

DC ELECTRICAL CONDUCTIVITY OF IODINE DOPED OF BRIDGED TETRAPYRAZINOPORPHRAZINEVANADYL OXIDE

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ABSTRACT

A bridged compound from TetrapyrazinoporphrazineVanadyloxide and p- Dicyanobenzene was synthesized. A thin surface film from the bridged compound and the complex were cast on a glass substrate and its dc electrical conductivity was measured. The two thin surface films from the two complexes were doped with Iodine vapour for one night. The excess iodine was removed by heating at 110 °C for one hour and their dc electrical conductivity were measured and compared. The electrical measurement shows that the iodine doped thin film have higher conductivity than the undoped due to the oxidation of the complex by the Iodine. The bridged complex with p-Dicyano benzene has lower dc conductivity than the unbridged, which could be attributed to the separation gap between the ring groups by p-Dicyanobenzene.

KEYWORDS: Tetrapyrazinoporphrazinevanadyl Oxide, Its Bridged Complex, Iodine doping and electrical Properties

INTRODUCTION

Tetrapyrazinoporphrazine (Pz) which is also calledazaphthalocyanines (AzaPc) ⁽¹⁾, have investigated intensively in many directions due to their potential applications as biomedical agents, chemical sensors, liquid crystals and non-linear optical materials (2, 3).

The increasing attention of the phthalocyanines and semiphthalocyanines due to strong correlation between the nature of the electronic and optical properties of the macro cyclic ring system and the substituents (peripheral and central metallic elements) ⁽²⁾.

The Azaphthalocyanines show good solubility in organic solvent compared to phthalocyaninecomplexes ⁽⁴⁾. In an another hand, and due to the extended π -conjugated system in phthalocyanine and Azaphthalocyanines, they exhibit a high tendency for aggregation, which causes the decrease of solubility and difficulty of purification, characterization, broadening of Q-band and the low ability to generate the singlet oxygen which is the active agent in photodynamic therapy(PDT)⁽⁵⁾. The dc electrical studies show its semiconducting properties.

Doping of phthalocyanines and semiphthalocyanines is well known as a mean of decreasing of resistance. Doping could be carried out by many doping agents such as halogens, quinones and their derivatives ⁽⁶⁾, AsF₅⁽⁶⁾, XeF₂⁽⁷⁾ and others ⁽⁸⁾. Pressed pellets of Fluorine bridged phthalocyanines doped withnitrosonium salts have conductivities as high as 10 ohm⁻¹. cm⁻¹⁽⁹⁾.

In this work a bridged complex of Tetrapyrazinoporphrazinesvanadyl oxide (PzVO) was with p- dicyanobenzene was prepared and doped with Iodineotherand characterized by CHN analysis, IR, and UV- Visible spectroscopy. Their dc electrical conductivities were measured.

PREPARATION OF THE COMPOUNDS

Preparation of Dicyanopyrazine⁽¹⁰⁾, DCP

A mixture of 1 ml (2.18 mmol) of Glyoxal, 2ml ethanol and 25 drops acetic acid was added to generate a flask containing 2.36 g (0.0218 mol) of Diamino Photodynamic (DAMN) dissolved in 25 ml of ethanol. The reaction mixture was refluxed for four hours and then left for two days. The solid precipitate was filtered and recrystallized from (1:1) mixture of Hexane and Acetone and filtered again. The product is a pale yellow crystalline solid with a yield of 1.6 grams (56.21%). MP: 133-135°C. CHN, calculated (C₆H₂N₄): C: 55.33, H: 1.53, N: 43.24 Found C: 54.48, H: 1.26, N: 42.24. The preparation reaction is shown in Figure 1.

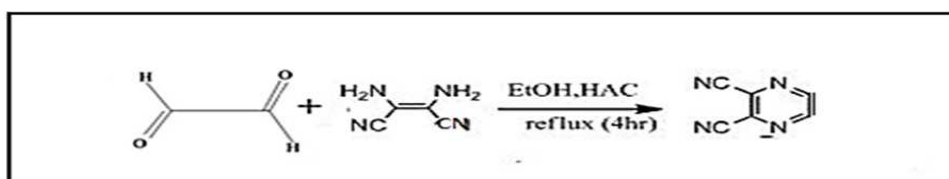
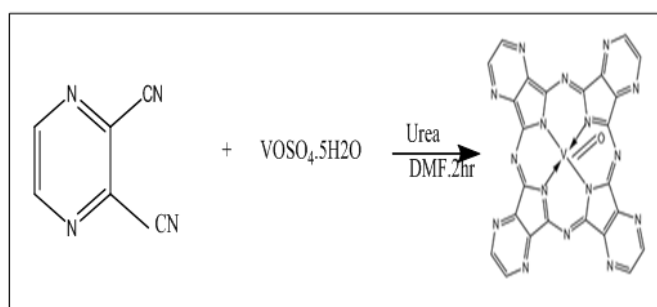


Figure 1: Preparation of DCP

Preparation of Tetrapyrazinoporphrazinevanadyl Oxide, PzVO (IV)⁽¹¹⁾

0.52 g (4 mmol) of DCP was dissolved in 10 ml DMF in a round bottomed flask containing 0.253 g (1mmol) of hydrated Vanadyl sulfate (VOSO₄·5H₂O). 0.24 g of urea then added to the mixture, the reaction mixture was refluxed for two hours with magnetic stirring. The reaction mixture then cooled and filtered and then dissolved in 10 ml of chloroform and the mixture then purified by adding the mixture drop-wise with stirring to a beaker containing 100 ml of ethanol. The solid product then filtered and the purification process was repeated three times. The product is a pale Bronze powder with a yield of (0.38 g, 64.72%). Decomposition temperature is 237-239°C. CHN, CHN, calculated (C₂₄H₈N₁₆VO) C: 49.07, H: 1.36, N: 38.16; Found C: 49.98, H: 1.31, N: 37.13. The reaction is shown in Figure 2.



PzVO

Figure 2: Preparation of Preparation of Tetrapyrazinoporphrazine Vanadyl Oxide Bridged with p- Dicyanobenzene, [PzVO (DCB)]_n

Dicyanobenzene (0.128 g, 1 mmole) was added to a solution of PzVO (0.1174g, 2mmole) soluble in 10 ml of ethanol in a conical flask. The mixture then refluxed for 7 days, cooled and filtered. The solid product was purified by dissolving it in 2 ml of THF and added drop-wise with stirring to a beaker containing 50 ml of Hexane. The solid product was then filtered and dried. The purification was repeated for 3 times. The solid product then dried at 110°C filtered. The yield was (0.79 g, 59.9%). Yellowish orange solid decomposes after 175°C. CHN analysis, (C₃₂H₁₂N₁₈VO) calculated: C: 53.63, H: 1.67, N: 35.19; Found C: 52.96, H: 1.51, N: 34.22.

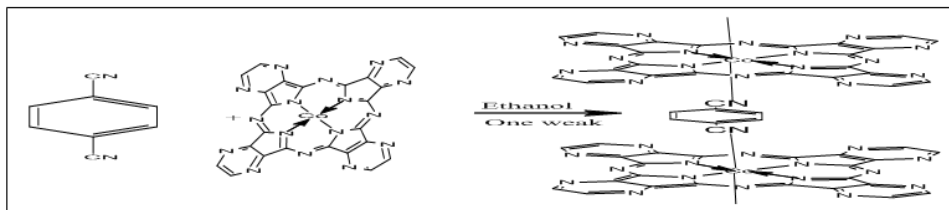


Figure 3: Preparation of the Bridged Compound

RESULTS AND DISCUSSIONS

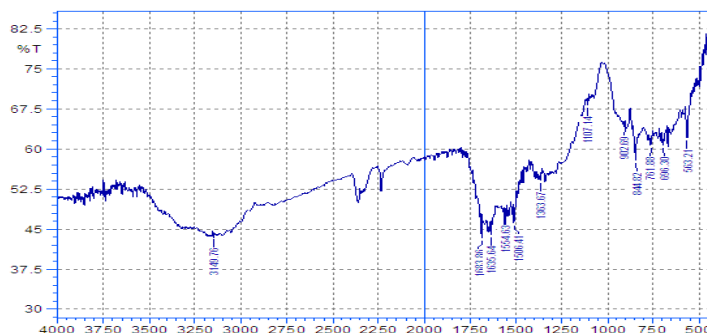


Figure 4: The IR Spectrum of PzVO (KBr Disc)

IR: The disappearance of the Nitrile peak at 2240 cm^{-1} is the most characteristic appearance in the Vanadyl Oxide complex ⁽¹²⁾, Figure (4). The bridged compound shows the re-appearance of the Nitrile peak in 2200 and 2250, Figure (5). The complexes show the characteristic C-H is stretching at 3149 for Vanadyl oxide complex and at 3275 cm^{-1} for the bridged complex. Figures 4 and 5

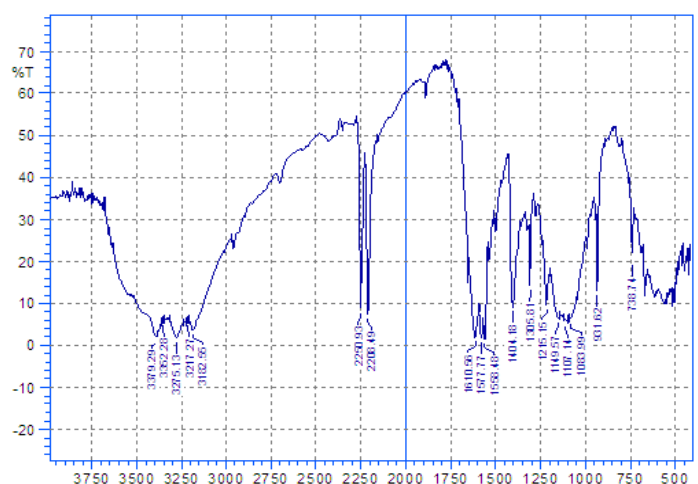


Figure 5: The IR Spectrum of the Bridged PzVO with p-Dicyanobenzene (in KBr Disc)

The electronic spectra of the complexes, PzVO⁽¹¹⁾, and the bridged complex with p-dicyanobenzene, show the characteristic (Soret band) at 430 nm and 450 nm, respectively, due to $\pi\text{-}\pi^*$ and $n\text{-}\pi^*$ transitions, and Q band at 635 nm and 650, respectively, which is due to $\pi\text{-}\pi^*$ ^(1,11) and weak d-d transition of the central metalatom hidden inside the Q-band, with an extinction coefficient (ϵ) range $0.62 \times 10^4 - 1.3 \times 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. The solvent DMF was used to prevent or reduce aggregation of the complex molecules. Figures 6.

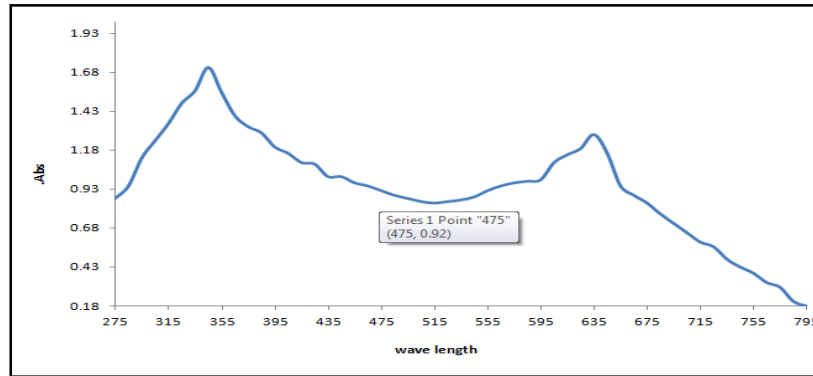


Figure 6: The Electronic Spectrum of Bridged Compound of PzVO with p-Dicyanobenzene (in DMF, 25⁰C)

THE ELECTRICAL PROPERTIES

Preparation of the Samples

The samples were prepared as thin films cast on glass substrate. The aluminum electrodes were evaporated on the glass substrates (2×0.5) cm². The substrate is wrapped with copper wire (0.0325 cm diameter) in the middle of the substrate. The cell constant is (0.5cm⁻¹). The samples were doped by iodine vapor in a closed vessel for one day with covering the electrodes. The cells were dried in an oven at 100⁰C. The dc electrical conductivity is measured in cryostat supplied with heating element and cell electrode holder connected to a cell containing variable voltage supply, voltmeter and ammeter⁽¹²⁾.

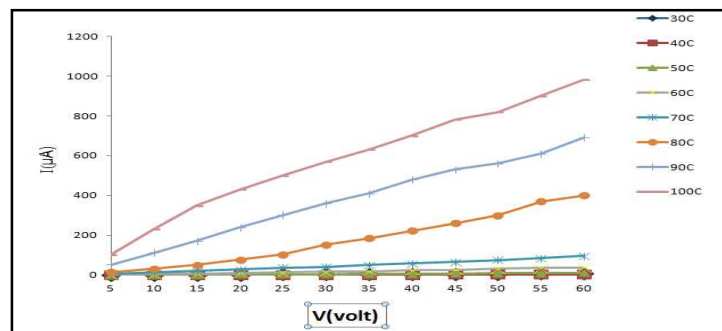


Figure 7: I/V Curve at Different Temperatures for Bridged PzVO

Figure 7, shows the V/I curve for the bridged complex of PzVO with p-dicyanobenzene at different temperatures and voltage range from 5-60 volts. It shows the ohmic relation especially at lower voltages where there is no space charge limited current.

Figure 8 shows the relation between \ln dc conductivity ($\ln \sigma$) and the reciprocal temperatures at different temperatures and under voltage of 7 volts for unbridged PzVO complex (2, 4) and a bridged complex with p-dicyanobenzene (1, 3) for both doped and undoped with Iodine vapour. The graph shows, in general, a higher dc conductivity of the Iodine doped in comparing to the Iodine undoped for bridged and unbridged complexes, and the bridged complex shows lower dc electrical conductivity than the unbridged which could be attributed to the presence of the bridging ligand which makes the inter-planner spacing between the Pz planes widely separated which reduces the charge carrier transfer.

The Iodine doped unbridged complex has higher conductivity than the undoped which could be attributed to the oxidation of the complex by the electron acceptor (the Iodine is oxidizing agent). The activation energy of the doped is lower than the undoped for both, the complex TpPzVO and the bridged compound.

The oxidizing agent, Iodine (I₂), reduces to form I⁻³ and I⁻⁵ Structures^(14, 15). The natural logarithm of dc conductivity against reciprocal absolute temperature was drawn according to Arrhenius equation, $\ln \sigma = \ln \sigma_0 - \frac{\Delta E}{kT}$, where σ and σ_0 are the dc conductivity and pre-exponential factor respectively. K is the Boltzmann constant ($8.61733 \times 10^{-5} \text{ eV/K}$) and ΔE is the activation energy, $-\frac{\Delta E}{k}$ is the slope of the straight line. From the slopes we calculate the activation energy in eV. The measured voltage was 7 volts to ensure that there is no space limited current. The activation energies of both PzVO unbridged and bridged PzVO complexes are 0.2 and 0.4 eV respectively, which could be attributed to the bridging ligand. The activation energy of the doped complexes decreases by about 0.1 eV.

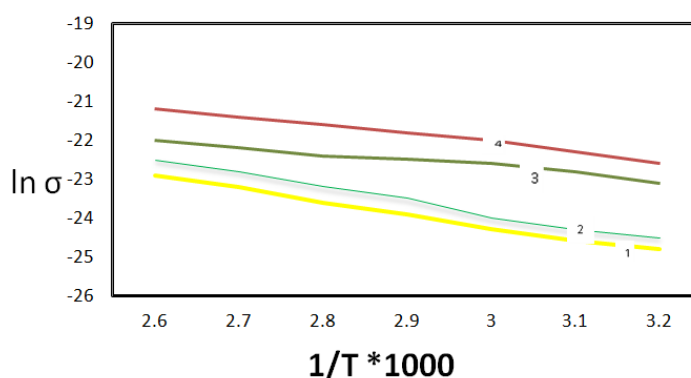


Figure 8: The Relation between $\ln \sigma$ and Reciprocal Absolute Temperature for the Iodine Undoped (2) and Doped (4) Complex TpPzVO and the Undoped (1) and Doped (3) of the Bridged Compound

CONCLUSIONS

We can conclude from this study that the complex, TpPzVO, behaves as semiconductor and its Iodine doping increases its conductivity while bridging of the complex with p- dicyanobenzene reduces its conductivity due to the gap separation between the porphrazine rings. Iodine doping of the bridged complex is also increase the conductivity due to oxidation of the molecules by Iodine.

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