

Synthesis Characterization and Study of Some Electrical Properties of Compound Substituted Bridged Polymeric 4- amino Phthalocyaninato Iron (III) Fluoride

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Abstract: The study included the preparation some bridged polymeric phthalocyanine which are substituted with amino groups of the formulae $[(4-NH_2)_4 PcFeF]_n$. The prepared compound were characterized by Infrared, UV-visible spectroscopy and x-ray. Electrical conductivity of the polymer was measured by using the iodine doping. It was found that the electrical conductivity increased up to $(10^{-4} \text{ ohm}^{-1} \cdot \text{Cm}^{-1})$

Keyword: Bridged polymeric (pc), losing doping, and electrical conductivity

1. Introduction

Phthalocyanine is the second most important class of colorant and iron phthalocyanine is the largest volume colorant sold. Phthalocyanine have also found extensive use in many modern high technologies ⁽¹⁾ for intence they are used as catalyst in the merox process and photoconductor xerographic double layers of laser printers and copy machines .

Also some infrared absorbing phthalocyanines cover many important high technical application including the phthalocyanine therapy if cancer, optical data storage and reverse storable absorbs ⁽²⁾

Phthalocyanine rings may either be separate units, such as metal free or copper phthalocyanines, or linked with other

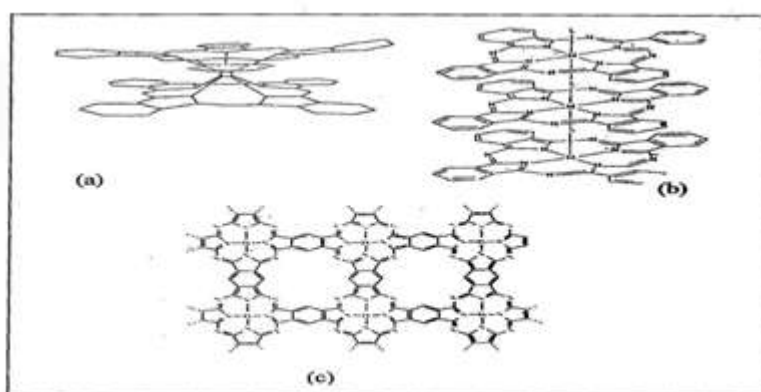
phthalocyanine rings in the form of dimer, oligomers or polymers. There are three known types of linkages in phthalocyanines

1- dimeric Forms have the metal sandwiched between the two phthalocyanine rings . This kind of linkage is found in the phthalocyanine complexes of lanthanides and actinides ⁽³⁾

2- A two dimensional eka-linked phthalocyanine polymer ⁽⁴⁾, these materials are usually prepared from tetracyano benzene where the

3- μ -Bridged phthalocyanine polymers, where a ligand is used, I which can act as a bridge between two macrocycles via the central metal atoms ⁽⁶⁾.

This will give cofacially stacked face to face phthalocyanine units with a rigid structure.



شكل (3) انواع من مركبات الفثالوسيانين من حيث الارتباط

Figure 1: Types of linkages in Phthalocyanine

2. Experimental

A: Chemical Materials

FeCl₃, Urea , 4-Nitrophthalic acid , Ammonium Molybdate , Nitro benzene Methanol, Na₂S₉H₂O, HCl , NaOH, HF, C₅H₅N, NH₄OH (%25), I₂.

B: Instruments

F.T-infra-red spectrometer made by shimadzu model (5400 S) in the range (4000- 500cm⁻¹) was used, U.V-visible spectrometer was recorded on a thermo supertonic IteeliosV(4-60). The X-ray diffraction measurements were recorded using PW-1320 X-ray diffraction. Electrical conductivity

(Voltmeter, Power supply, Resistance, Temperature, Recorder, and measured sample cell) was used under vacuum measurement, were carried out in Department of Chemistry, College of Education, Basrah University.

Synthesis of iron (III) tetranitro phthalocyanine:

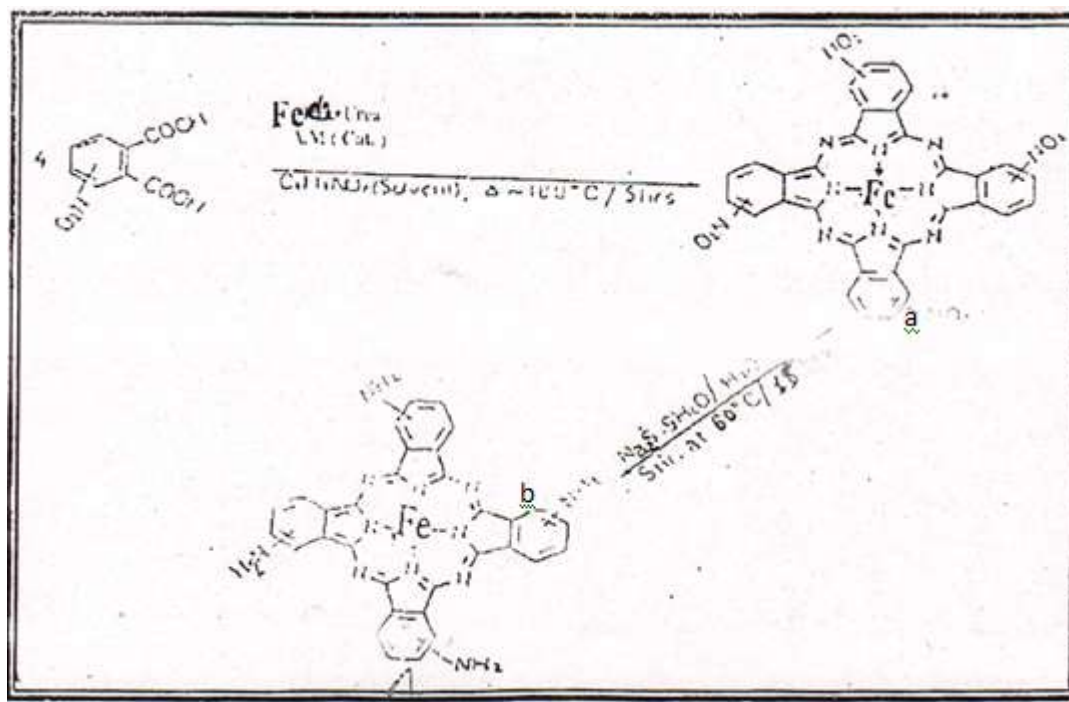
5.54 g (0.092 Mole) urea. 3.289 (0.018 mol) iron (III) chloride and 0.075 g of ammonium Molybdate were dissolved and mixed with nitrobenzene.

After mixing, It was refluxed at (185 - 190 C°) for (5h), the product was purified in three steps by (6ml) HCl, 20% NaOH solution and then washed with hot water. Iron (III)

tetranitrophthalocyanine shown in the scheme (1-a) is only one of the possible structural isomers of the complex ⁽⁸⁾

Synthesis of iron (III) tetra aminophthalocyanine:

4g (0.005 Mole) from compound was dissolved in (100ml) water and (20g) of Na₂S. 9H₂O was added. The Mixture was stirred under reflux at (300) for 11h, the solid product separated by centrifuge and treated with 100 ml (1N HCl, 1N NaOH), tire product was washed with water to remove the (HCl, NaOH). Iron (III) tetra amino phthalocyanine was filtered and dried at (50C°) in a vacuum oven ⁽⁹⁾ Scheme (1-b) show the preparation and reduction of iron (III) tetranitro phthalocyanine.

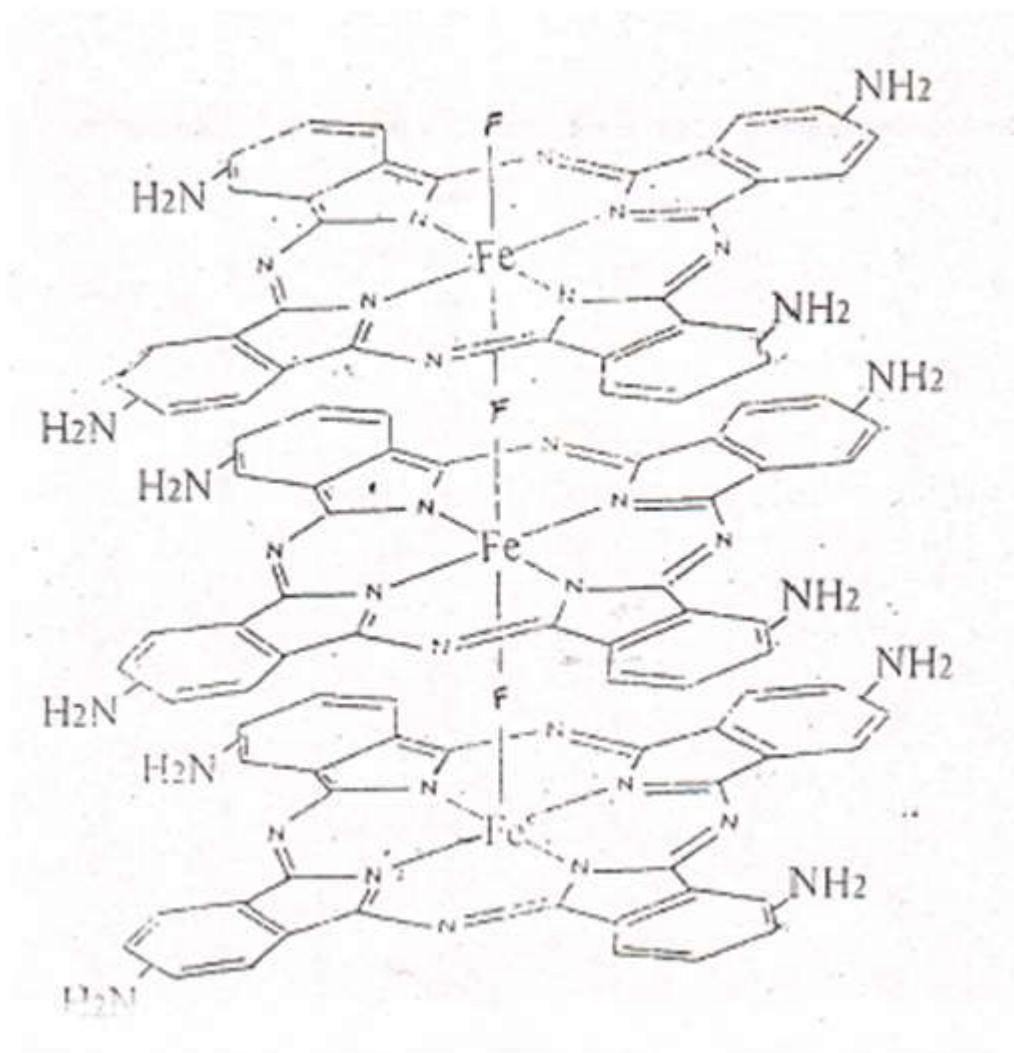


Scheme (1)

Synthesis of 4- amino phthalocyanine iron { III } fluoride

A mixture 1.5 g (0.024 Mole) of 4-tetra amino phthalocyanine iron (III), (concentrated ammonium hydroxide (50 ml), and pyridine (25 ml) was refluxed for (7 h). The reaction product was filtered , and the solid was washed with pyridine , concentrated ammonium hydroxide and hot water and dried at 110 C° A portion of this product ,

assumed to be (4-NH₂)₄ Pc Fe OH-XH₂O (1g) was evaporated to dryness on a steam bath with two separate portions of 48% hydro fluoride acid (15 - 20 ml each time) the resulting solid was washed with water , Methanol , Pyridine and acetone and dried at 110 C° ⁽¹⁰⁾ Scheme (2) shows. Only one of the structural isomer of the polymer.

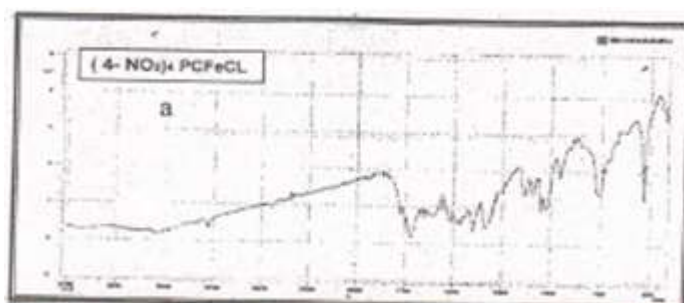


Scheme (2)

3. Result and Discussion

The synthesis of iron (III) tetranitrophthalocyanine phthalocyanine and 4-tetra amino phthalocyanine Iron fluoride were confirmed by IR spectra⁽¹¹⁾ taken in KBr. The nitro phthalocyanine complex show characteristic NO_2 peaks at 1340 cm^{-1} and 1546 cm^{-1} . The characteristic nitro peak at 1340 cm^{-1} disappeared after reduction and the NH_2 stretching peak appeared in the polymer at 3450 cm^{-1} .

The aromatic (C-H) stretching band appeared in ranged at 3000 and show a strong in the range of (at $1602, 1620\text{ cm}^{-1}$ due to (C=C) stretching band, in all spectra of the prepared complex there are several bands $1506, 13173, 1396, 937, 816, 667\text{ cm}^{-1}$, and appearance of a broad band in the range ($400\text{--}600\text{ cm}^{-1}$ which are attributed to the stretching vibration of the (M-F) bond. These band refer to the bridging structure of these polymers.



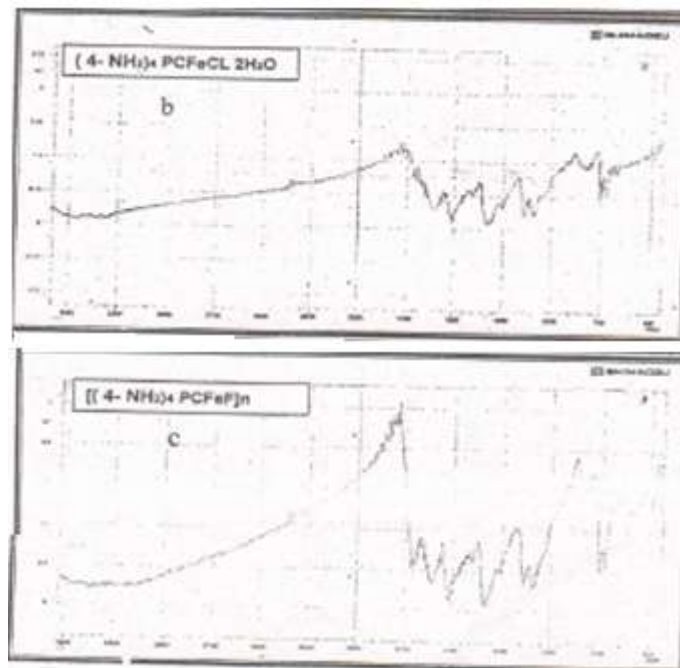


Figure 2: infra-red spectrum of compounds a,b,c

The UV - visible spectra ⁽¹²⁾ are characterized by the appearance of two absorption bands, the first or two absorption at the range (600 - 700) nm which is called Q - band and the second at the range (300- 400) nm which is called B or soret - band . These bands are attribute to $\pi - \pi'$ transition which belong to the hetro-aromatic system of the phthalocyanine Molecule.

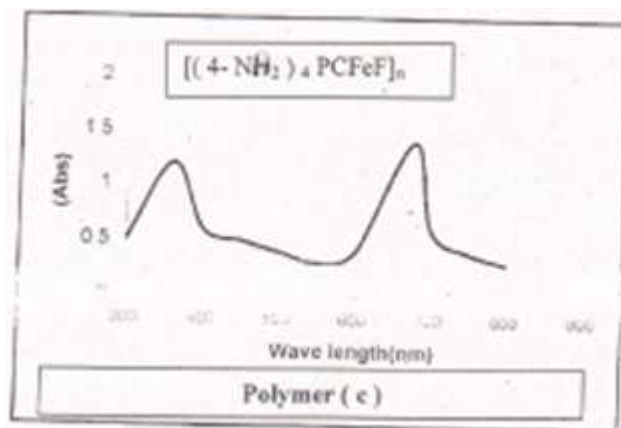
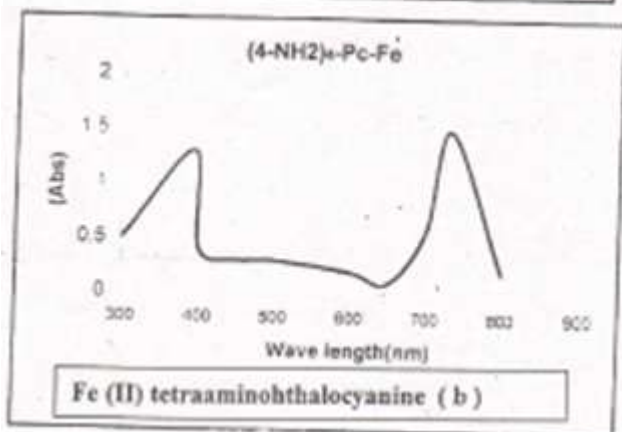
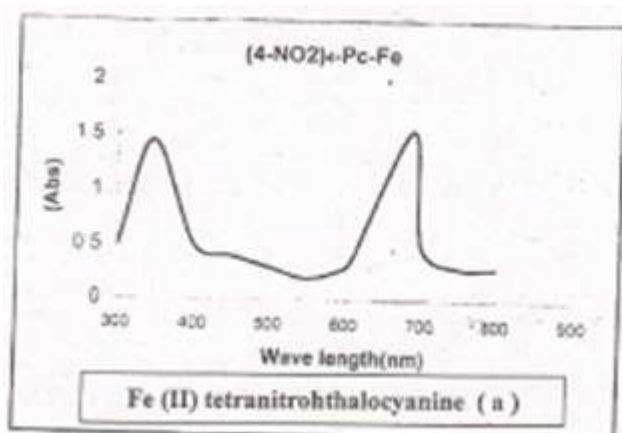


Figure 3: UV-visible spectrum of compounds a, b, c



X-ray diffraction can be used to determine the degree of crystallization of the polymer. Figure (4) shows the powder x-ray diffraction spectra. This Figures show the crystalline nature of the solid compounds Table (1) shows that the inter planner spacing ranges are 2.40, 5.05Å°

Table 1: The inter planner spacing of the polymer

Compounds	Values d inÅ
polymer	5.05, 4.44, 3.34, 2.40

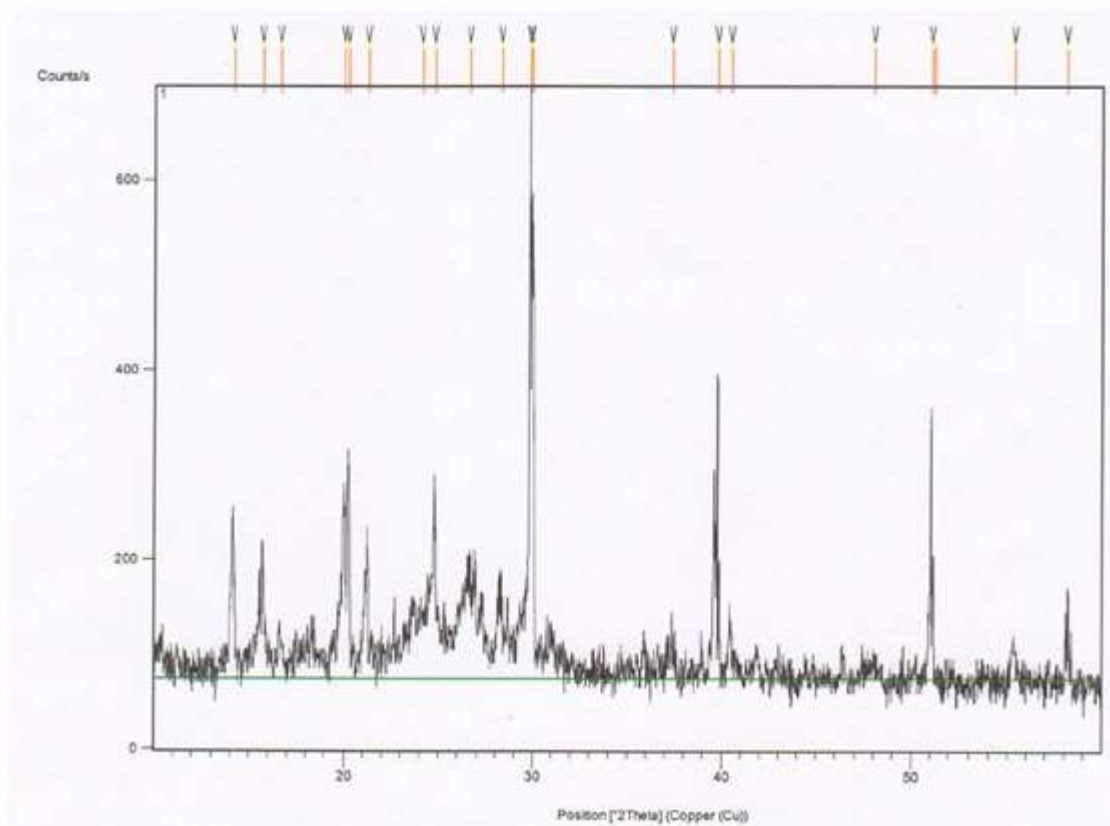


Figure 4: x-ray for the polymer

Electrical conductivity

The electrical properties of phthalocyanine and related compounds depend very much up on the Morphology of the Macro cyclic systems, to achieve good semiconducting or even conducting properties.

Doping of the polymer Iodine was achieved by the dissolved of polymer in CCl_4 and stirrer at (79C) for t(72h), after that the polymer doping was filtered and dried in vacuum oven at (50C) the maximum conductivity of the doped polymer samples is $3.52 \times 10^{-4} \text{ ohm}^{-1}$. It increases conductivity by

the overlap of the Λ phthalocyanine orbitals of rings, A high electrical conductivity has been reported by Wohrle⁽¹³⁾ for iodine - doped $[(4-NH_2)_4pcFeF]_n$ and was explained by assuming that the eclipsed ring structure persists in the partially oxidized Material.

Table 2: Shown the Values ΔE and σ^0

sample	ΔE (eV)	σ^0 ($\text{ohm}^{-1}\text{cm}^{-1}$)
polymer	0.57	1.2×10^{-4}
Iodine-doped polymer	0.54	8.30×10^{-4}

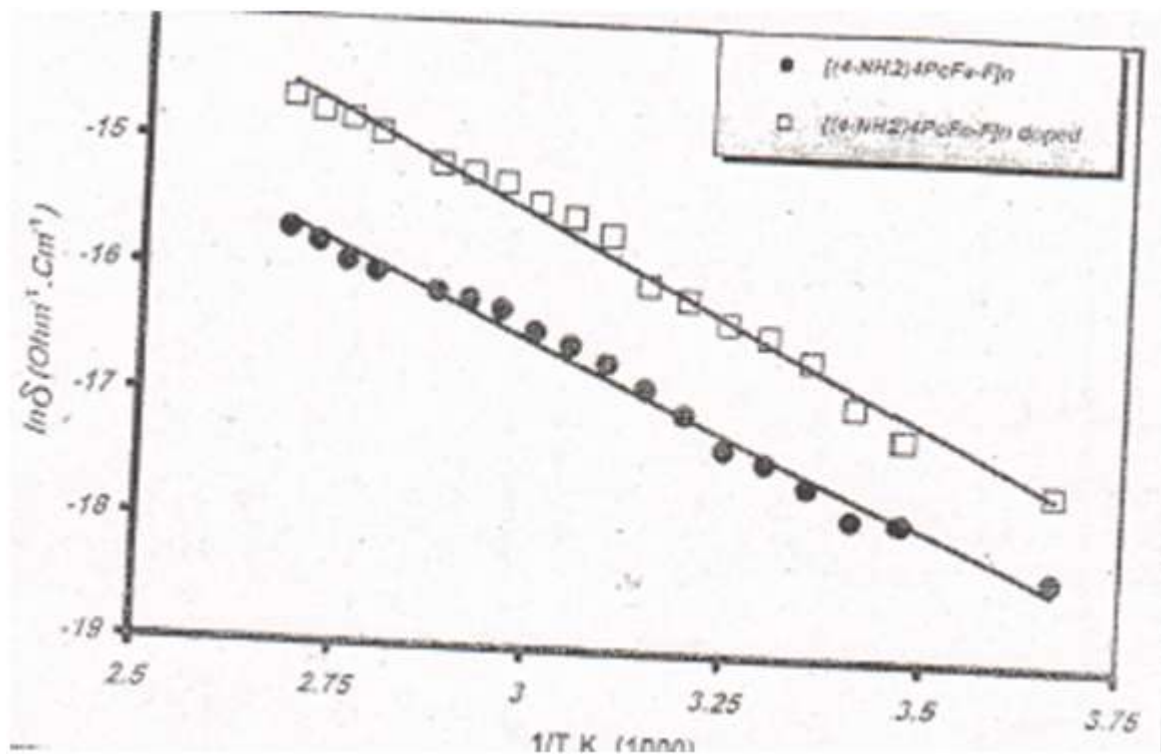


Figure 5: The DC conductivity of polymer and doped polymer

4. Conclusions

In this study of compound bridges polymeric phthalocyanine preparation and characterized which are substituted with amino group of the formula $[(4-NH_2)_4pcFeF]_n$

The I.R spectra for the polymer showed broad peaks at the vibration $500-600\text{ cm}^{-1}$ which is related to (M-F) stretching group showing the polymeric bridged structure. The UV - visible spectra are characterized by the appearance of two absorption bands, The first at the range (600 - 700) nm which is called Q-band the second at the range (300 - 400) nm which is called B or solet -band and x-ray diffraction can be used to determine the degree of crystallization of the polymer. The results showed a higher conductivity for the prepared polymers that substituted with both nitro and amino groups. The iodine doping effect on the electrical conductivity of the polymers and the values of (ΔE) and (σ) were calculated to the polymer and iodine -doped polymer that it's showed in table (2).

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