

SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF BRIDGED TETRAPYRAZINO PORPHRAZINE IRON (II)

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ABSTRACT

Abridged complex structure of Tetrapyrazinoporphrazine, PzFe (II) with 1, 4-dicyanobenzene was prepared. The study shows that the complex has the structure (PzFeDCN) n . It is analyzed by elemental analysis and spectroscopic methods (IR, Uv-Visible and $^1\text{H NMR}$) in addition to the thermo gravimetric method and X- ray diffraction method. The dc electrical conductivity measurements show that the complex has a semiconducting behavior with activation energy of 1.12 eV compared with the activation energy of PzFe which is 0.9 eV which could be related to the PzFe plane separation in the bridged complex..

KEYWORDS: Bridged Tetrapyrazino Porphrazine, Dc Electrical Conductivity

INTRODUCTION

Tetrapyrazinoporphrazines (Pz, PcM) are semiphthalocyanine compound have two nitrogen atoms at equivalent 1,4 positions of the phthalocyanine benzene rings(1). Due to the additional nitrogen atoms, Pz is less electron rich than the corresponding phthalocyanine (2). Both Pc and Pz have remarkable thermal and chemical stability and advantageous optical, absorption and emission properties and have many applications such as photodynamic therapy (PDT), organic solar cells, chemical sensors (3, 4). Bridging of phthalocyanines and tetrapyrazinoporphrazines with different bridging ligands is well known, such as bridging with Fluorine atoms, bipyridine, CN, groups which effect solubility, aggregation, optical and electrical properties (5-11).

In this work we prepared a complex of tetrapyrazinoporphrazine Iron (II) and bridged with 1, 4-dicyanobenzene. The complex then identified by spectroscopic methods, thermal and X-ray diffraction and studies the effect of bridging on the electrical properties.

PREPARATION OF THE COMPOUNDS

1- Preparation of Dicyanopyrazine, DCP ⁽¹²⁾

A mixture of 2.18mmol(1ml) of Glyoxal, 25 ml ethanol and 25 drops of acetic acid was added to a conical flask containing 2.36g of diaminimalonitrile (DAMN) soluble in 25 ml of ethanol. The reaction mixture then refluxed for 4 hours and then left for two days to precipitate the solid product which then filtered and recrystallized from 1:1 mixture of acetone/ hexanol. The product is pale yellow crystalline material mp (222-225 0C), (yield is 1.6g, 56.1%). CHN, calculated (C₆H₂N₄): C: 55.33, H: 1.53, N: 43.24 Found C: 54.48, H: 1.26, N: 42.24.

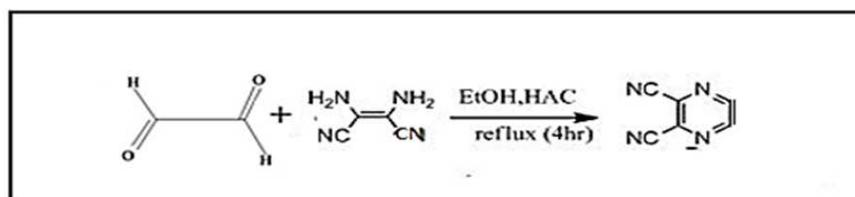


Figure 1: Preparation of DCP

2- Preparation of Tetrapyrazinoporphrazine Iron (11), PzFe:

0.52 g (4mmole) of DCP was dissolved in 100 ml flask containing of 0.278g (1mmole) of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.24g (4 mmole) of Urea. The mixture then refluxed with magnetic stirring for two hours and then cooled to room temperature and filtered (13). The solid product then purified and by dissolving it in 2 ml of chloroform and added drop wise with stirring to 100 ml of ethanol. The purification process was repeated for three times and the solid product was dried at 100°C.

The product is pale bronze powder, mp (254-257). Yield is 0.46g (58.44%). CHN, calculated ($\text{C}_{24}\text{H}_8\text{N}_{16}$): C: 50.01, H: 1.40, N: 38.90; Found C: 49.35, H: 1.35, N: 35.40.

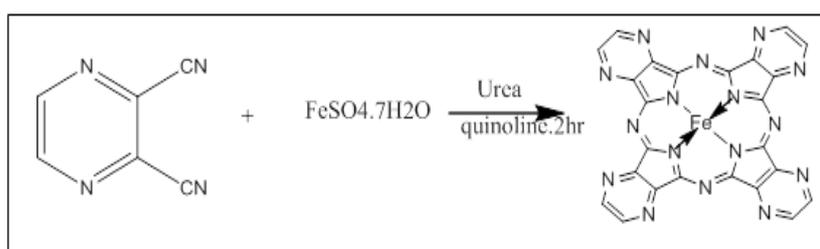


Figure 2: Preparation of PzFe

3- Preparation of Tetrapyrazinoporphrazine Iron (11) Bridged with p- Dicyano benzene (PzFeDCB)n:

0.128g (1mmole) of 1, 4- dicyano benzene was added to a round bottomed flask containing 0.576g in 10 ml of ethanol. The mixture then refluxed for a week and cooled and purified by dissolving it with 2ml of THF and added portion wise with stirring to a beaker containing 100 ml of hexane. The precipitate then filtered and dried at 100 °C. The product is dark bronze powder. The yield is 0.48g (36.09%). CHN, calculated ($\text{C}_{56}\text{H}_{20}\text{N}_{34}\text{Fe}_2$) C: 54.54, H: 1.57, N: 37.19; Found C: 52.66, H: 1.4, N: 36.5

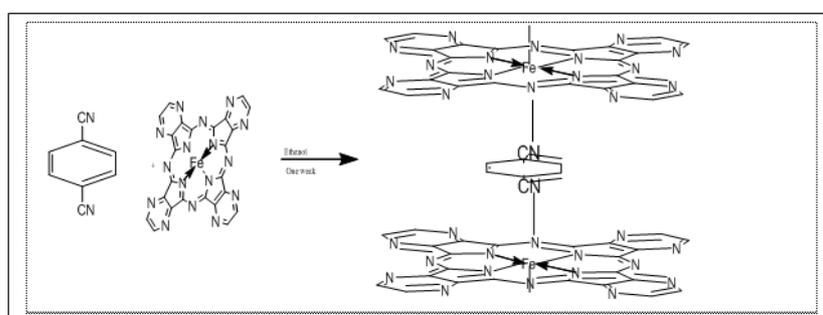


Figure 3: Preparation of (PzFeDCB) n

IDENTIFICATIONS OF THE COMPOUNDS

The little differences between the calculated and experimental values are due to mainly that the molecules are big and the difficulty of the purification.

Spectroscopic Identification: a-

IR: Figure (4), shows the IR spectrum of the complex PzFe. It shows the distinctive aromatic C-H stretching vibration at 3193 cm⁻¹ and aromatic C-H bending in plane 1037 cm⁻¹ and out of plane at 769 cm⁻¹. The band at 1635 cm⁻¹ stretching

Vibration for C=N band. The stretching vibration at 1498 cm⁻¹ is related to the aromatic C=C. The stretching of the C=N bands for both pyrrole and pyrazine mix strongly to form a wide band. Due to the moisture a wide band is appeared (14, 15).

Figure (5), shows the IR spectrum of the bridged complex of PzFe with DCN. It shows a band at 2250 cm⁻¹ which it attributed to the C≡C of the cyanide of DCB Bridge (15).

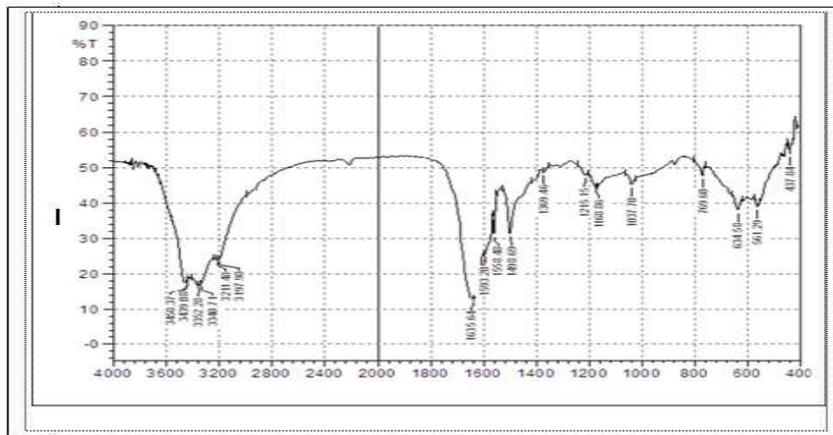


Figure 4: IR Spectrum of the Complex PzFe

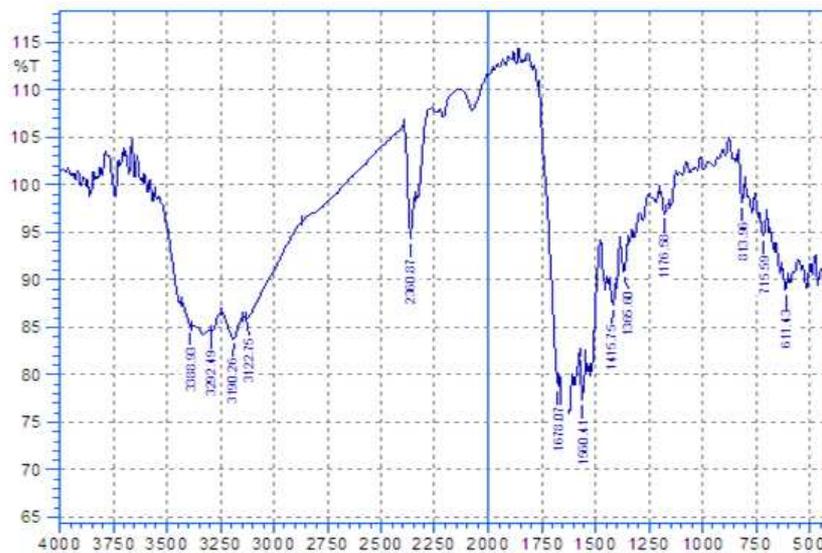


Figure 5: IR Spectrum of (PzFeDCB) n

¹H-NMR: Figures (6) and (7) show the ¹H-NMR spectra of the complex PzFe and its bridged structure with DCB in DMSO. Figure(6) Shows a chemical shift at 8.3 ppm which is attributed to the protons of the pyrazine rings in the complex while figure(7) shows two chemical shift values at 7.9 and 8.5 ppm which are attributed to the protons of the benzene ring and the protons of the pyrazine rings respectively. The protons of the DMSO and the moisture show two chemical shifts at 3.75 and 2.48 ppm respectively (15).

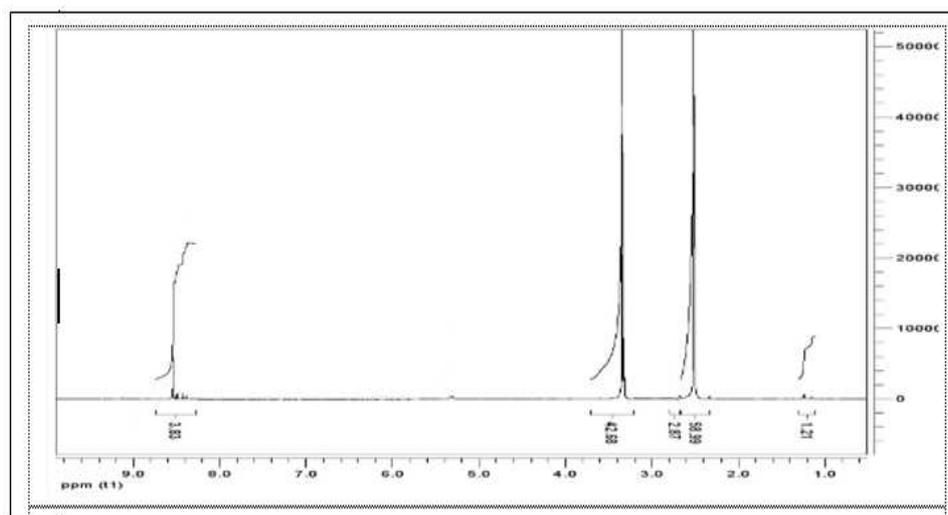


Figure 6: The ¹H-NMR Spectrum of PzFe

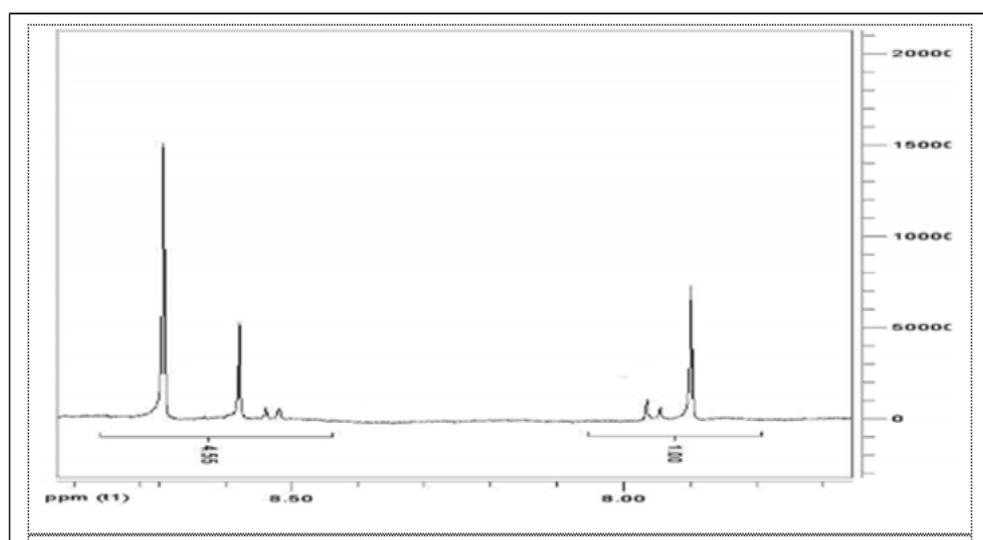


Figure 7: The ¹H-NMR Spectrum of the Complex PzFe with DCB

THE ELECTRONIC SPECTRA

Figures (8) and (9) show the electronic spectra of the complex PzFe and its bridged structure with the DCB. Figure (8) shows at the Q-band at 650 nm ($\epsilon = 0.45 \times 10^5 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$) and the Soret 330nm ($\epsilon = 0.81 \times 10^5 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$), while figure (9) shows the Q band at 635 nm ($\epsilon = 0.82 \times 10^5 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$) and the Soret band at 355 nm ($\epsilon = 0.43 \times 10^5 \text{ l.mol}^{-1} \cdot \text{cm}^{-1}$) (16, 17).

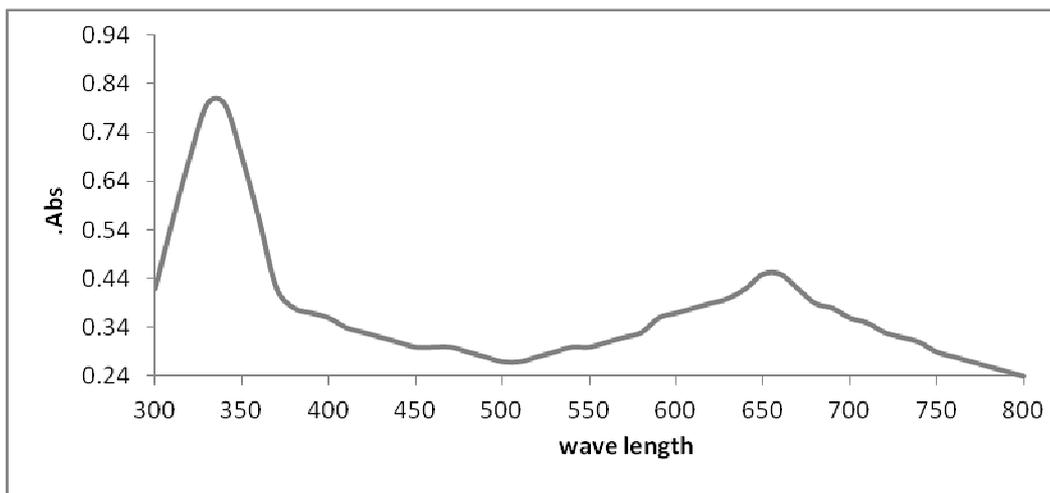


Figure 8: the Electronic Spectrum of the Complex, PzFe

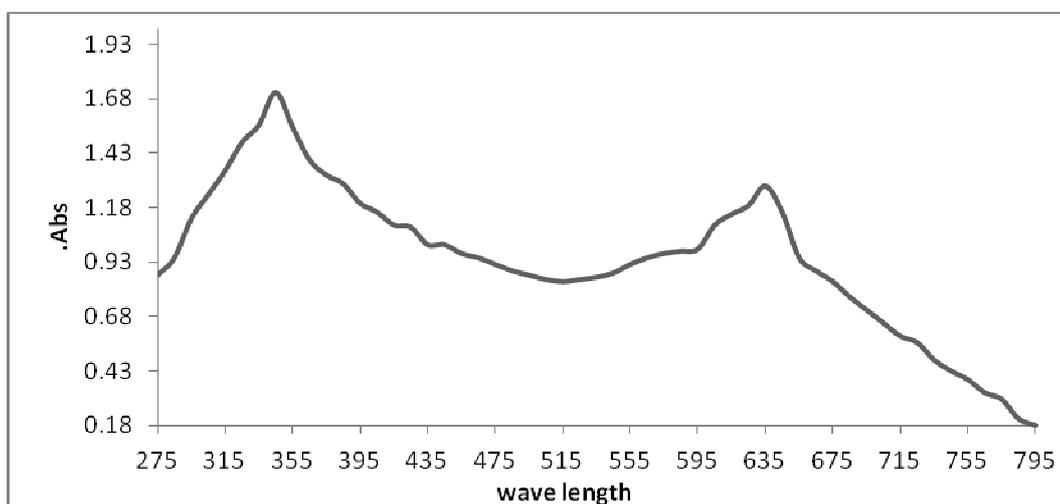


Figure 9: the Electronic Spectrum of the Complex Bridged with DCB

B- THERMO GRAVIMETRIC ANALYSIS

Thermo gram in figure(10) shows three steps of the weight loss of PzFe complex: 1- At (64_158)0C and Tmax at 125.550C with percent loss 4.9% (calculated 5.8%) which refers to the loss of water molecule(18,19). 2- At 181-2940C with Tmax at 285.300C and percent loss of 14.01%(calculate 13.36%) which refers to the loss of ethylenediamine and ammonia molecules.3- At 305-6600C with Tmax at 585.360C and percent loss of 35.77%(calculate 36.07%) which refers to the loss of three molecules of ethylene diamine.

Figure (11) shows a thermo gram of the complex of (PzFeDCB)_n. It shows three steps of the weight loss of the bridged complex:1- At (64_150)0C and Tmax at 107.120C with percent loss 1.66% (calculated 1.38%) which refers to the loss of water molecule(18,19). 2- At 186-3430C with Tmax at 291.450C and 322.170C and percent loss of 6.26% (calculate 6.01%) which refers to the loss of ethylenediamine and ammonia molecules. 3- At 349-6540C with Tmax at 584.330C and percent loss of 13.39% (calculate 13.467%) which refers to the loss of two molecules of ammonia molecule and a molecule of 1-4 dicyanobenzene.

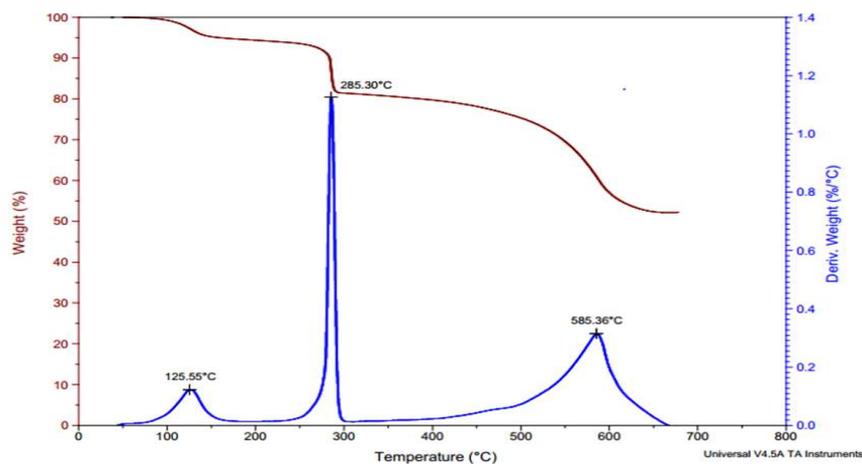


Figure 10: Thermogram of PzFe

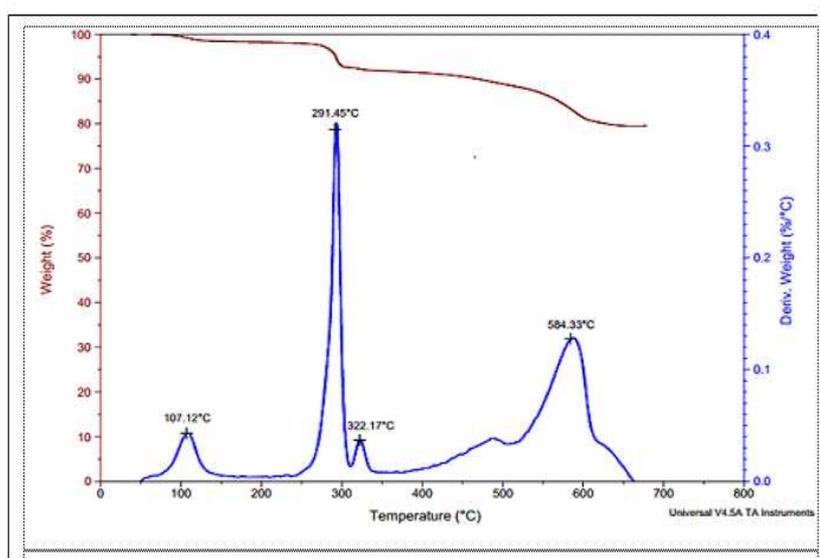


Figure 11: Thermogram of (PzFeDCB) n

C- X-RAY DIFFRACTION ANALYSIS

Figures (12) show the X-ray diffraction of PzFe using $\text{CuK}\alpha$ (1.5406\AA) as X-ray energy source and using powder method. The estimated d-spacing is 3.27\AA ($2\theta=27.25$) with relative intensity 100% and 4.49\AA ($2\theta=19.8$) with relative intensity 33.79% and 6.76\AA ($2\theta=13.1$) with relative intensity of 11.13%. The d-spacing is calculated using Bragg's law (20). Figure (12) shows the X-ray diffraction of (PzFeDCB). The estimated d-spacing is 5.8\AA ($2\theta=15.27$) with relative intensity 100% and d-spacing 3.33\AA ($2\theta=26.71$) and relative intensity of 70.1%.

The main d-spacing of 100% intensity for both compounds shows that the bridged compound has bigger d-spacing which is the bigger separation between the two parallel PzFe planes in the bridged complex.

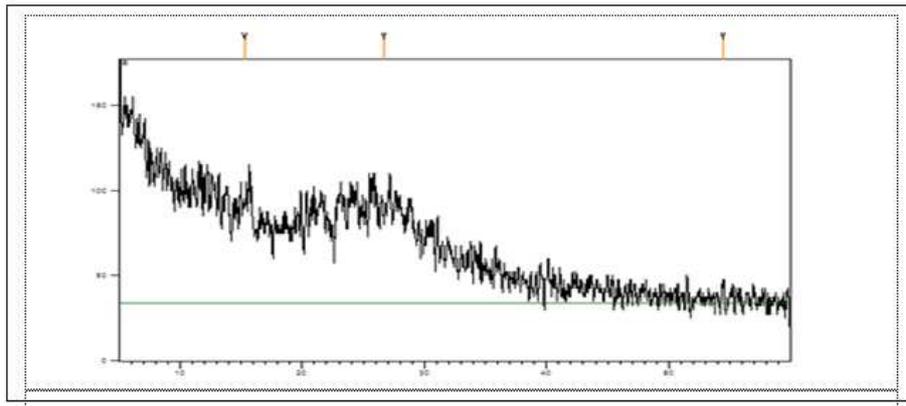


Figure 12: The x- Ray Diffraction of PzFe

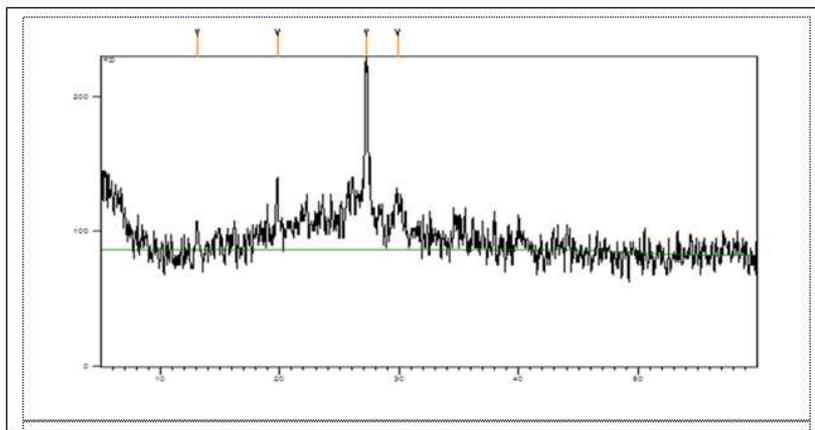


Figure 13: X-Ray Diffraction of (PzFeDCB) n

D-ELECTRICAL PROPERTIES

The dc electrical properties were measured using a system containing a cryostat, power supply, voltmeter, ammeter and temperature measurement system. The cryostat contains a tube in which the sample is inserted and connected to conducting wires. The tube can be evacuated and heated. The temperature is measured by a thermocouple. The sample is a surface film casted on a glass substrate. The conductivity was measured under a vacuum of 10⁻⁴ torr. Figure (14) shows the V-I characteristic curves at different temperatures. It shows a clear ohmic relation in the first 10 volts.

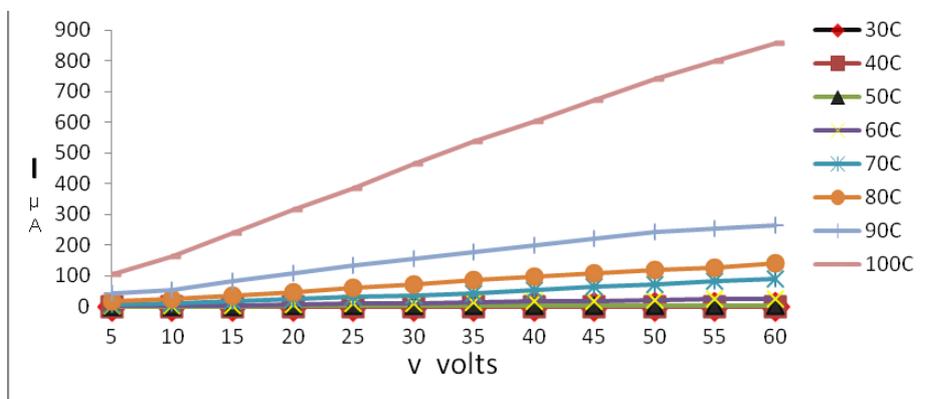


Figure 14: The V-I Characteristic Curve for (PzFeDCB) n (I Current, μ A)

Figure (15) shows the relation between the dc conductivity ($\ln \sigma$) and the inverse temperature, at 10 Volts, according to Arrhenius question ($\ln \sigma = \ln \sigma_0 - \frac{\Delta E}{kT}$) where $\sigma_0, \Delta E, k$ and T are the pre-exponential factor, activation energy, Boltzmann constant and absolute temperature respectively (21). The activation energy between valence and conduction bands was estimated from the slop to be 1.12 eV compared to the activation energy estimated for PzFe which is equal to 0.9 eV (22). The higher activation energy of the bridged complex might be due to the wider separation between the PzFe complex planes in compared to the stacked structure of the PzFe (9).

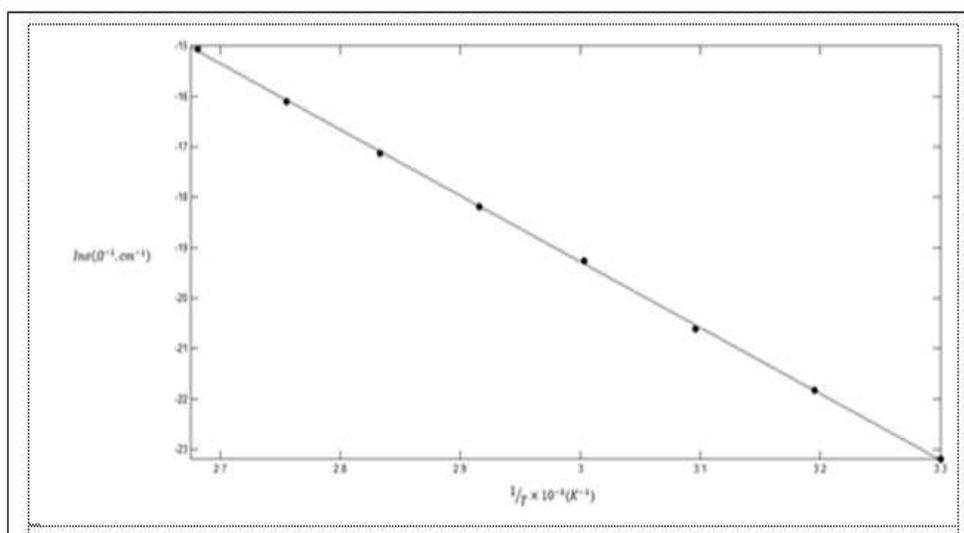


Figure 15: The Relation between and Inverse Temperature for the Complex (PzFeDCB) n

CONCLUSIONS

From the study we can conclude that the prepared complex is of the bridged structure (PzFeDCB) n and behaves as semiconductor.

REFERENCES

1. K. M. Kadish, K. M. Smith, R. Guilard; "The Porphrazine handbook" Vol. 1- 10 San Diego, Academic Press, 2000.
2. J. Kim, Jae Yan Jaung and Heejoon Ahn; Macromolecular research, 16(4), 367(2008).
3. S. V. Kudrevich, M. G. Galpern, J. E. van lier" Synthesis, 779 (1994).
4. F. H. Moser and A. L. Thomas;"The phthalocyanines" Vol.1 and 2 CRC press Boca Raton (1983).
5. Eva. H Morkved, Lars T. Thomas, Helge Kjosjen and George Hvistendhal: Acta Chemica Scandinaviah, 50, 1153(1996).
6. B. Keskin and y. Koseoglu; polyhedron, 27, 1155(2008).
7. S. D. kocak and E. Conca; J. fluorine chem., 131, 1322 (2010).
8. E. Gonea; Inorg. Chem. commum, 8, 343(2005).

9. J. P. Linsky and T. R. Paul; *Inorg. Chem*, 19, 3131 (1980)
10. M. Casstevents M. Samok and J. P. fleyer; *J. chem. phys.* 92, 2019(1990).
11. M. S. Rodrigues and P.A. Stuzhin; *Journal of porphyrans and phthalocyanines*, 8, 129(2004).
12. P. A. Barrett, C. E. Dent, and, R. P. Linstead; *J. chem. Soc*, 14, 1719 (1936).
13. Nazar A. Hussein and Hassan S. Jabore, *International Journal of Chemical and Petrochemical Technology*, 5(1), 1, 2015.
14. A. S.T. Al Salami, "M.Sc. Thesis", University of Basrah, Iraq (2009).
15. R. M. Silverstein and F.X-Webster, "Spectroscopic Identification of Organic Compounds", 6th Ed, John Wiley and Sons, Inc., New York (1996).
16. J. Simon and J. J. Andr'e;"Organic Semiconductors" John and Willy, London (1985).
17. M. Kostka, P. Zimcik, M. Miletin, P. Klemra, K. Kopecky and Z. Musil, *J. Photochemistry and Photobiology A: Chem.*, 178, 16 (2006).
18. Aida. L. El-Ansay and Nora. S. Abdel-Kader: *Int. J. Inorg. Chem.*, Article ID 901415 (2012).
19. G.G. Mohamed; M. M. Omer and A. M. Hindy, *Turk.J.chem.* 30, pp.361-382 (2006).
20. M. Bouvet, E. Lukyanets and J. Simon: *J .porphyrins and phthalocyanines*, 3, 501(2001).
21. J. B. Webb and D. F. Williams, *J. Physic: Solid State phys*, 12, 3173 (1979).
22. Hassan S. Jabur, PhD thesis, Basrah University, Iraq (2015)

