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# DC ELECTRICAL CONDUCTIVITY OF TETRA-DIIMINOBENZENE-P-AMINOBENZENEPHTHALOCYANINATO METAL (II) & (III)

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**Abstract:**

In this work a complex of Schiff base of tetra-diiminobenzene-P-amino benzene-phthalocyaninato with tetra diimino-benzene as peripheral groups. The compounds were synthesized with different central metal ions(Al, Fe, Cu and Zn) were synthesized, identified by elemental analysis and spectroscopically, their dc electrical conductivity of their thin films were measured with and without iodine doping. The dc electrical conductivity of iodine doped thin films of the compounds were compared with iodine un-doped thin films of the compounds. The study shows that the measured dc electrical conductivity of the doped Schiff base has higher dc conductivity than un-doped. It shows that the conductivity of the bridged phthalocyanines of aluminum Schiff base has higher dc conductivity than the others, while planar phthalocyanines of zinc Schiff bases has lower dc conductivity. The study, also, shows that the peripheral groups on the phthalocyanine rings as the Schiff base have clear influence on the dc conductivity of all compounds. The stacking and the bridging of the phthalocyanine rings has also effect on the dc electrical conductivity. The bridged compounds have higher conductivity than unbridged compounds.

**Keywords**: Cyanobacteria, Fatty Acids, Biodiesel Du, Gc, Biodiesel Cn.

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**Introduction:**

The dc electrical conductivity of metallic phthalocyanine compounds (PcM, where Pc is the phthalocyanine rings and M is a central metal atom) is intrinsically related to their electronic structure and the morphology of the phthalocyanine molecules[1,2]. Generally, phthalocyanine compounds in the solid state (crystalline arrangement) behave as insulators with a very low conductivity, often around $10^{-9}ohm^{-1}.cm^{-1}$ at room temperature[1]. That is because the molecular distance between phthalocyanie rings does not allow a sufficient over-lap of the π-molecular orbitals of adjacent phthalocyanine molecules and therefore reduce conduction and hence, reduce the charge carrier mobility in these molecules [1,3]. Conduction in these structures occurs as in other organic conductor, via electron hopping as a result of electric field. That is the only mechanism which allows the mobility of charge carries. This kind of electrical conductivity is temperature dependent [1,4]. To increase the conductivity of such molecules is to build polymeric stacking of phthalocyanine molecules$(PcML)_n$, where the phthalocyanine molecules bridged together by some ligands(L). This system will modify the charge carriers hopping via the band gap(5).

The conductivity is also increased by means of oxidation-reduction agents which increase the charge carrier density and their mobility, by structural rearrangement of the molecules. Although the monomeric structure of the (PcML)n [L=pyrazine (pyz), tetrazine (taz), F…etc ], shows insulating behavior, it can be seen that the ligand (L) has a significant effect on the conductivity of the bridged complexes [1,6,7].

An increase in conductivity is observed for the pyrazine bridged compounds [PcM(pyz)]n, which its conductivity lies in the low semiconducting region. However, by changing the bridged ligand from pyrazine to S-tetrazine the conductivity is increased by 3-5 order of magnitude without external oxidative doping) [8

In phthalocyanines the conduction band is partially filled at normal temperature. By increasing the temperature, the conductivity increases due to increase of the charge carriers so they shows semiconducting properties[9, 10].
In order to get good conductivity, the charge carriers are generated either by oxidation or reduction reactions with dopants( either donors or acceptors[1]. In this work the dc electrical conductivity for a stacked and non-stacked complexes of Schiff bases with different central metal atoms were measured after and before doping.

Synthesis of the compounds:

Synthesis of 4,4',4'',4'''–tetraamino-phthalocyaninato metal(III)and(II), $(NH_2)_4PcM$, (NH2)4PcMCl

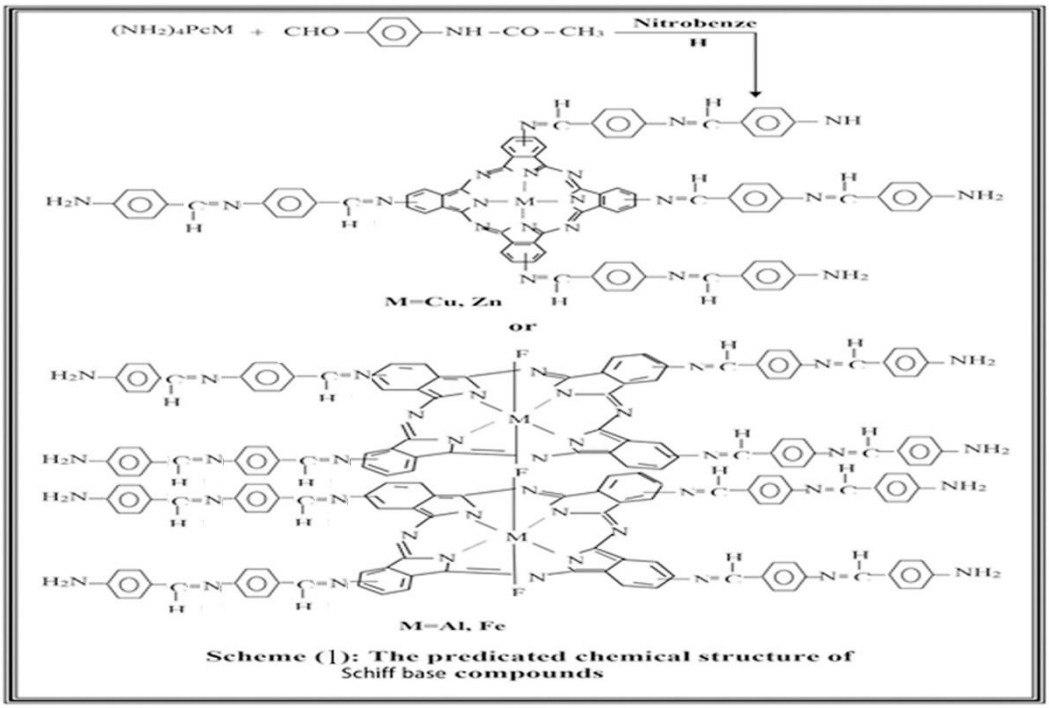
This compound was synthesized according to J. P. Linsky etal in three steps, for M=Cu Zn, Al, Fe) [11,12].

Synthesis of 4, 4', 4'', 4'''–tetraaminophthalocyaninato fluoro Metal (III), $(NH_2)_4PcMF$, for M= Al, Fe. (

A mixture of 4,4',4'',4'''–tetraamino-phthalocyaninato metal (III) 1.5g, (0.024mole) for M=Al and 1.0g (0.024mole) for M=Fe, ammonia solution 25ml and pyridine 50ml were refluxed for 7hours. The product then filtered and washed with hot water and the solid product dried at 110 $^0$C. The product is 4,4',4'',4'''–tetraaminophthalocyaninato hydroxyl metal (III), $(NH_2)_4PcM(OH).XH2O$. Then 1g of this product was mixed with hydrofluoric acid (HF) (38-40%) and evaporated in a plastic dish over vapor bath. The product is 4,4',4'',4'''–tetra amino-phthalocyaninato flouro-metal (III), $(NH_2)_4PcMF)n$. Both products [M=Al, Fe] were blue powders. These compounds are known with their stacked structure [12-14]. (

Synthesis of Schiff base of 4, 4', 4'', 4'''–tetra-diiminobenzene-P-aminobenzenephthalocyaninato Metal (II) & (III).

A mixture of 4,4',4'',4'''–tetraaminophthalocyaninato cupper(II)[ $(NH_2)_4PcCu$] (0.656g, 0.001mol) and 4-acetoamidobenzaldehyde (1.304g, 0.008mol) in nitrobenzene (20ml) and a few drops of HCl were refluxed for 12 hours. The solid product was filtered and purified by reflux with 50ml of absolute ethanol, then the solid products (Schiff base) [11,13, 15]) was filtered and dried at 110$^0$C. The product is dark black powder and the yield is 56%. The procedure was repeated with other metals. $(NH_2)_4PcFeF$, gives product of brown power, with yield of 56.8% . The product is dark brown power with yield of 59.5%. $(NH_2)_4PcZn$, the product is brown powder with yield of 57.3, and (NH2)4PcAlF, the product is dark blue with yield of 60%. The predicted chemical structure is shown in scheme1. The results of elemental analysis of the prepared compounds are shown in table 1.




Scheme (1): The predicated chemical structure of Schiff base compounds

**Note: For the reaction below the references 11, 13 was depended:**

$$(NH_2)_4PcMF + 8CHO\text{-}Ar\text{-}NH\text{-}CH_3 \longrightarrow PcMF(\text{-}N{=}CH\text{-}Ar\text{-}N{=}CH\text{-}Ar\text{-}NH_2)_4 + HCOCH_{3)4}$$

In this reaction a molecules of acedamido-benzaldehyde reacts aminophthalocyanine to form first Schiff base which then react with another molecule of acedamido benzaldehyde to for the second Schiff base[ 13,14 ].

**Table 1: The elemental analysis data of the studied compounds**

| No. | Compound | Calculated% | | | Found% | | |
|---|---|---|---|---|---|---|---|
| | | C | H | N | C | H | N |
| 1 | Schiff-base (Cu) | 71.7 | 4.9 | 19.02 | 71.58 | 4.83 | 18.79 |
| 2 | Schiff-base (Zn) | 71.6 | 4.95 | 19.0 | 71.49 | 4.91 | 18.8 |
| 3 | Schiff-base (Al) | 72.5 | 5.01 | 19.2 | 72.25 | 4.93 | 19.05 |
| 4 | Schiff-base (Fe) | 71.1 | 4.91 | 18.8 | 71.12 | 4.88 | 18.66 |

**The CHN analyses were carried out in Micro Analytical Center/ Faculty of Science, Cairo University/ Egypt.**

**Spectroscopic study:**

IR spectra:

The I.R spectra of all compounds were recorded on KBr discs using Infra-Red Spectrophotometer 14500, with wave number range (3500-400)cm-1.

The spectra show general features of the IR spectra of amino and Schiff base derivatives of phthalocyanine compounds (4). The amino derivatives show the main IR peaks which include –N-H symmetric and asymmetric stretching vibration at 3290-3190 $cm^{-1}$.

It shows show the C=N stretching vibration of the imino group of the Schiff base at 1600-1608 $cm^{-1}$ as a new band as compared to the spectra of amino derivatives [12,16]. They also show the C-H stretching of imino group at 2900-2350 cm-1. An expected weak band at 500-200 cm-1 is related to carbon metal stretching vibration which is difficult to be identified due to the crowded region[12,17].

**The electronic spectra:**

The electronic spectra were recorded in the range (200-800)nm, using L.R1156 Spectrophotometer. The spectra of the compounds were recorded in DMF, using 1cm quartz cell at ($25^0$C-$28^0$C). The measurements were carried out at Physics department/ College of Science/ Basrah university.

The electronic spectra for the synthesized compounds show the general features of spectra of phthalocyanines compounds with two main peaks at (637-734)nm (Q-band) and at (320-460)nm (B-band) (sort band) [4]. Each figure show a blue shift of both peaks position on going from amino phthalocyanine to the Schiff base.

**Iodine doping of the Schiff base Compounds:**

The synthesized compounds with central metal atoms, Cu, Zn, Al and Fe) compounds were doped chemically by iodine, by treating them with iodine (1.5g,0.74 mole) (mole ratio 1:6) (as excess for iodine) in $CCl_4$ and then heated over water bath at71$^0$C with mechanical stirring for 3hours and then the solid products were filtered and left to dry at 100 $^0$ C to be ready for dc electrical measurements[12].

**Dc electrical conductivity**

Results and discussion

The semiconducting properties of phthalocyanines were first discovered by D.D. Eley.[9] and Vartanian [18]. The conductivity is given by Arrhius relation:

$$=\sigma \quad \frac{-Ea}{kT} \quad \ldots\ldots (1)$$

where σ is the conductivity at temperature T, $\sigma_o$ is the pre-exponential conductivity, $E_a$ is the activation energy for the conduction and k is Boltzmann constant.

For intrinsic conduction, the behavior may be described by the band theory equation [1,19].

$$=\sigma_c \quad \frac{-\Delta E}{2KT} \quad \ldots\ldots (2)$$

where ΔE is the intrinsic band gap. The conductivity is varying with temperature.

The dc. conductivity ($\sigma_{dc}$)ohm$^{-1}$.cm$^{-1}$ can be calculated from the equation (3).

$$\sigma_{dc} = \frac{1}{R_x} \quad \frac{L}{A} \qquad \ldots\ldots\ldots\ldots (3)$$

where L/A is cell constant, L is the distance between the electrodes (thickness of the sample) in cm, A is an area of the electrodes in cm$^2$, $R_x$ is the resistance of the sample.

ΔE and $\sigma_o$ can be calculated according to equation (2) by plotting $ln\sigma_{dc}$ as a function of a reciprocal temperature (1/T), which gives linear relation, the slope is $\frac{\Delta E}{kT}$ and the intercept is $ln\sigma_o$ [1,12,20].

The dc electrical conductivity measurements of the samples were carried out for 1.25cm diameter pressed disc for a finely ground polycrystalline material which were prepared by using Pye-Unicam die. Thickness of 1-2 mm (measured by virnier micrometer) was obtained with a pressure of 3.92x10$^6$ Pascal. All measurements were carried out in college of science/ Basrah university.

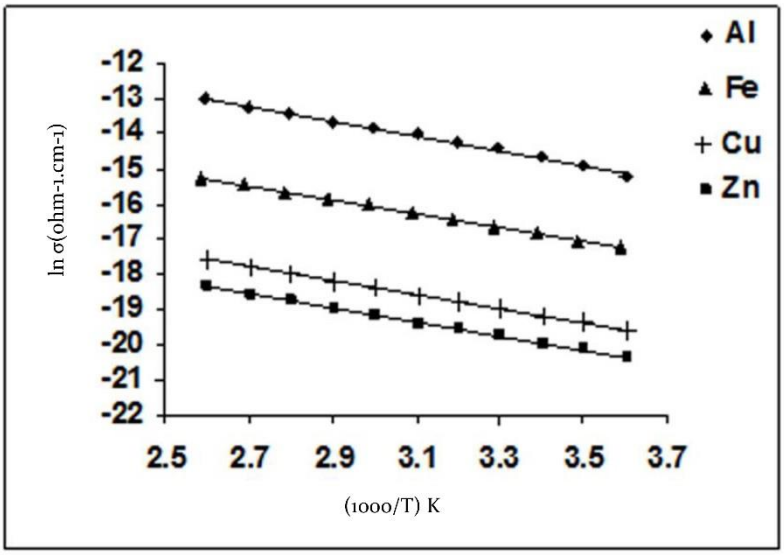



**Figure 1: Dc electrical conductivity of un-doped Schiff bases.**

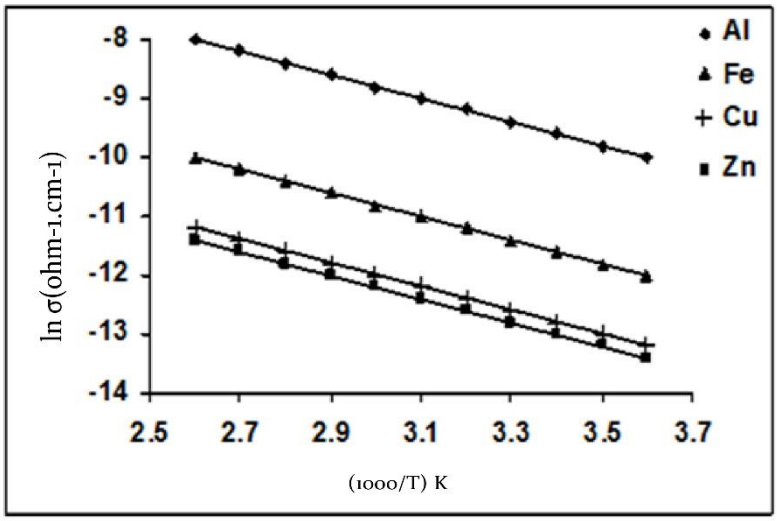



**Fig.2: Dc electrical conductivity of doped Schiff bases.**

Figure1 shows the relation between the dc electrical conductivity and the reciprocal temperature of the synthesized Schiff bases of Al, Cu, Zn and Fe as central metal atoms. It shows the sequence of electrical conductivity as follows:

PcAlF(-N=CH-Ar-N=CH-Ar-$NH_2$)$_4$ >

PcFeF(-N=CH-Ar-N=CH-Ar-$NH_2$)$_4$

**PcCu(-N=CH-Ar-N=CH-Ar-NH2)$_4$ >**

**PcZn(-N=CH-Ar-N=CH-Ar-NH2)$_4$**

The highest dc conductivity of (PcAlF(-N=CH-Ar-N=CH-Ar-NH2)$_4$ is may be due to the highly stacking of phthalocyanine ring which is due to the polymeric fluoride linkage that reduce the gap between the phthalocyanine rings. The small aluminum ion($Al^{+3}$) in compared to ($Fe^{+3}$) makes the gap between the phthalocyanine rings smaller in the case of aluminum than that of the Ferric ion that makes the conductivity of aluminum Schiff base is higher. The fluoride linkage in the case of Aluminum and iron make them of higher conductivity than the case of copper ion($Cu^{+2}$) which is planner without fluoride linkage. The filled d-orbitals of zinc ion($Zn^{+2}$) makes copper Schiff base is higher conductivity than that of the Zinc Schiff base.

Peripheral groups might have same effect on all compounds which might reduce the conductivity due to reduction of the planarity of the overall structures.

Figure 2 shows the dc conductivity as a function of reciprocal temperature for the iodine doped Schiff bases of Al, Fe, Cu and Zn central metal atoms.

The figure shows that the conductivity sequence is the same as of the un-doped Schiff bases..

which is due to the oxidation of the compounds with iodine as donor impurities, forming a reduced form of iodine $I^{-3}$ or $I^{-5}$ [12].In this case a charge carriers are generated by oxidation reduction reaction. At low temperatures electrons occupy these the donor levels through relatively low energies of excitation to the condition band. The donor levels makes the system n-type semiconductor[20,21].

The effect of iodine doping is the same on all compounds that makes no change in the conductivity sequence but with higher conductivity.

Table 2 shows the conductivities and activation energies at room temperature for the studied compounds before and after doping.

Table 2: the conductivities and activation energies at room temperature for the studied compounds before and after doping.

| Compounds | $\sigma_{dc}$ before doping at $40^0$C ohm$^{-1}$.cm$^{-1}$ | $\sigma_{dc}$ after doping at $40^0$C ohm$^{-1}$.cm$^{-1}$ | $\sigma_o$ befor doping ohm$^{-1}$.cm$^{-1}$ | ΔE (eV) before doping |
|---|---|---|---|---|
| Schiff-base of Al | $5.50*10^{-7}$ | $1.12*10^{-6}$ | $2.60*10^{-6}$ | 0.179 |
| Schiff-base of Cu | $4.50*10^{-9}$ | $1.02*10^{-8}$ | $2.70*10^{-8}$ | 0.308 |
| Schiff-base of Zn | $1.68*10^{-9}$ | $5.60*10^{-9}$ | $1.80*10^{-8}$ | 0.548 |
| Schiff-base of Fe | $3.40*10^{-10}$ | $1.68*10^{-9}$ | $2.20*10^{-9}$ | 0.342 |

**Conclusion**

The measured dc conductivity shows that the sequence of conductivity of doped with iodine and un-doped is:

Schiff base of Al > Schiff base of Fe > Schiff base of Cu > Schiff base of Zn

But the doped with iodine Schiff bases have higher conductivity which is due to oxidation with iodine.

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