Journal of Thi-Qar University No.3 Vol.4 December/2008

Synthesis , characterization and study of some electrical properties of compound substiuted bridged polymeric 4-amino phthalocyaninato iron (II) fluoride

Thi - Qar Director of Education
Hassan sabbeh Jabur
Physical chemistry

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 Infer-red and UV-visible spectroscopy.

Electrical conductivity of the polymer was measured by using the iodine doping . It was found that the electrical conductivity increased up to (10^{-4} ohm $^{-1}$, cm $^{-1}$).

Introduction:

Phthalocyanine are 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 doubic 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 absorbes (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 form tetracyano benzene where the macrocyeles are linked via the peripheral conjugated systems to give a layer type structure (5)**
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 .

Several different types of ligands are used to act as bridging units , such as F (μ -fluoro), O(μ -oxo), CN(μ -Cyano) , pyrazine (pyz) and others (7)

Experimental

A: chemical Materials :

FeCl2, Urea , 4-Nitrophthalic acid , Ammonium Molybdate , Nitro benzene , Methanol, Na2S.9H2O , 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 recored on a thermo supertonic Iteelios V(4-60) .

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

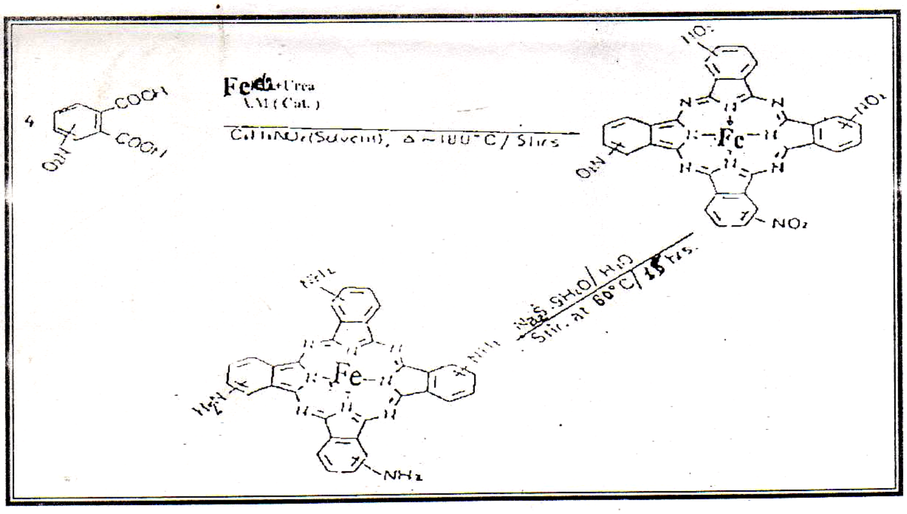
Synthesis of iron (II) tetranitro phthalocyanine

5.54 g (0.092 Mole) urea . 3.28g(0.018 Mole) iron (II) 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 Methanol (6ml) HCl , 20% NaOH solution and then washed with hot water . Iron (II) tetranitrophthalocyanine shown in the scheme (1) is only one of the possible structural isomers of the complex (8)

Synthesis of iron (II) 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 (60c) for (15h) , the solid product separted by centrfuge and treated with 100Ml (lN HCl), the product was washed with water to remove the (NaCl , NaOH). iron (II) tetra amino phthalocyanine was filtered and dried at (50C) in a vacuum oven (9) Scheme (1) show the preparation and reduction of iron (II) tetranitro phthalocyanine



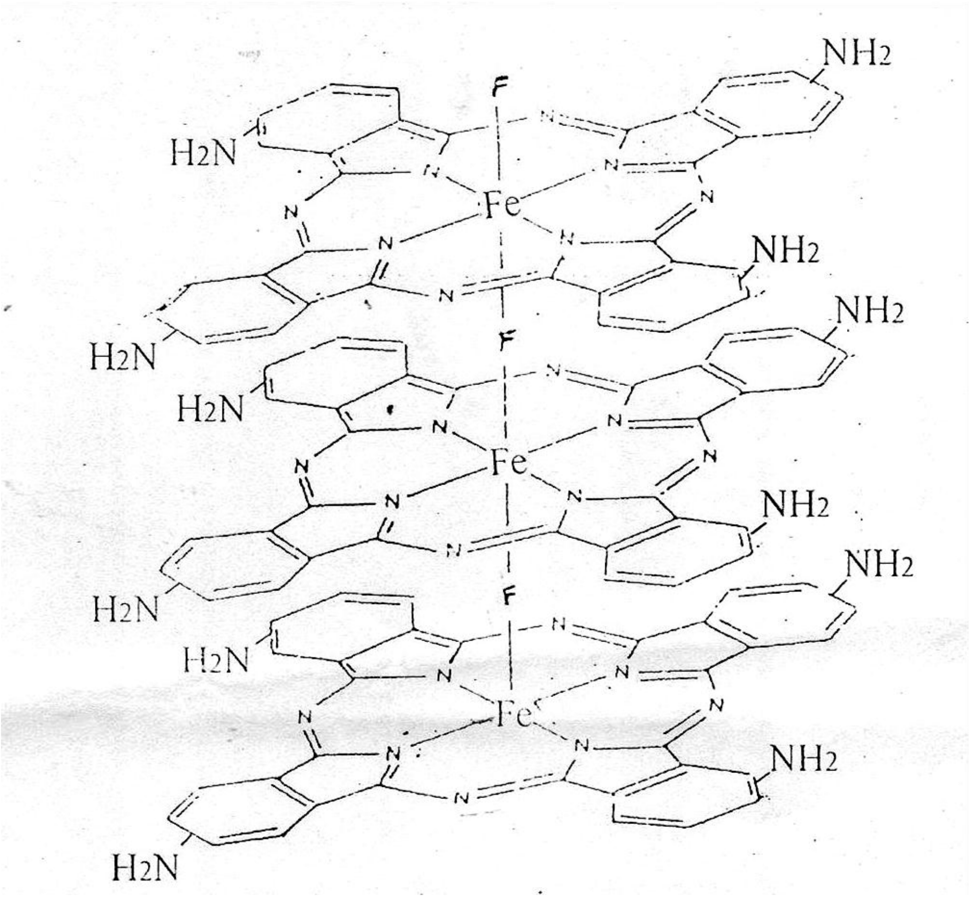
Scheme (1)

Synthesis of 4- amino phthalocyanine iron (II) fluoride

A mixture 1.5 g (0.024 Mole) of 4-tetra amino phthalocyanine iron (II), (concentrated ammonium hydroxide (50 ml) , and pyridine (25 ml) was refluxed for (7 h) . The reaction product was filtered , and the solide 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% hydrofluoride acid (15 – 20 ml each time) the resulting solid was washed with water , Methanol , Pyridine and acetone and dreid at 110 C (10)

Scheme (2) shows only one of the structral isomer of the polymer.



Scheme (2)

Results and discussion

The synthesis of iron (II) tetranitrophthalocyanine , Iron (II) tetra amino phthalocyanine and 4- tetra amino phthalocyanine Iron (II) fluoride were confirmed by IR – spectra (11) taken in KBr . The nitro phthalocyanine complex show characteristic – NO2 peaks at 1340 cm $^{-1}$ and 1540 cm^{-1} . The characteristic nitor peak at 1340 cm $^{-1}$ disappeared after reduction and the – NH_2 stretching peak appeared in the polymer at 3450 cm $^{-1}$ C-H at 3000 and 749 cm^{-1} c=c peak at 1602 , 1620, 1506 , 4173 , 1396 , 937 .816 . 667 , and appearance of abroad band in the range (400-600) cm^{-1} which are attributed to the stretching vibration of the (M-F) bond . These band refer to the bridging structure of these polymers

The UV – visible spectra(12) are characterized by the appearance of two absorption bands , the first 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 Λ - Λ transition which belong to the hetro – aromatic system of the phthalocyanine Molecule .

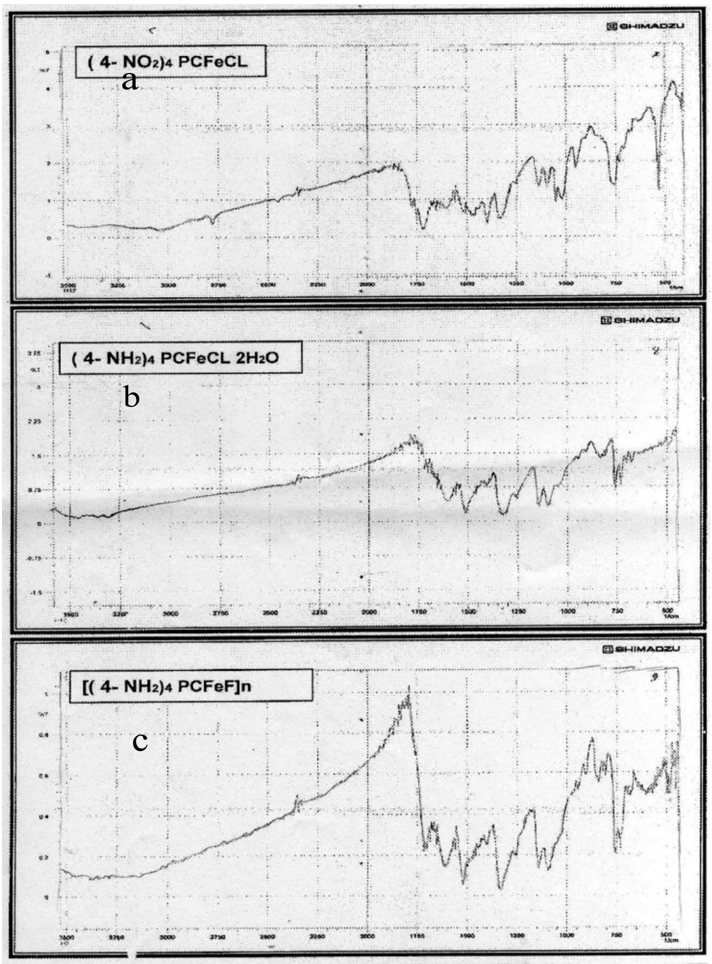
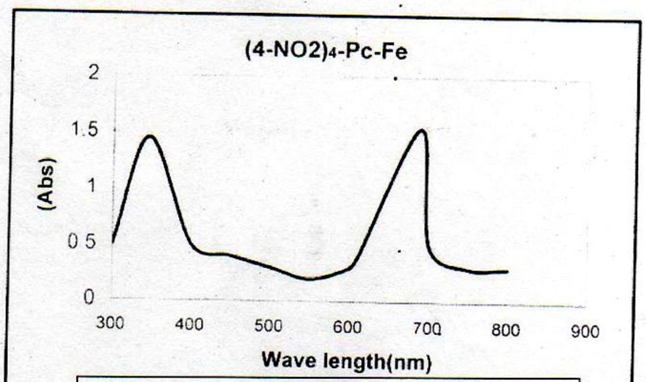
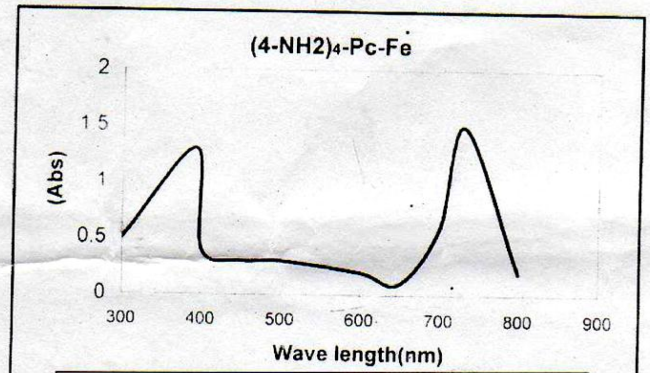


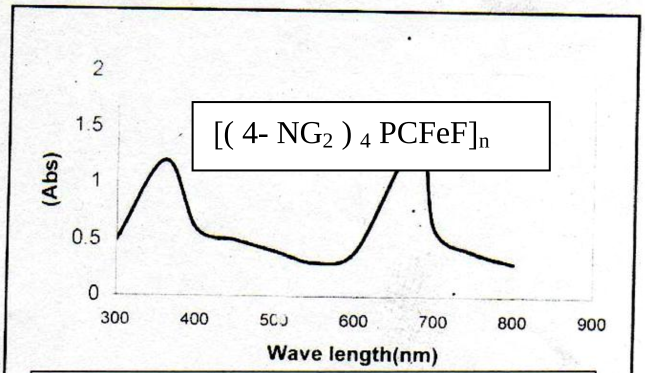
Figure (1) infra-red spectrum of compounds a,b,c



Fe (II) tetranitrohthalocyanine (a)



Fe (II) tetraaminohthalocyanine (b)



Polymer (c)

Figure (2). uv – visible spectrum of compounds a , b , c

Electrical conductivity

The electrical properties of phthalocyanine and related compounds defend very much up on the Morphology of the Macrocyclic systems , To achive good semiconducting or even conducting properties .

Doping of the polymer Iodine was acheaved by the dissolved of polymer in CCl4 and stirrer at (70c) for (72h) , after that the polymer doping was filtered and dried in vacuum oven at (50 C) the maximum conductivity of the doped polymer samples is 3-52 X 10 $^{-4}$ ohm^{-1} . It increases conductivity by the overlap of the Λ orbitals of phthalocyanine rings , A high electrical conductivity has been reported by wohrle (13) for iodine – doped [(4-NH2)4pcFeF]n and was explained by assuming that the eclipsed ring structure persists in the partially oxidized Material .

Conclusions :

In this study of compound bridges polymeric phthalocyanine preparation and characterized which are substituted with amino groups of the formula [(4-NH2)4pcFeF]n

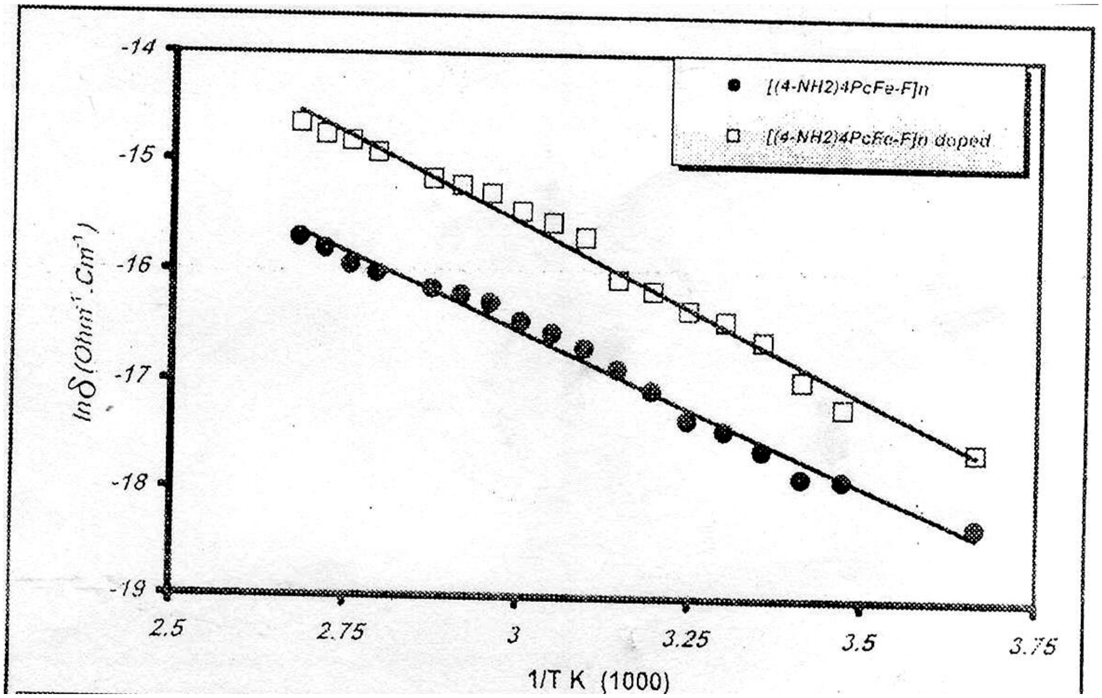
The I.R spectra for the polymer showed broad peaks at the vibration 500-600 cm^{-1} which is related to (M-F) stretching group showing the polymaric bridged structure.

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 and the second at the range (300 – 400) nm which is called B or soret – band .

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 (6) were calculated to the polymer and iodine –doped polymer that it's showed in table(1)

Table (1) shown the values ΔE and 6

Sample	ΔE (eV)	6 (ohm^{-1} (cm^{-1})
Polymer	0.57	1.21X10^{-4}
Iodine – doped polymer	0.54	8.30X10^{-4}



Fig(3) conductivity of polymer doped and un doped

References

1. **Gegory , P,J, porphyrins phthalocyanine 4 , 432 (2000)**
2. **Lever, A,B et al ; Journal of porphyrines and phthalocyanines , 3, 488 (1999)**
3. **Bouvet , M Bassoul , P and simon , J; Mol cryst , Lig , cryst 31 , 252 (1994)**
4. **Willis , M , R , mol. crys , lig , 17 , 217 (1989)**
5. **Jong , R , and Hannack , M ; synthesis 2, 1387 (2001)**
6. **Hielmeire , C, H , and Harison , S, E; phys , Rev , 132 , 2012 (1963)**
7. **Hanack, M,and levernz ; A; Sxnth Met,22,9(1987)**
8. **Nuchter .M ; Microsynth synthesis application notes (2001)**
9. **Vogel , H ; practical organic chemistry 9,837, (1969)**
10. **Linsky , J, P and paul , T:R;Inorg chem. 19 , 3131 (1980)**
11. **somani ,P.R, Materials chemistry and physics 77,117 (2002)**
12. **Hanack , M and Metz , J , Inorg – chem. , 23 , 1065 (1984)**
13. **whorle , D; Adv polymer sei , 50 , 46 (1983)**