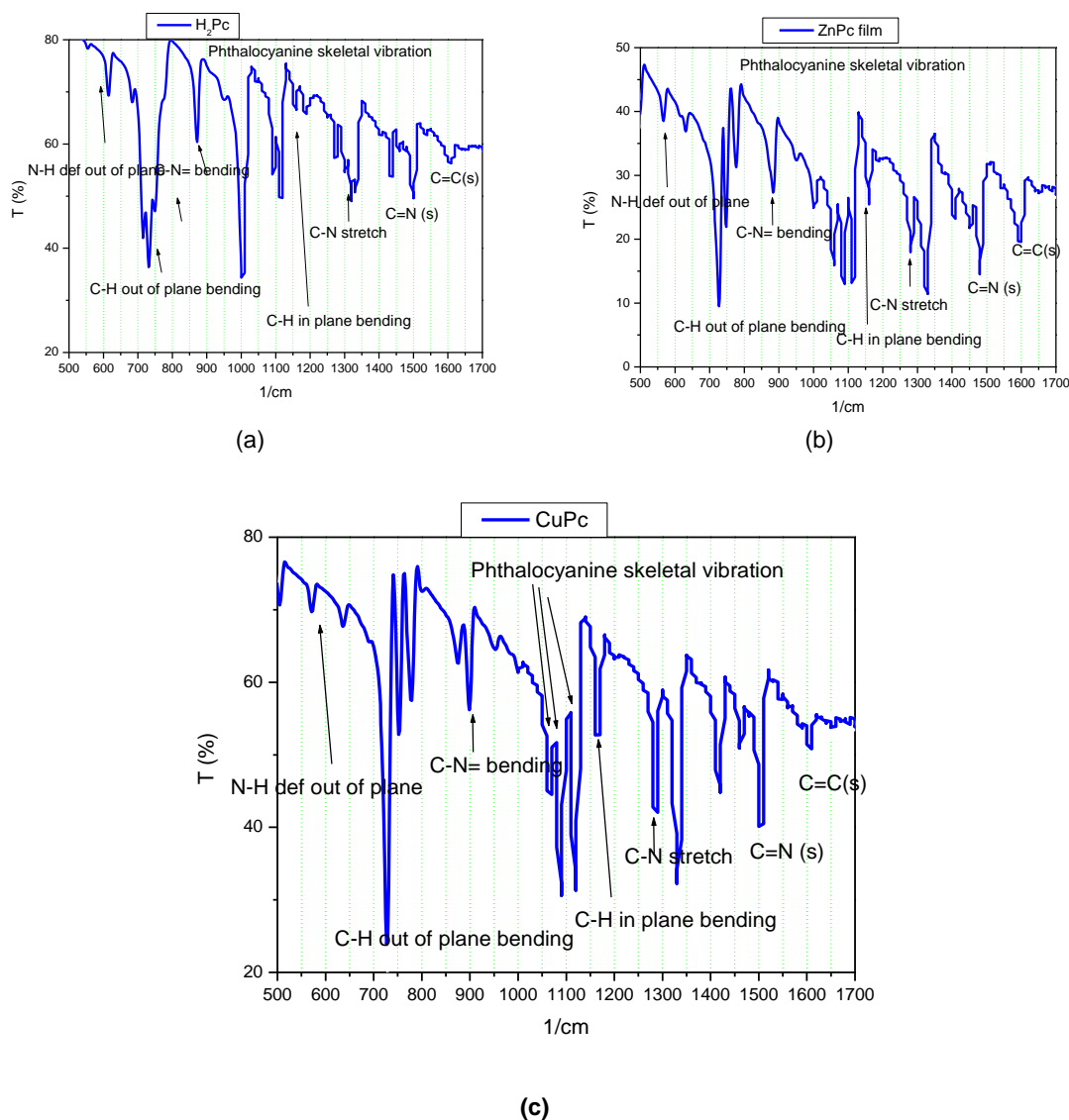


Fig. 2: FTIR spectra of (a) H₂Pc, (b) ZnPc and (c) CuPc

The shift is systematically to the higher frequencies in the sequence of the phthalocyanines: $\nu(\text{Zn}) < \nu(\text{Cu})$. The spectrum of the metal-free pigment differs in some respects from that of the metal-containing ones. This shows that the introduction of a central metal atom affects the whole array of the bonds in the organic part of the molecule. The spectrum of the metal-free phthalocyanine possesses a narrow absorption maximum at 3298 cm^{-1} ($30,300 \text{ \AA}$) belonging to the NH frequency of two such bands at the N atoms of the pyrrole rings.

The position of this maximum is a normal one, as is the case for an imino or amino group and does not suggest the presence of two protons shared in common by all the four nitrogen atoms of the central ring [11]. For IR spectra we sublimed all Pcs and then formed palates with KBr powder. The FTIR measurements were done with the help of "Nicolet 5100 FTIR" instrument. The spectra of H₂Pc, ZnPc and CuPc are shown below in Fig.2. (a), (b) and (c).

The region 1500 cm^{-1} to 4000 cm^{-1} remain same for all the Pcs, Effect of metal substitution in Pcs is visible in finger print region 500 cm^{-1} to 1700 cm^{-1} therefore only this region is given attention for discussion. From ZnPc to CuPc all the vibrations shifts towards higher energy vibration. Results are

shown in Table 1 below.

Table 1: Correlation FTIR absorption Table of H₂Pc, ZnPc and CuPc

Type of band	H ₂ Pc (1/cm)	ZnPc (1/cm)	CuPc (1/cm)
C=C (s)	1604	1597	1605
C=N (s)	1497	1480	1505
C-N (s)	1277	1277	1283
C-H(in plane)	1157	1159	1163
C-N= (bending)	872	882	901
C-H (out of plane)	751, 731, 712	773, 748, 725	778, 751, 730
N-H (out of plane)	612	565	569

The metal phthalocyanines have elicited considerable interest concerning the nature of the chemical bonding between the central metal atom and the great organic ring structure surrounding it. In particular, attention has been given to the bonding of the central metal atom to the surrounding four nitrogen atoms which form the corners of a square. Two types of bonding are possible: electrovalent and covalent. The electrovalent bond is characterized by its ionic character and relative weakness. For example, atoms forming an ionic bond do readily separate into cations and anions in an aqueous media. The covalent bond is known for its non-ionic character and relative strength. In electrovalent bonding, the electropositive atom readily donates an electron to the electronegative atom. In covalent bonding both the electrons involved in the bonding are tightly held and are shared in common by the atoms involved. An extension of the covalent bond is the coordinate covalent bond in which both electrons forming the covalent bond are donated by only one of the atoms involved. In addition to bivalent CuPc, bivalent ZnPc may be considered to be covalent salts [12]. The fact that ZnPc is held by lower covalencies, than CuPc as suggested by with Fajans principle, according to which "in the same periodic group of metals the tendency to form covalent compounds decreases with rise in atomic number". It is also of interest that, where comparison is possible between pairs of metals in the same group, a metal of higher atomic number enters the phthalocyanine complex more reluctantly and leaves it more readily. Still another criterion by which to discriminate between covalent and electrovalent bonding is the diameter of the metal atom. Generally the metals whose diameters are approximate the dimensions of the square gap between the four isoindole nitrogen atoms, form stable or covalent bonds. However, the metals of the diameters larger or smaller than the central void tend to form electrovalent bonds [12].

Conclusion

Organic semiconductor comes under the category of soft materials. Formation of OSCs from organic semiconductors is a multi step process. When organic semiconductors undergo via different steps from powder form to complicated layer by layer structures most of the properties of these materials get changed and obtained performance of OSCs is not only because of the bulk properties of these materials but a combined effect of all layers. The performance of OSCs also depends on the changes which generates at the time of device formation and because of the device structure.

Cu metal atom has one less electron than Zn atom, except this thing all the entire structure of CuPc and ZnPc are same. By UV-Visible absorption and IR-Spectroscopy we are able to see the difference in absorption and structural properties between these materials. Both materials are good absorber of solar spectrum in UV-visible range, and are good candidate for solar cell applications. By IR spectroscopy we observe that CuPc require high energy for transition which indicate more covalent character in CuPc than ZnPc.

Acknowledgment

I did this experimental work at NPL New Delhi, when I was doing my Ph.D. This work develops understanding for fundamental properties of Phthalocyanine and their impact on physics behind the working of OPV devices. I would like to pay my heartfelt gratitude to my supervisor Dr. S. Chand for their kind help and support. I heartily thank him for providing me the facilities and a healthy working environment at NPL

References

1. R. P. Linstead, *Brit. Assoc. Advance. Sci., Rep.*, 465-6 (1933).
2. A. Braun, J. Tchermiac, *Ber. Deut. Chem. Ges.* **40**, 2709 (1907).
3. A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.* **7**, 27 (1965).

4. M. K. Engel, *Report Kawamura Inst. Chem. Res.* (1996).
5. R. P. Linstead, *J. Am. Chem. Soc.* **56**, 1016(1934). (b) R. P. Linstead, A. R. Lowe, *J. Am. Chem. Soc.*, **56**, 1022 (1934).
6. J. M. Robertson, *J. Chem. Soc.*, **57**, 615 (1935). (b) J. M. Robertson, *J. Chem. Soc.*, **58**, 1195 (1936). (c) J. M. Robertson, T. Woodward, *J. Chem. Soc.*, **59**, 219 (1937).
7. F. H. Moser, A. L. Thomas, "*The phthalocyanine – properties*", Vol. 1, CRC Press: Florida, (1983), (b) F. H. Moser, A. L. Thomas, "*The Phthalocyanines – Manufacture and Applications*" Vol. 2, CRC Press: Florida, (1983),.
8. C. C. Leznoff, A. B. P. Lever, "*Phthalocyanines: Properties and Applications*", Vol. 1-4, Eds.VCH: New York, (1989-1996),.
9. N. B. McKeown, "*Phthalocyanine Materials: Synthesis, Structure and Function*", CambridgeUniversity Press: New York, (1998).
10. (a) R. O. Loutfy, A. M. Hor, C. K. Hsiao, G. Baranyi, P. Kazmaier, *Pure Appl. Chem.* **60**, 1047 (1988). (b) O. Stenzel, A. Stendal, K. Voigsberger, C. Borczykowski. *Sol. Energy Mater. Sol. Cells*, **37**, 337 (1995).
11. A. N.Terenin, A. N. Sidorov, *Spectochim. Acta Suppl.*, 573 (1957).
12. P. A. Barrett, C. E. Dent, R. P. Linstead, *J. Chem. Soc.* **382**,1719 (1936).

