Alternative Current Electrical Conductivity of Octaphynyl Tetrapyrazino Porphrazine Zinc

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Abstract. The alternative current (Ac) conductivity of octaphynyl tetrapyrazino porphrazine Zinc (opTpPzZn) was measured in the frequency rate of 5 X 10^3 to 5 X 10^3 Hz of and temperature rate (303 to 423)K. The dc conductivity was carry out in the same temperature range, which consists of frequency independent (Dc conductivity) and frequency dependent part. This type of conductivity results from hopping of cargo carriers between localized sites around Fermi levels. The jump position is indication of the degree of imperfection in the crystal. of crystallation degree . The number of the jump position was calculated using Webb and William equation which is estimated to be 1 x 10^20 ev^-1 cm^-3.

1. Introduction

Studies of temperature dependence of the electrical conductivity of some compounds show an agreement with Arrhenius behavior, can be clarified as the result of the presence of states in the band gap (about Fermi level). According to which most of the conductivity is a consequence of the trapping of the hole and its polarization, which was effected by the frequency of the field and affected the temperature. AC conductivity measurements assumed the existence of localized sites between which electrons may hope. in response to the alternating field. The hoping conduction is frequency dependent. The sample which show significant crystal distortion or disorder (trapped holes), show a significant frequency depend on conductivity in addition to the frequency independent. that makes an assumption of both hole and electron motilities and their temperature dependence. Such behavior has been in many compounds, including Phthalocyanines and polymers. In this work, Tetrapyrazino porphrazine Zinc (OpTpPzZn) was prepared and its dc and ac electrical conductivity were studied.

2. Preparation of the Compounds

2.1 Synthesis of (2, 3-Dicyano-5,6-Diphenyl Pyrazine)(DCP)

1 gm (4.7x 10^-5 mole) of Benzil was dissolved in 25 ml of ethanol and 25 drop of concentrated acetic acid and added to a round bottomed flask containing 0.5 gm (4.6 x 10^-3 mole) of diaminomalonitrile (DAMN) dissolved in 25 ml of ethanol. The mixture then refluxed for 4 hours and the reaction mixture was left for 2 days to be precipitated. The solid product then filtered and the product was pale brown solid which is then recrystallized from 1 : 1 mixture of hexanol. The yield was 75%, mp (250-251 C°). The reaction equation is shown in figure 1.
2.2 Synthesis of Octaphenyl Tetrapyrazino Porphrazine zinc\(^{(8)}\) (OpPzZn)

5.85gm(0.04 mole) of DCP 1.6lgm(0.01 mole) of dihydrated zinc dichloride\((\text{ZnCl}_2\).6\(\text{H}_2\text{O}\)), 10gm of urea, and 0.01 gm of Ammonium Molybdate dissolved in 5ml of quinolone. The reaction mixture then refluxed for 5 hours. The precipitate then filtered to dissolve the impurities. The solid then dried at 110°C. The product is dark blue solid decomposes at about 285°C. The yield is 51.5%. The preparation is shown in figure 2.

3. Results and Discussion

CHN \((\text{C}_{72}\text{H}_{40}\text{N}_{16}\text{Zn})\) calculated C:72.78%, H:3.36%, N: 18.87%, found: C:72.60, H:3.20, N:17.99.

IR: The disappearance of the nitrile peak at 2240 cm\(^{-1}\) and the carbonyl group at 1700 cm\(^{-1}\) and the band around 3100 is due to C-H aromatic stretching are the characteristic IR spectrum of Octaphenyl Tetrapyrazino porphrazine, the width of the around 3400 cm\(^{-1}\) might be due to moisture. The peak at 1640 cm\(^{-1}\) is due to the C=N stretching\(^{(9)}\) Figure 3
Figure 3: IR Spectrum of TpPzZn (KBr Disc)

The electronic spectra of the complexes, Octaphenyl Tetrapyrazino Porphazine zinc, shows the characteristic (Soret band) at 353 nm and, due to \( \pi^* - \pi \) and \( n - \pi^* \) transitions, and Q band at 680.5 nm, which is metal atom due to \( \pi^* - \pi \) and weak d-d transition of the central metal atom hidden inside the Q-band\(^{10}\), with an extinction coefficient \( (\varepsilon) 1.3 \times 10^4 \text{ L.mol}^{-1} \text{ cm}^{-1} \). The solvent DMSO was used to prevent or reduce aggregation of the complex molecules.

Figure 4: The electronic spectrum TpPzZn

4. Electrical Properties

Preparation of the samples

The samples were casted as sandwich cells on fluorine doped tin oxide (FTO) glass substrate which is conducting from one side with 1cm² surface area. The thickness of the casted film is 0.45 mm and then the cell constant is \( 10^{-3} \text{ cm}^{-1} \). The sample cell is put in cryostat which is supplied with variable heating element.
and cell electrode holder and voltage supply. The cryostat is connected to voltmeter and ammeter\(^{(11)}\) to measure the voltage and the current. The temperature was measured using copper-constantan thermocouple placed near the sample. The dc electrical conductivity measurement were carried out in the temperature range of (303-423) K and at 3 volts. The Ac electrical measurement were measured in the frequency range (5 -50) KHz and temperature range of(303 - 423) K. The ac electrical conductivity was measured using 4800A vector impedance. The I/V characteristic curve study for the complex (OpTpPzZn) , in the voltage range 0-10 volts and 30°C shows an ohmic relation especially at lower voltages where there is no space charge limited current.

Figure 5: I/V Curve at different Temperature for (OpTpPzZn) The electronic spectrum TpPzZn

Figure 5 shows the relation between log conductivity (log\(\sigma\)) and log angular frequency (log \(\omega\)) and different temperatures for the complex. where \(\omega\) is the angular frequency (2\(\pi\)f), and f is in hertz. The figure shows the increase of ac conductivity with frequency and temperature. Figure 6 shows the variation of log conductivity with inverse temperature at different frequencies for both dc conductivity at different frequencies. It shows that the measured ac conductivity is higher than dc conductivity, and dc conductivity, is approaching the ac conductivity at lower frequency. The ac conductivity increases with increasing temperature and frequency.

The measurement shows that the measured conductivity (\(\sigma_T\)) contains ac and dc conductivities \(^{(2,11)}\).

\[
\sigma_T = \sigma_{dc} + \sigma_{ac}
\]

Where \(\sigma = \omega \ n\) (varies with frequency \(n\) is constant), and \(\sigma_{dc}\) follows Arrhenius equation,

\[
\sigma_{dc} = \sigma_0 \ e^{\Delta E/\kappa T}
\]

Figure 7, shows the variation of \(\log\) Capacitance (\(\log\ C\)) with \(\log\ \omega\) in Hertz. The figure shows the increase of the capacitance with temperature and decreases with frequency. Which tend to approach common value.

Figure 8, shows the variation of \(\log\ (C_{\infty}-C)\) with \(\ln\ \omega\) at different temperature according to Kramer Kronig relation\(^{(3,5)}\),

\[
C = C_{\infty} + A \ \omega^{n-1}
\]

Where C is the capacitance at any frequency and \(C_{\infty}\) the capacitance at infinity (which means at common value of capacities) which is assumed to be at 105 Hz. A and n are constants. using Mott and Davis equation\(^{(12,13)}\),

\[
\sigma_{ac} = \frac{4\pi}{3} (\ln 2) e^2 K T N(E_F)^2 \alpha^{-5} [\ln \frac{\nu F}{\omega}]^4 \omega
\]
N(Ef), the number of energy states around Fermi level, is estimated to be $9.6 \times 10^{19}$ ev$^{-1}$ cm$^{-1}$ where charge of electron is $4.8 \times 10^{-10}$ e.s.u. $k$ is $8.617 \times 10^{-5}$ ev/k. $T$ is taken as 303 K, $a$ is the reciprocal inter planner spacing which is calculated from X-ray diffraction with Cu as anode and CuKα of wavelength of 1.5406 (Figure 9, $2\theta=240$) $\omega_{ph}$ is the phonon frequency taken as 1012 Hz and $\omega$ is taken as 5 kHz.\(^{(14,15)}\)

![Figure 6](image1.png)

**Figure 6:** Relation between $\log \sigma$ and $10g \omega$ at different Temperature for OpTnPzZn

![Figure 7](image2.png)

**Figure 7:** The Relation between $\log C$ and $10g \omega$ at different Temperature for OpTnPzZn

![Figure 8](image3.png)

**Figure 8:** Relation between $\log(C_{00-c})$ and $10g \omega$ at different Temperature for OpTnPzZn
Conclusions
A sandwich thin film of Tetrapyrazino Porphrazine Zn acts as a semiconductor. Ac conductivity increases with frequency and temperature and its Capacitance decreases with both Frequency and Temperature. The number of energy states around Fermi level is estimated to be $7.6 \times 10^{18}$ ev$^{-1}$ cm$^{-3}$.

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