The study of optical and structural properties of a novel ligand (5-ClCPAI) thin films by spray pyrolysis method .

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Abstract

The study in cludes the preparation of new dye azo heterogeneous of the ring derived from imidazole of the ligand :

2-[2-(5- Chloro carboxyl phenyl)azo]-imidazole and the identification of ligand (5-ClCPAI)were identified and analyzed by using ^{1}H-NMR,mass spectrum ,FT-IR ,UV-Vis ,XRD, SEM and EDX

The membranes of ligand prepared of concentration of (0.05,0.1,0.3) M membrane pure and doped of 10%Zno of concentration (0.05M) was prepared of membranes with thikness (1000 ±10) nm the preparation of membranes by method spray pyrolysis .

The study of optical properties of membranes pure and doped study spectral of absorbance and transmittance within the wavelength (200-800)nm, the results show of the transmittance decrease of the molar concentration increase and doped and the absorbance increase with increase molar concentration and doped and energy band gap decrease with increase molar concentration and doping , the study of structure properties of the membranes prepared through(XRD) where the results show membranes multiple crystallization and preferred trend of growth is (101) particle

Key words: Azo imidazole , Thin films , Spray pyrolysis .

1- Introduction

Azo compounds: these compounds are made up of two homogenous or heterogeneous group that are bound by the azo group on both ends, (1) this type structures characterized by its high stability(2) , this is due to the double bond between the two nitrogen atoms of the azo group(3) they are commonly used as reagents because of their properties and multi –use properties due to their high stability and rapid reaction with metal ions as well as their high sensitivity and selectivity(4) , azo imidazole compounds are characterized by being heterogeneous compounds and contain nitrogen and carbon catalyst that contribute to the alignment with the transition element(5) , one of the most important uses of azo imidazole compound is use in spectral mapping to estimate the very small quantities of transitional element(6) , as such imidazole compounds are use in pharmaceutical preparation(7) , such as anti fungal agents , the hetrocyclic of azo dye imidazole compounds of the important in in spectral of determination of filed the trace amount elements of metal ions because of azo dye high selectivity(8) , the present work we report the preparation and spectral identification of new heterocyclic cyclic of new azo dye ligand 2- (2-(5-chloro carboxyl phenyl)azo)imidazole (5-Cl CPAI) the present study report the preparation and spectral characterization of new azo imidazole ligand (5-ClCPAI)), the term thin film is used to describe layer or several layers of atoms of ascertain substance whose thickness less than 1um ,thin film application in electronic resistances(9) , transistor and solar cell ,spray pyrolysis is versatile technique for deposition of ligand (5-ClCPAI) because of its cheapness and process control which gives the possibility of obtaining films(10) .

2- Experiment

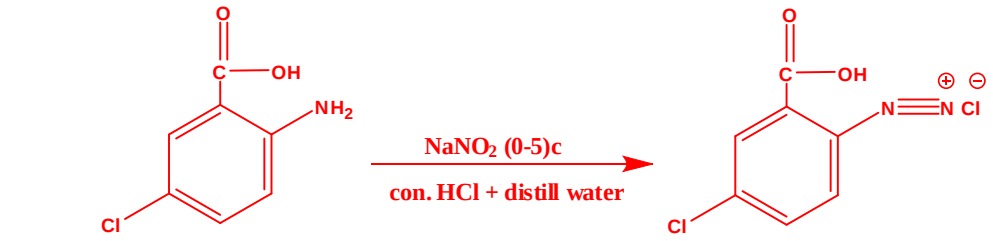
2-1 **Chemicals and method**

All chemicals used the work are the 2-amino-5-chloro benzoic acid, imidazole, NaOH , HCl, $NaNO_2$ and ZnO produced by (Sigma ,Fluka and Aldrich) company , In addition to use of ethanol ,DMSO,DMF and THF as a solvent ,azo dye ligand (5-ClCPAI) characterized by analytical data. H-NMR spectra were recorded in DMSO-d6 on a bruker 300 MHZ spectrophotometer using TMS as an internal reference ,mass spectrum was obtained using shimadzu Agilent technoliges , the IR spectra of azo dye ligand recorded in KBr medium using shimadzu 8400 FT_IR spectrophotometer in wave number at rang (4000-400) cm-1 , x-ray diffraction (XRD)technigue using a shimadzu x-ray diffractometer with CuK_(k=1.5418°A) radiation for 2theta values in the rang of 20–60° ,the electronic spectra of ligand and thin film ligand were recorded on a shimadzu double beam UV-Vis spectrophotometer the range of (200-1100)nm in absolute ethanol solution , scanning electron microscopy (SEM) images of azo dye ligand using micrograph zeiss em 3200,energy dispersive-x-ray (EDX) of azo dye ligand .

2-2 **Synthesis of azo dye ligand(5-ClCPAI)**

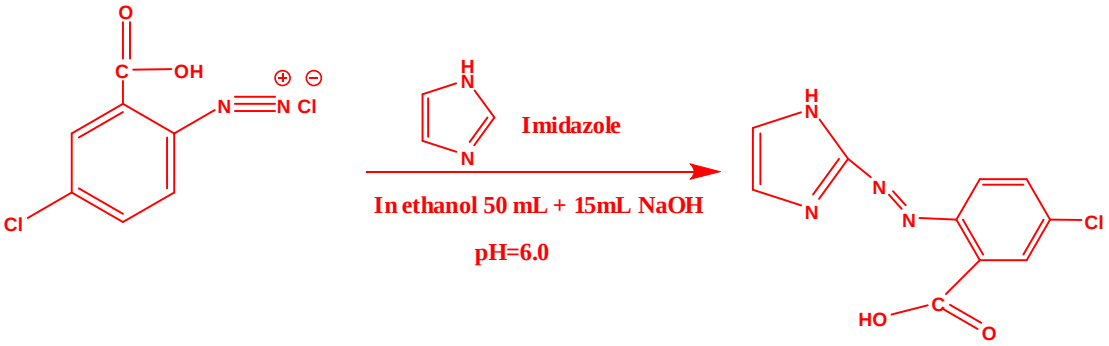
Preparation of ligand with some 1,2g (0.01mol) of 2-amino-5-chloro benzoic acid dissolved in a mixture of 5ml hydrochloric acid 30 ml distilled water and 5ml ethanol the mixture with continuous stirring and not temperature above (5 °c) the mixture added to 0.9g Sodium nitrite dissolved to 30ml distillated water added drop wise at (0-5°c) continuous stirring for 25min the added of diazunium salt solution with continuous added drop wise with cooling at (0-5°c) into 0.9g (0.012mol) of imidazol was dissolved in mixture 50ml ethanol and 10 ml Sodium hydroxide .

for coupling after had been stirring two hour at (0-5°c) to PH=6.0 the precipitate



2-Amino -5-Chloro benzoic acid

Diazonium salt



2-[2-(5-Chloro carboxy phenyl)azo] imidazol

(5-Cl CPAI)

Scheme 1.synthesis of azo dye ligand (5-ClCPAI)

3-2- Preparation of ligand (5-ClCPAI) thin films

Ligand thin films pure from a solution with different molar concentration (0.05M,0.1M,0.3M) in 100ml of deionzed water and thin film distortion of 10%ZnO of concentration(0.05M) ,thin films were prepared by spray pyrolysis , solution was sprayed with spray rates of 1ml min into preheated glass substrate at 130°C , using compressed air as acarrier gas . the nozzle to substrate distance was about 45cm . number of bribes 10 and time stop 1s .

3- **Result and discussion**

3-1 **H-NMR Spectra of ligand (5-ClCPAI)**

In the H-NMR of azo dye ligand (5-ClCPAI) used solvent DMSO and TMS internal reference the H-NMR of ligand shows a signal peak back to solvent DMSO δ=2.523ppm , singlet due to H7 into benzene ring δ=7.427ppm , singlet due to H10 into benzene ring δ=7.561-7.590 , signal due to H9 into benzene ring δ=7.739-7.747ppm , signal due to H5 into imidazole ring δ=7.767-7.775 ppm signal due to H4 into imidazole ring δ=7.837-7.845ppm, singlet peak due to H1 into imidazole ring δ=7.011ppm , singlet due to OH δ=13.191ppm .(11,12)

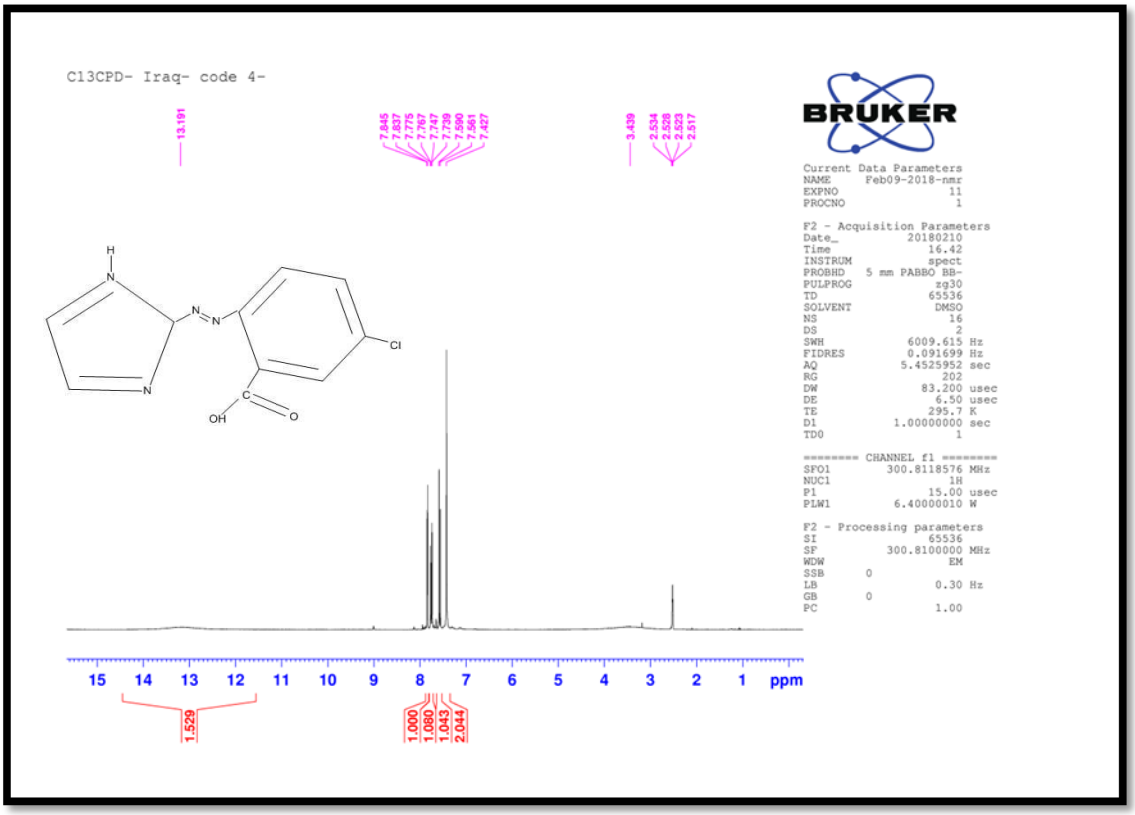


figure.1 H-NMR spectrum of azo dye ligand (5-ClCPAI)

3-2 **Mass spectra of ligand (5-ClCPAI)**

Recorded of mass spectrum of ligand (5-ClCPAI) and molecular ion peaks ,the mass spectrum of ligand(5-ClCPAI) showed peaks to the molecular ions m/z^+ at 250.9,248.8 204.9,176.9,141.0,127.9,61.9 for the structure [$C_{10}H_7N_4O_2$ Cl]

$[C_{10}H_5N_4O_2Cl]^+$, $[C_{10}H_5N_2OCl]^+$, $[C_9H_5N_2Cl]^+$, $[C_9H_5N_2]^+$, $[C_8H_4N_2]^+$, $[C_5H_2]^+$.(13,14)

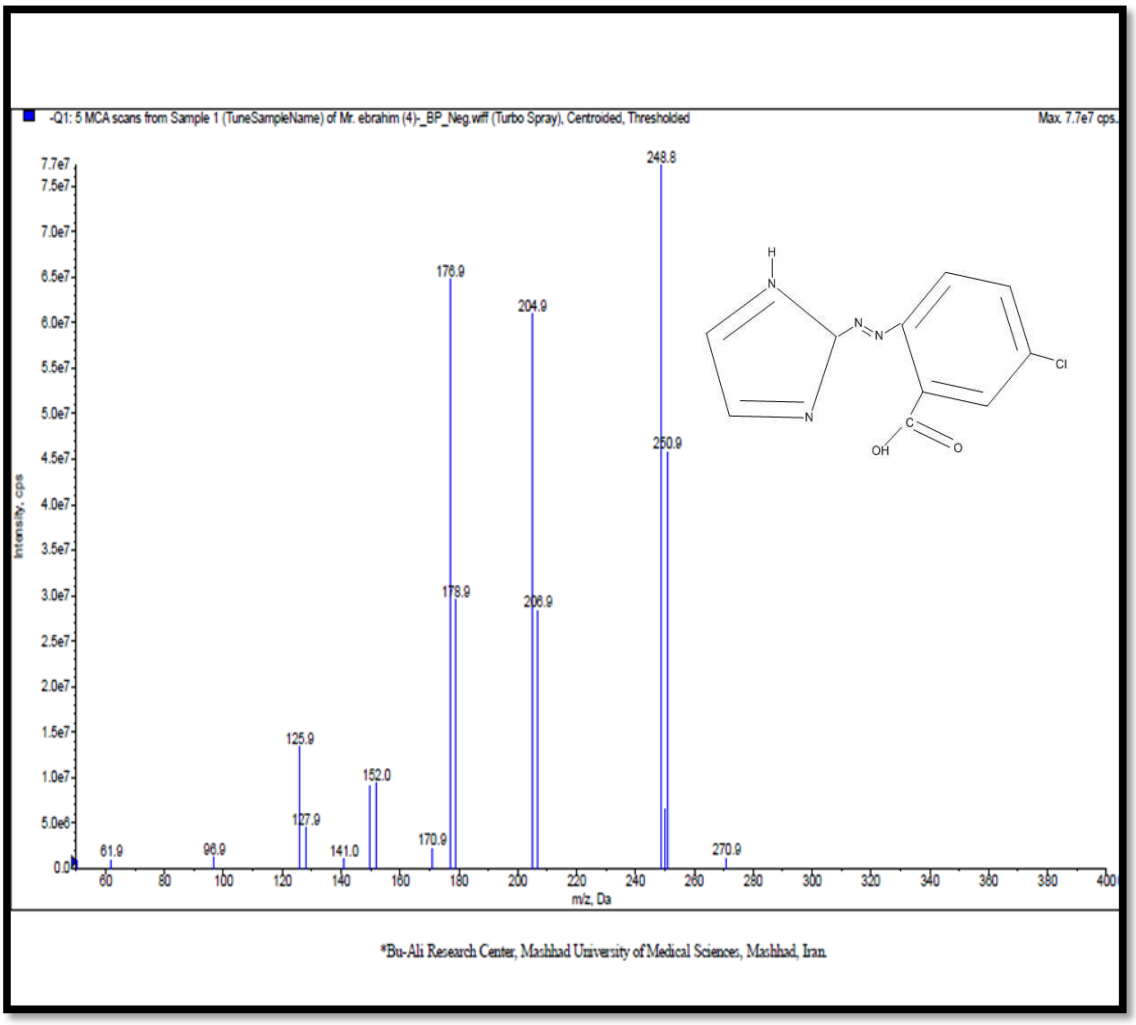
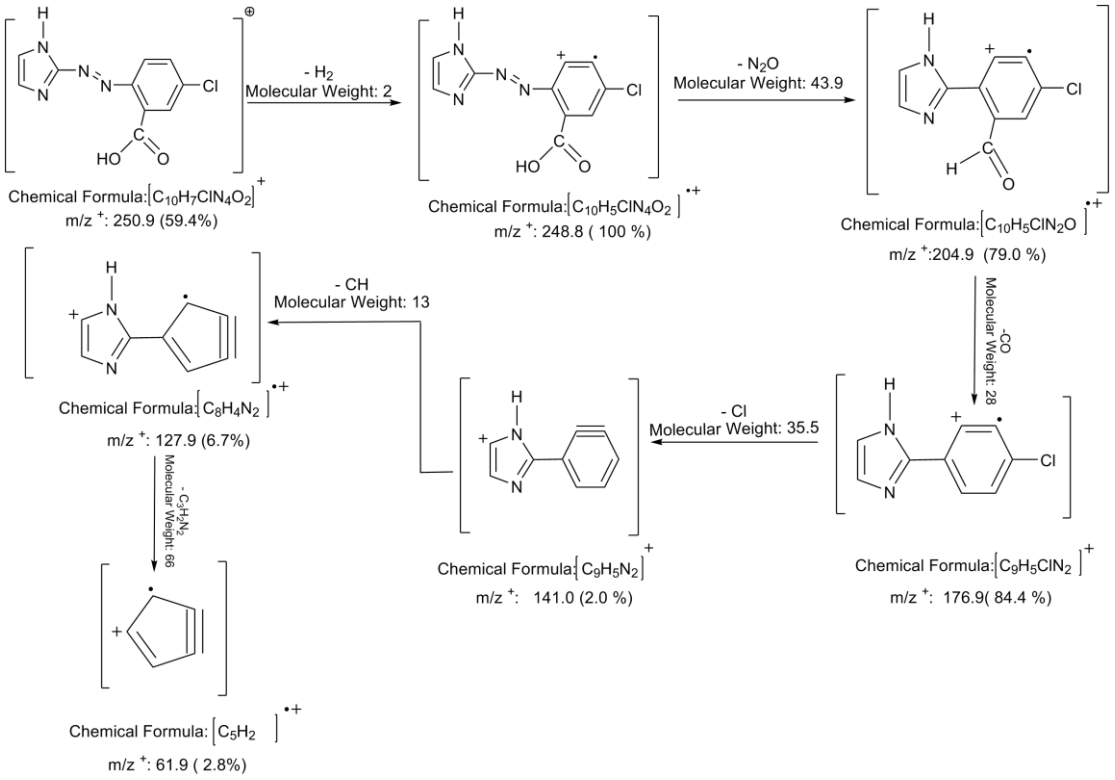


figure.2 .mass spectrum of ligand (5-ClCPAI)



figurer.3. Mass spectrum fragmentation of ligand (5-ClCPAI)

3-3 **Electronic spectral**

The electronic absorption of azo dye ligand (5-ClCPAI) and some metal complexes Co(III),Cu(II) , of the ethanol solution (0.0001M) and at room temperature ,the electronic spectrum is characterized by three absorption is band in UV-Vis these bands are appearing at the posit 256nm(41508) cm^{-1} ,296nm(30384) cm^{-1} can be attributed transition at $\pi \rightarrow \pi^*$ and band 465nm(19290) cm^{-1} can be attributed transition at $n \rightarrow \pi^*$ (15,16)this band showed at red shift on coordination with metal ions Co(III) shows three bands at 534nm(21235) cm^{-1} ,396nm(11568) cm^{-1} ,237nm(11347) cm^{-1} , the electronic spectra Cu(II)shows tree bands at 530nm(22146) cm^{-1} ,430nm (21457) cm^{-1} ,241nm(11368) cm^{-1} ,the UV-Vis spectra ligand and some metal complexes shows in figs4,5.(15,16)

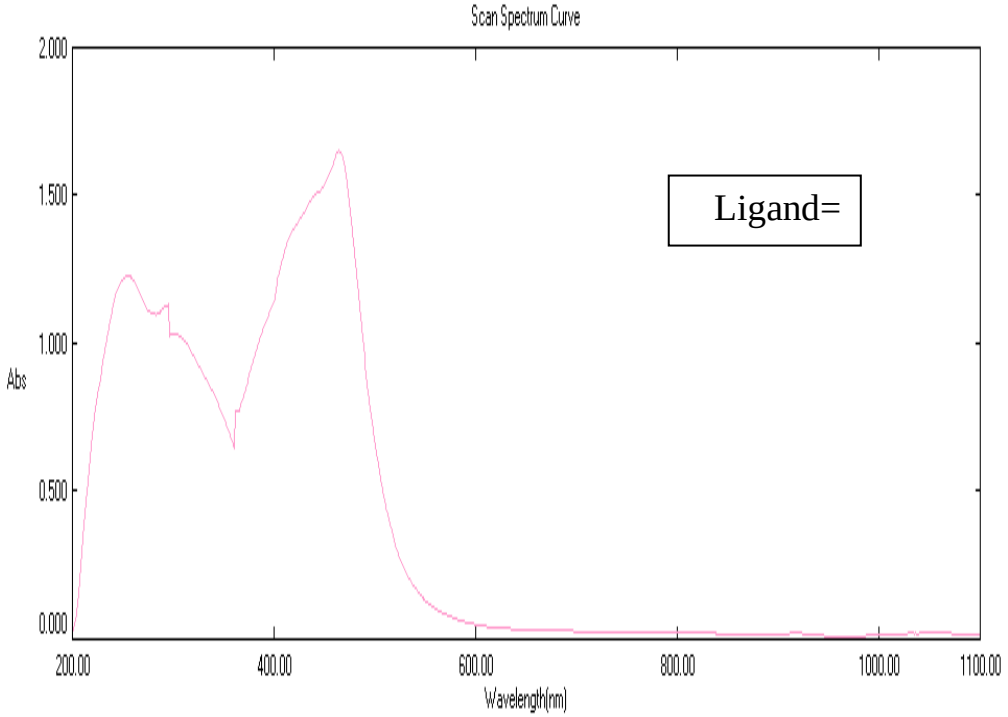


Figure.4. UV-Vis of azo dye ligand (5-ClCPAI)

3-4 **Infrared spectra**

Infrared spectral of the prepared azo dye ligand (5-ClCPAI) ,IR spectrum show absorption band in the region (3132) cm-1 due to stretching vibration (N-H) imidazole group ,disappear of (1458,1566,1149,1689,786,3411) cm^{-1} of (N=N),(C=C)aromatic (C-N),(C=O), (C-Cl) ,(O-H) carboxylic acid group.(17,18)

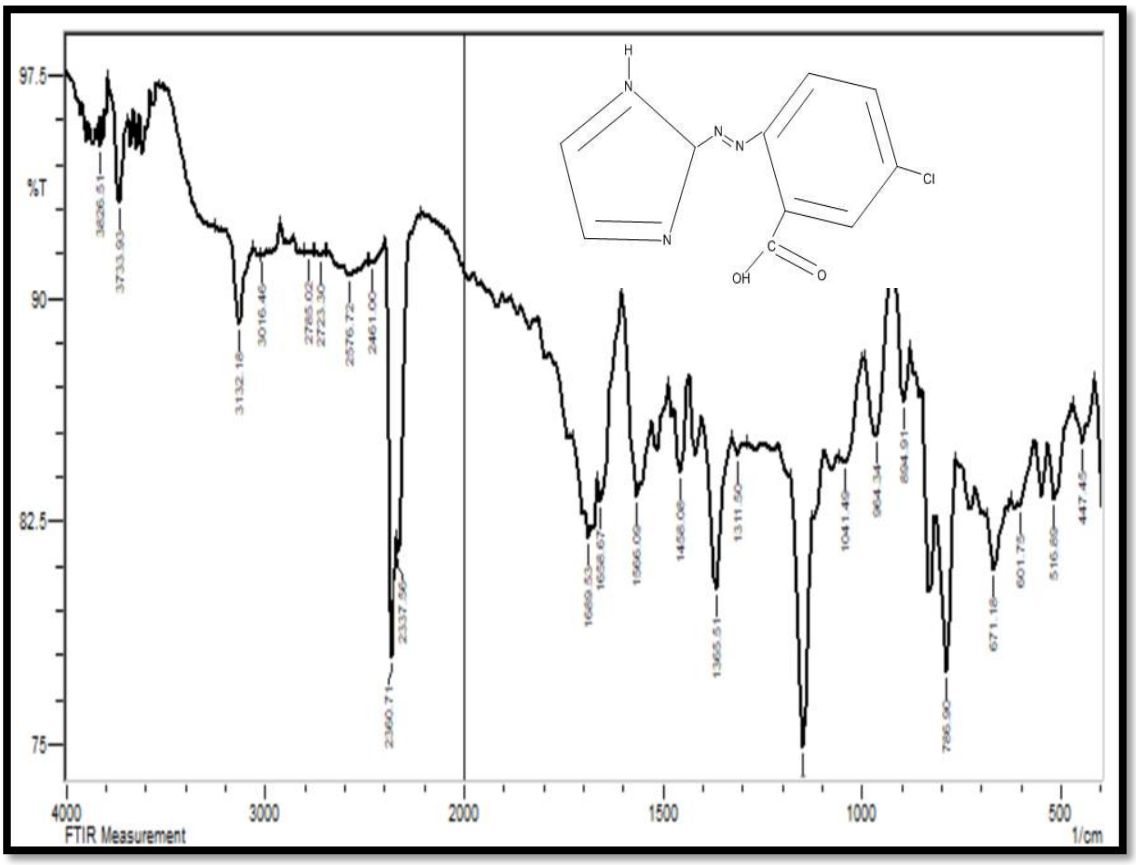


Figure.6.IR spectrum of azo dye of ligand(5-ClCPAI)

3-5 **Energy –dispersive -X-ray spectroscopy of ligand(5-ClCPAI)**

For the element analysis or chemical characterized of ligand (19)

Elements	Wight%
C	39.85
N	38.11
O	18.34
Cl	3.02

Table .3. The element found of ligand (5-ClCPAI)

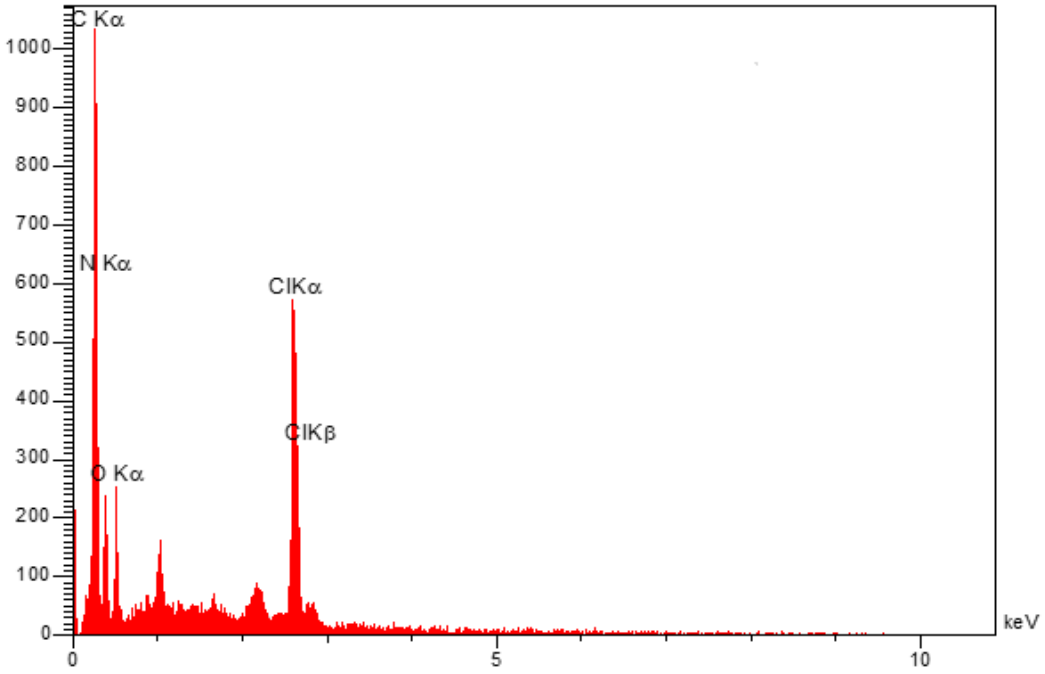


figure7. EDX of azo dye ligand(5-ClCPAI)

3-6 SEM analysis

The properties of the ligand(5-ClCPAI) like surface morphology distribution of particles aggregation and shape of the particle study by scanning electron microscopy (SEM) ,of the ligand (5-ClCPAI) have from micro flour shape with average size (32)um. (20)

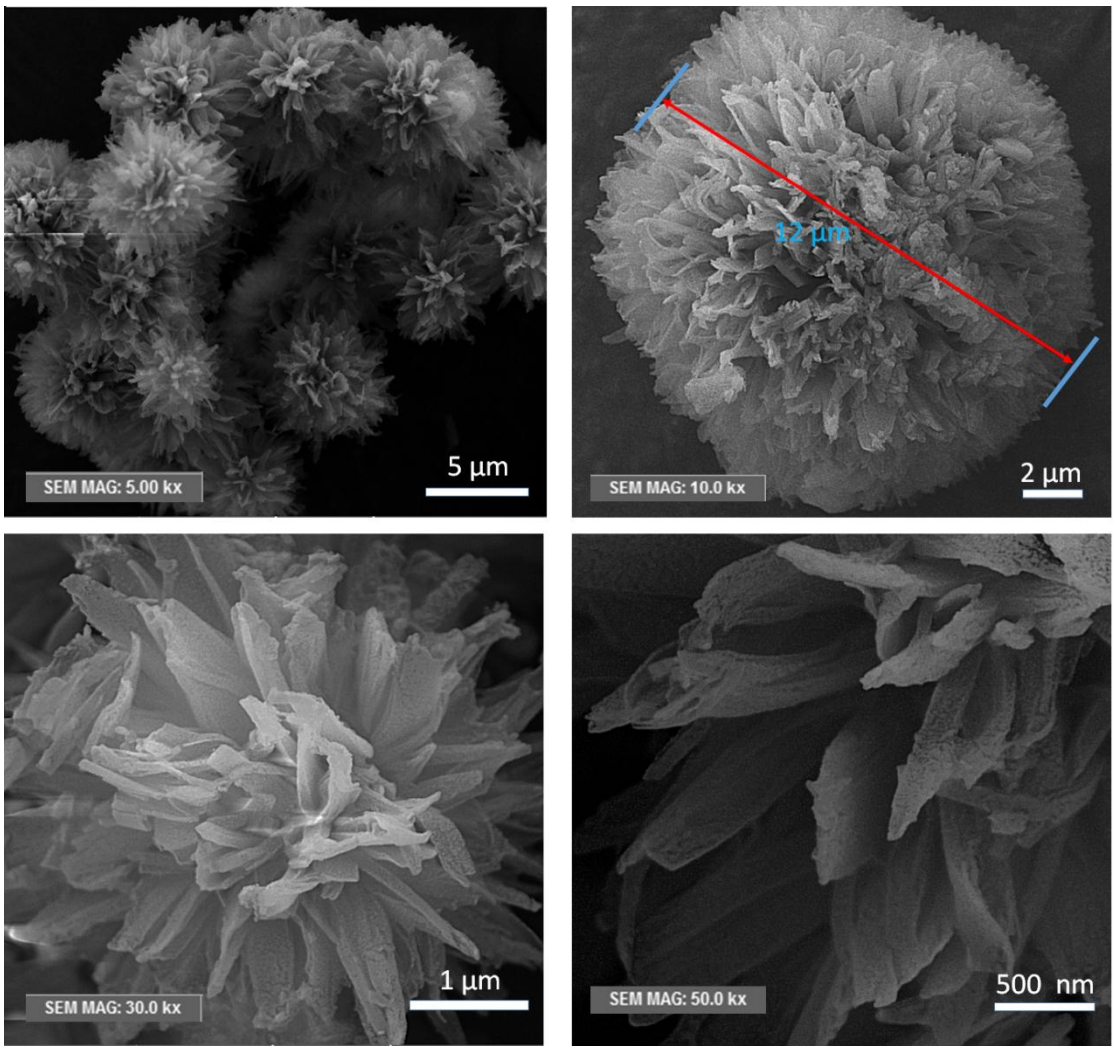


Figure.6: SEM of the ligand (5-ClCPAI)

3-7 X-Strcture properties of thin films of ligand(5-ClCPAI)

The diffraction patterns of ligand (5-ClCPAI) films deposited at 0.05M,0.1M,0.3Mand 10%ZnO of concentration 0.05M precursor concentration at substrate temperature 130°C , in nature with (101) preferred orientation ,(21), the crystallite size (D) of X-ray using Deby-sherrer formula. Equation (1) $D = \frac{k\lambda}{\beta \cos\theta}$

D is the grain size in a particular orientation, _ is the X-ray wavelength, _ is the diffraction angle
corresponding to the particular orientation, _ is the width at half maximum intensity (FWHM).

Molar Concentration (M)	2theta (degree)	FWHM (degree)	Crystallite Size D (nm)	hkl
0.05M	25.3	0.394	112	101
0.1 M	24.3	0.358	132	101
0.3M	26.2	0.325	143	101
0.05M Doping ZNO	23.9	0.376	146	101

Table:2 the crystallite size ,FWHM ,hkl ,2theta and d(A) of thin films of ligand (5-ClCPAI)

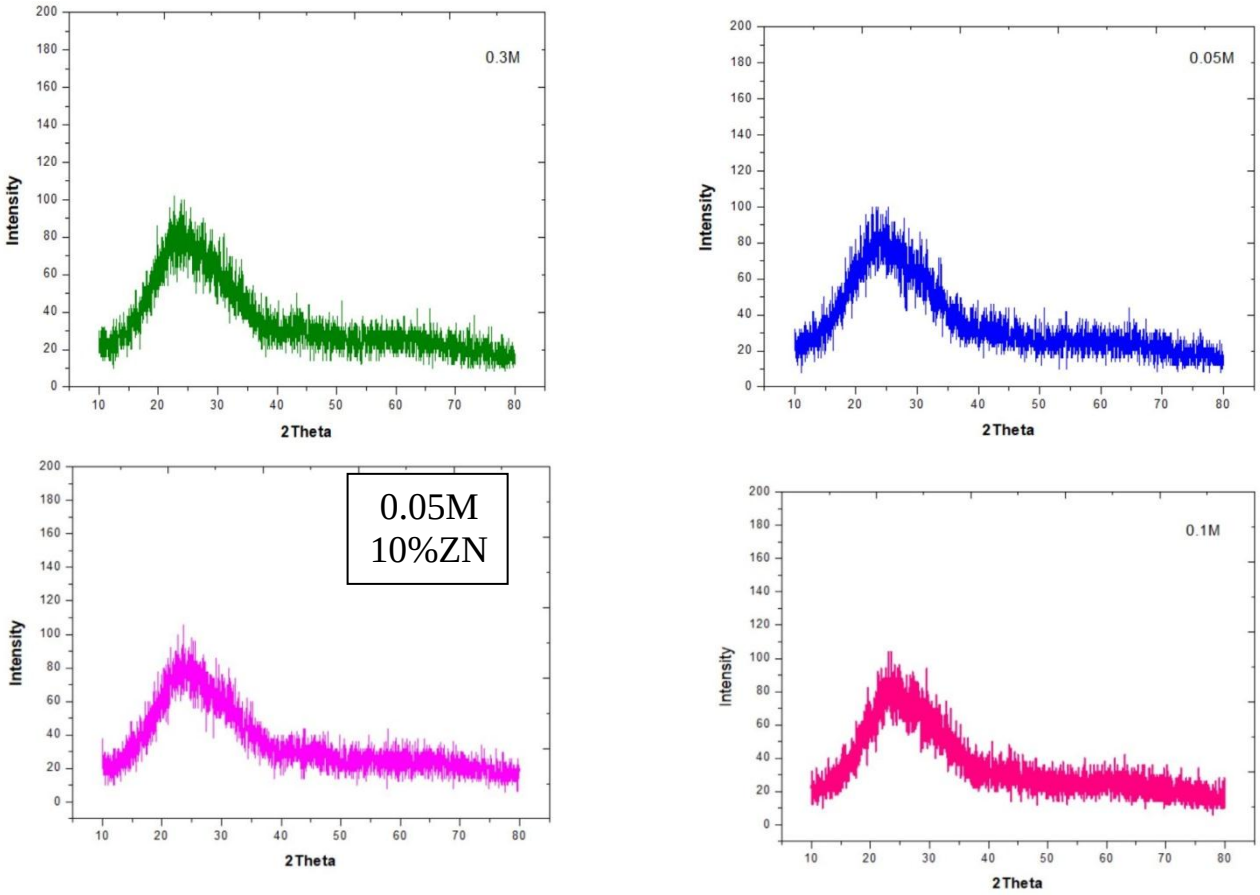


Figure:8: the (XRD) thin films of ligand(5-ClCPAI)

3-8 Optical properties of thin films of ligand(5-ClCPAI)

Transmission and absorbance curves of ligand (5-ClCPAI) thin films recorded as a function of wavelength in the range (200-

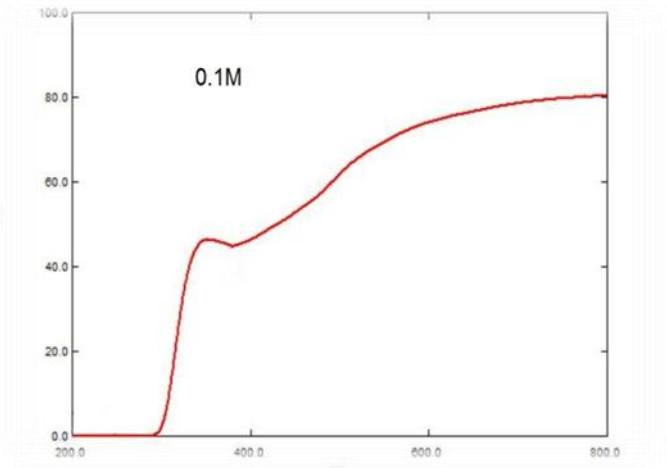
1100)nm ,the transmission goes down from 90% to 70% when concentration increased from 0.05 to 0.3 M and doping 10% ZNO , all the films are high absorbance in UV :the reduction of the transmission at high molar concentration may be attributed to the increased scattering of photons by increased of the roughness of the surface morphology .(22)

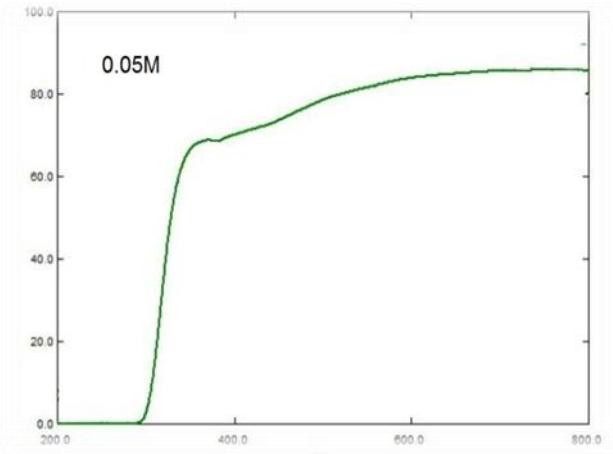
The optical band gap was determine using equation:

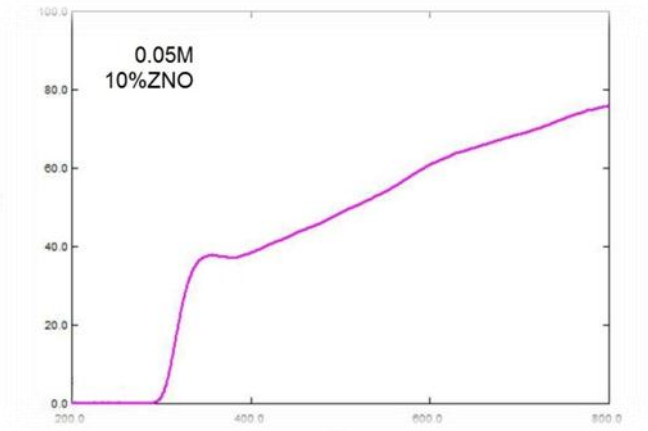
$$(ah)^2=C(h-Eg),..(2)$$

C is a constant; h is the photon energy and Eg is the optical band gap. The optical absorption coefficient (a)

The energy band gap decreased with increased molar concentration and doping 10% ZnO ,the energy band gap decrease from 3.21 to 3.021 ev , the band gap decrease with increase molar concentration and doping due to decrease in strain values . has been demonstrated earlier the correlation between the direct band gap and the compressive stress of the ligand thin films(23) .







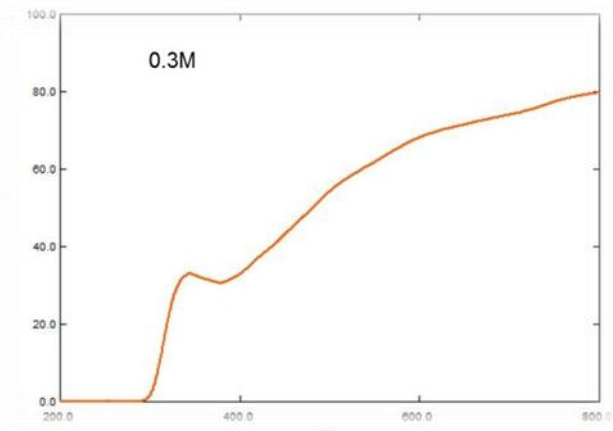
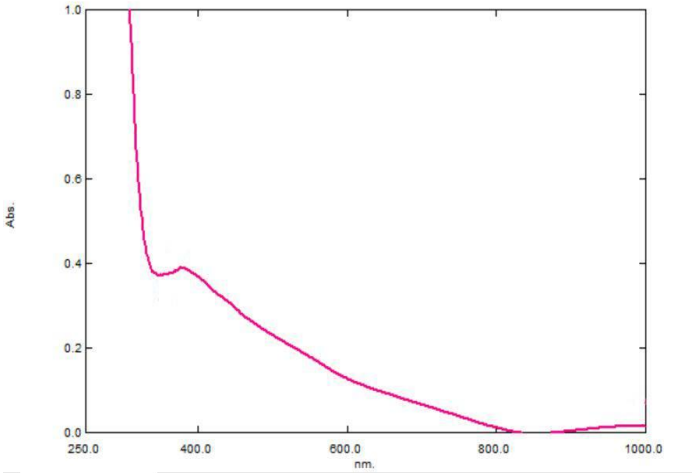
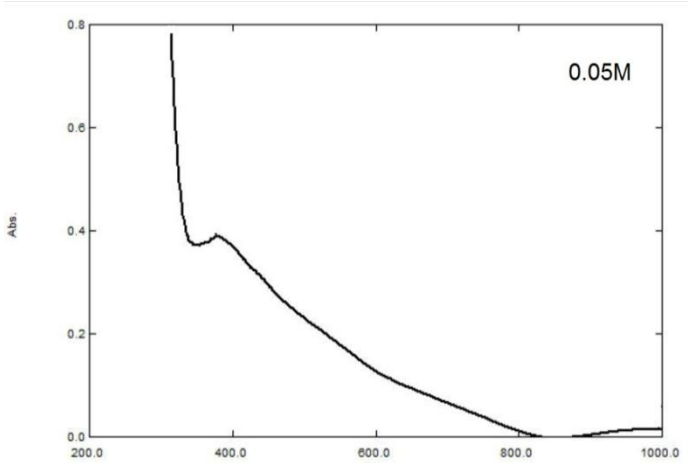
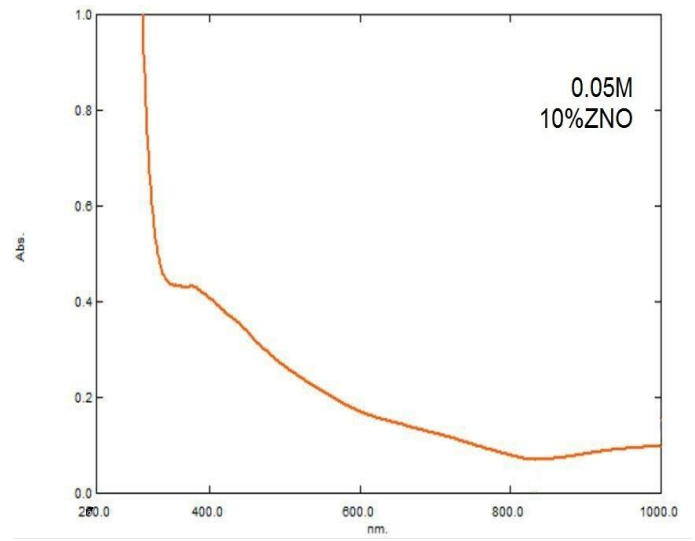


Figure 9.the transmission spectral thin films of ligand







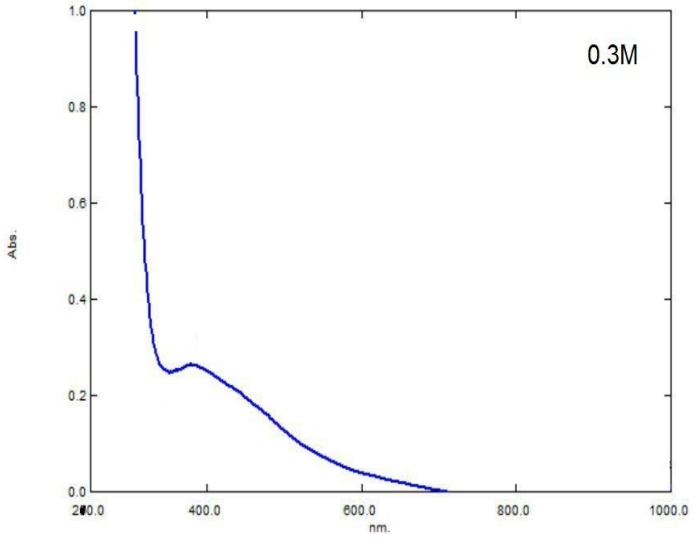


Figure 10.the absorbance spectral thin films of ligand

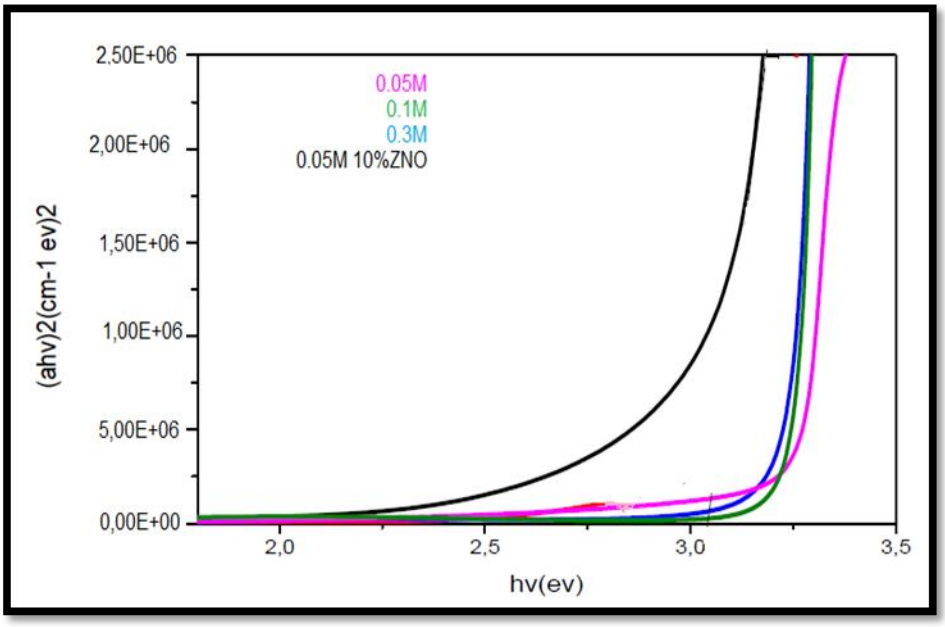


Figure 11.the energy band gap thin films of ligand

Concentration (M)	Eg (eV)
0.05M	3.218
0.1M	3.194
0.3M	3.125
0.05:10%ZnO doped	3.047

Table 3.energy band gap with different molar concentration and doping

4- Conclusion

We have synthesized of azo dye ligand (5-ClCPAI) derived from imidazole and the spectroscopy of ligand by analytical data. Mass spectrum ,H-NMR, FT-IR, electronic spectra and EDX ,SEM, the ligand (5-ClCPAI) thin films were deposited by a simple and cheap method spray pyrolysis. The X-ray diffraction show that films have a polycrystalline structure
with an orientation the (101) , The optical measurements have show a decrease in the transmission T (%) with an increase in
the molar concentration due to the surface roughness. The band gap values were decreased from 3.2 4 eV to
3.01 5 eV as molarity of increased for 0.05 M to 0.3 M and doping .

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