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Studying of Optical and Structural Properties of a Novel Ligand (5-ClCPAI) Thin Films by Spray Pyrolysis Method

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Abstract: The study includes 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 0.05 M was prepare 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, XRD, membranes, wavelength

INTRODUCTION

Azo dyes are organic substances made up of two organic groups that are connected by the reaction coupling with azo group to give colored compounds absorbed in UV-Vis region has been discovered debuty by Peter year 1888 (Khammas *et al*., 2015) this type structures characterized by its high stability (Pellei *et al*., 2018) this is due to the double bond between the two nitrogen atoms of the azo group (Samal *et al*., 2018) 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 (Patel and Patel, 2018), 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 (Chung, 2016) such as anti fungal agents, the hetrocyclic of azo dye imidazole compounds of the important in spectral of determination of filed the trace amount elements of metal ions because of azo dye high selectivity (Al-Hamdani and Hasan, 2016), the present study 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-ClCPAI) 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 <1 μm, thin film application in electronic resistances (Habiban *et al*., 2015), 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 (Emwanta *et al*., 2018).

MATERIALS AND METHODS

Chemicals and method: All chemicals used the work are the 2-amino-5-chloro benzoic acid, imidazole, (NaOH), (HC_l), ($NaNO_2$) 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. ^{1}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 FTIR spectrophotometer in wave number at rang 4000-400 cm^{-1},

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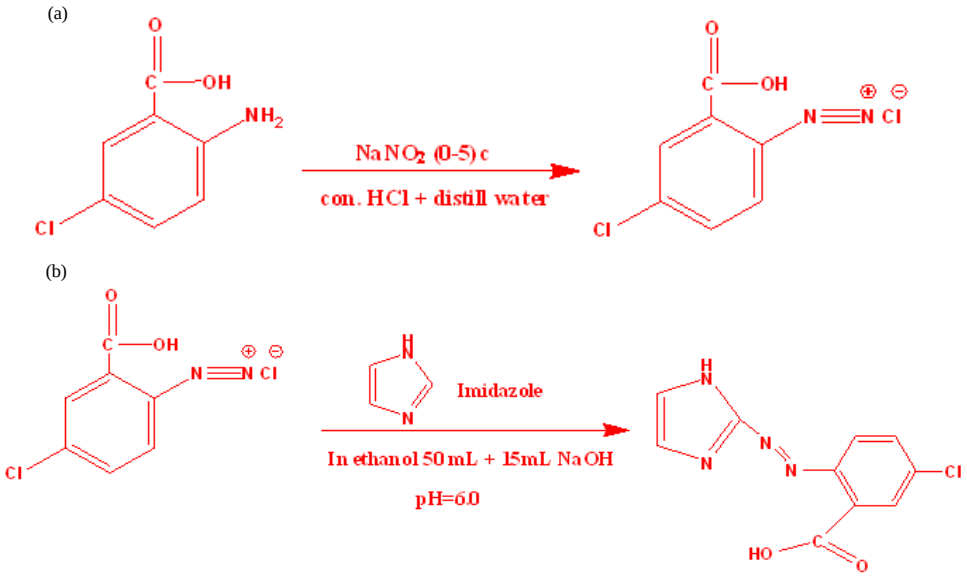

Fig. 1: Synthesis of azo dye ligand (5-ClCPAI); a) Amino-5-chloro benzoic acid and diazonium salt and b) [2-(5-Chloro carboxy plenyl)azo] imidazol (5-CICPAI)

X-Ray Diffraction (XRD) technigue using a Shimadzu X-ray diffractometer with CuK_(k = 1.5418°A) radiation for 2θ 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.

Synthesis of azo dye ligand (5-ClCPAI) 2-2: Preparation of ligand with some 1, 2 g (0.01 mol) of 2-amino-5-chloro benzoic acid dissolved in a mixture of 5 mL hydrochloric acid 30 mL distilled water and 5 mL ethanol the mixture with continuous stirring and not temperature above 5°C the mixture added to 0.9 g sodium nitrite dissolved to 30 mL distillated water added drop wise at (0-5°C) continuous stirring for 25 min the added of diazunium salt solution with continuous added drop wise with cooling at (0-5°C) into 0.9 g (0.012 mol) of imidazol was dissolved in mixture 50 mL ethanol and 10 mL sodium hydroxide. For coupling after had been stirring 2 h at 0-5°C- pH = 6.0 the precipitate (Fig. 1).

Preparation of ligand (5-ClCPAI) thin films: Ligand thin films pure from a solution with different molar concentration (0.05, 0.1, 0.3 M) in 100 mL of deionzed water and thin film distortion of 10% ZnO of concentration (0.05 M), thin films were prepared by spray pyrolysis, solution was sprayed with spray rates of 1 mL min into preheated glass substrate at 130°C, using compressed air as acarrier gas. The nozzle to substrate distance was about 45 cm number of bribes 10 and time stop 1 sec.

RESULTS AND DISCUSSION

H-NMR spectra of ligand (5-ClCPAI) 3-1: In the spectrum of ^{1}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 = 2.523 ppm, singlet due to H_7 into benzene ring δ = 7.427 ppm, singlet due to H_{10} into benzene ring δ = 7.561-7.590, signal due to H_9 into benzene ring δ = 7.739-7.747 ppm, signal due to H_5 into imidazole ring δ = 7.767-7.775 ppm signal due to H_4 into imidazole ring δ = 7.837-7.845 ppm, singlet peak due to H_1 into imidazole ring δ = 7.011 ppm, singlet due to OH δ = 13.191 ppm (Di Santo *et al*., 2017; Al-Adilee and Kyhoiesh, 2017).

Mass spectra of ligand (5-ClCPAI) 3-2: 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 $[C_{10}H_7N_4O_2Cl]$ $[C_{10}H_5N_4O_2Cl]^+$ $[C_{10}H_5N_2OCl]^+$, $[C_9H_5N_2Cl]^+$, $[C_9H_5N_2]^+$, $[C_8H_4N_2]^+$, $[C_5H_2]^+$ (Orojloo *et al*., 2015; Al-Adilee *et al*., 2013) (Fig. 2 and 3).

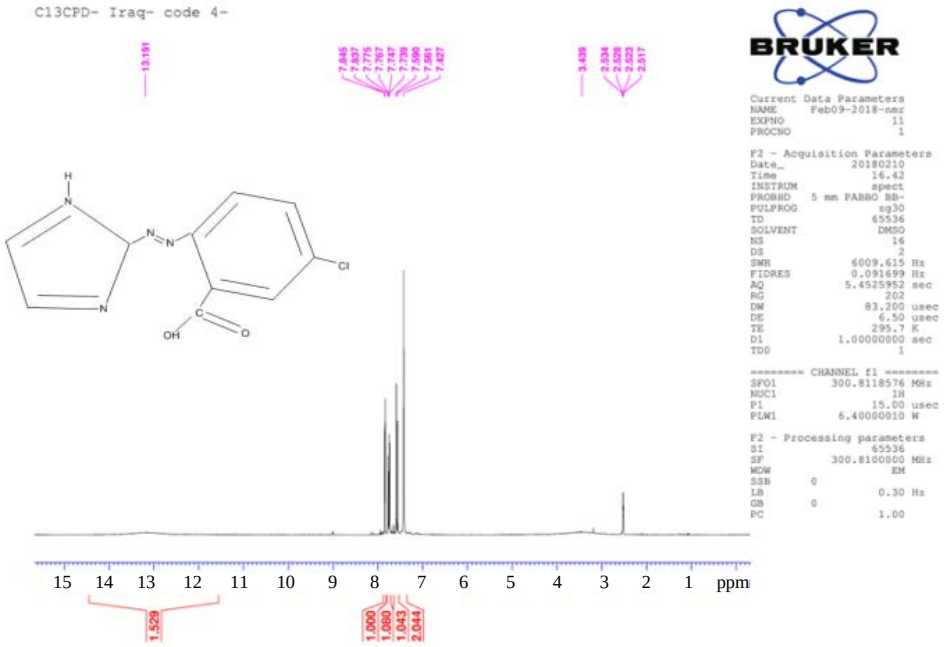

Fig. 2: H-NMR spectrum of azo dye ligand (5-ClCPAI)

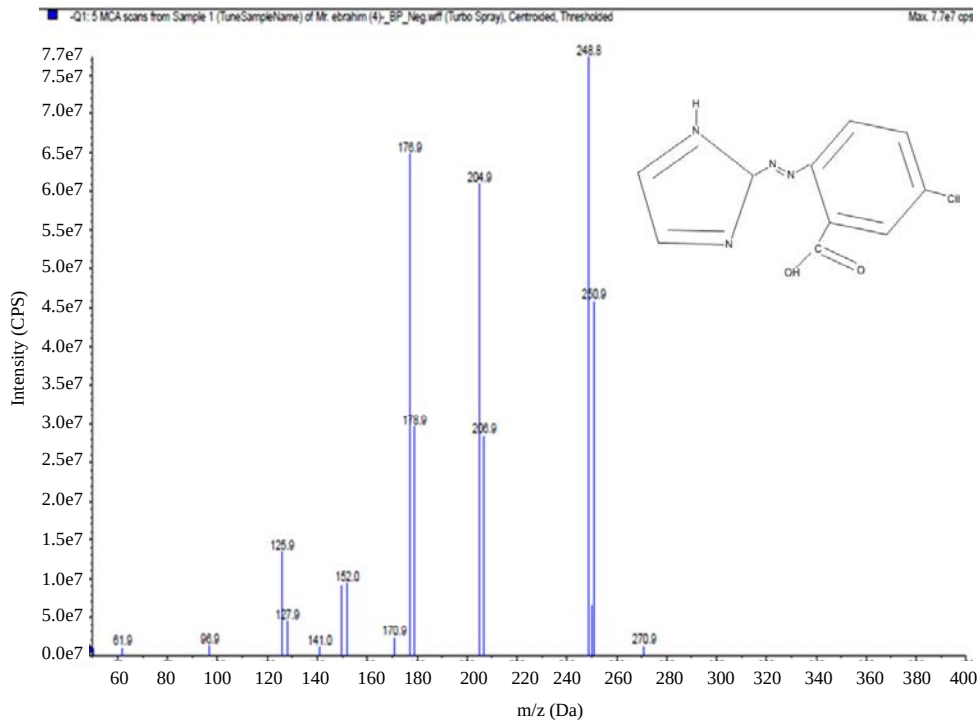

Fig. 3: Mass spectrum of ligand (5-ClCPAI); *Bu-Ali Research Centre, Mashhad University of Medical Sciences, Mashhad, Iran

Electronic spectral 3-3: The electronic absorption of azo dye ligand (5-ClCPAI) and some metal complexes Co(III), Cu(II), of the ethanol solution (0.0001 M) and at room temperature, the electronic spectrum is characterized by three absorption is band in UV-Vis these bands are appearing at the posit 256 nm 41508 cm^{-1}, 296 nm 30384

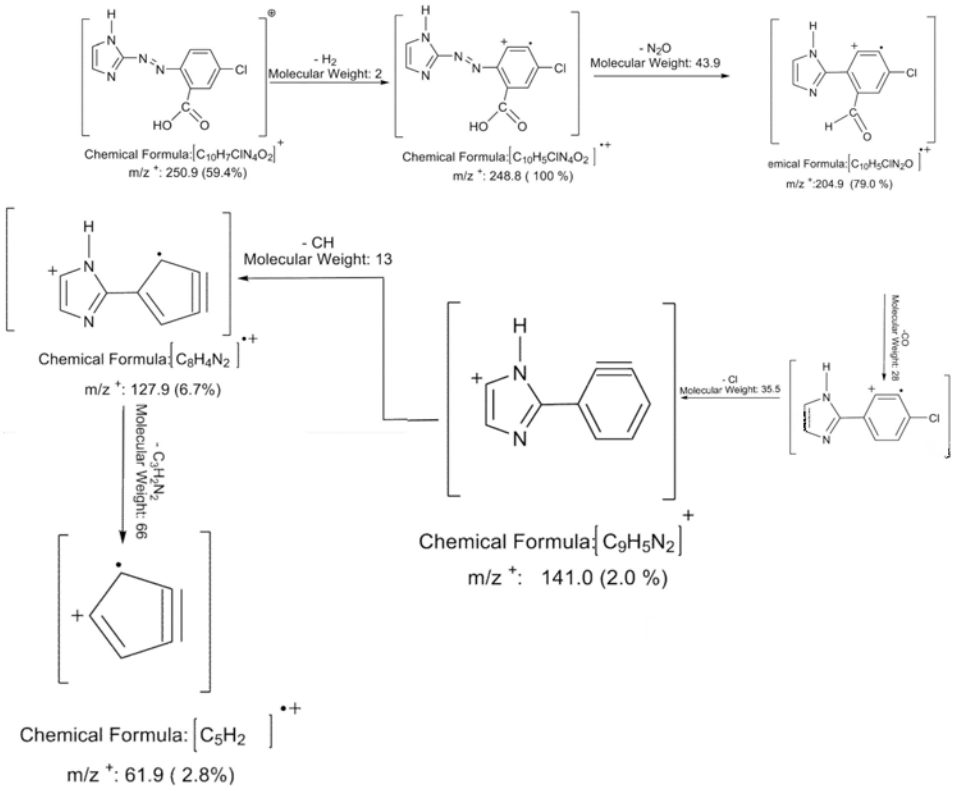

Fig. 4: Mass spectrum fragmentation of ligand (5-ClCPAI)

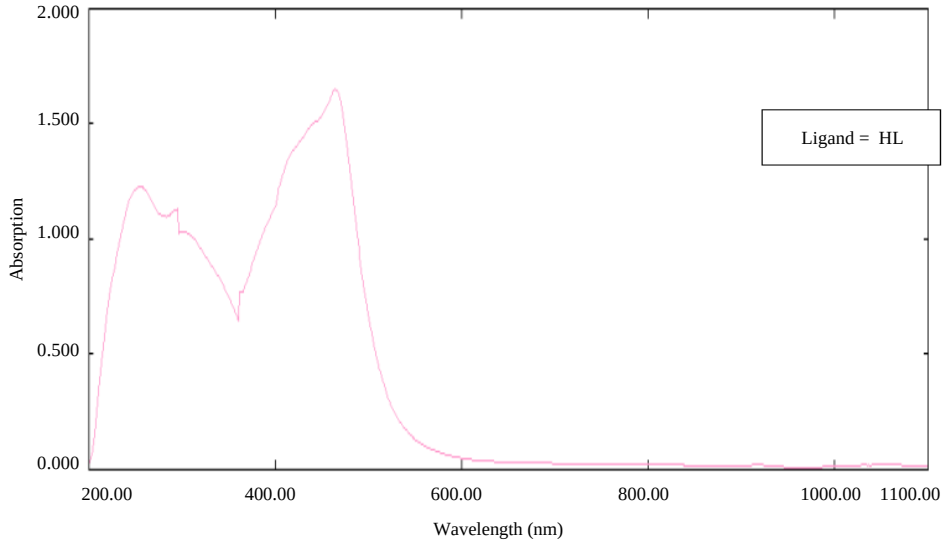

Fig. 5: UV-Vis of azo dye ligand (5-ClCPAI); Scan spectrum curve

cm^{-1} can be attributed transition at $\pi \rightarrow \pi^*$ and band 465 nm 19290 cm^{-1} can be attributed transition at $n \rightarrow \pi^*$ (Mostafa *et al*., 2013; Khan *et al*., 2018) this band showed at red shift on coordination with metal ions Co(III) shows 3 bands at 534 nm 21235 cm^{-1}, 396 nm 11568 cm^{-1}, 237 nm 11347 cm^{-1}, the electronic spectra Cu(II) shows tree bands at 530 nm (22146) cm^{-1}, 430 nm 21457 cm^{-1}, 241 nm 11368 cm^{-1}, the UV-Vis spectra ligand and some metal complexes shows in Fig. 4 and 5 (Mostafa *et al*., 2013; Khan *et al*., 2018).

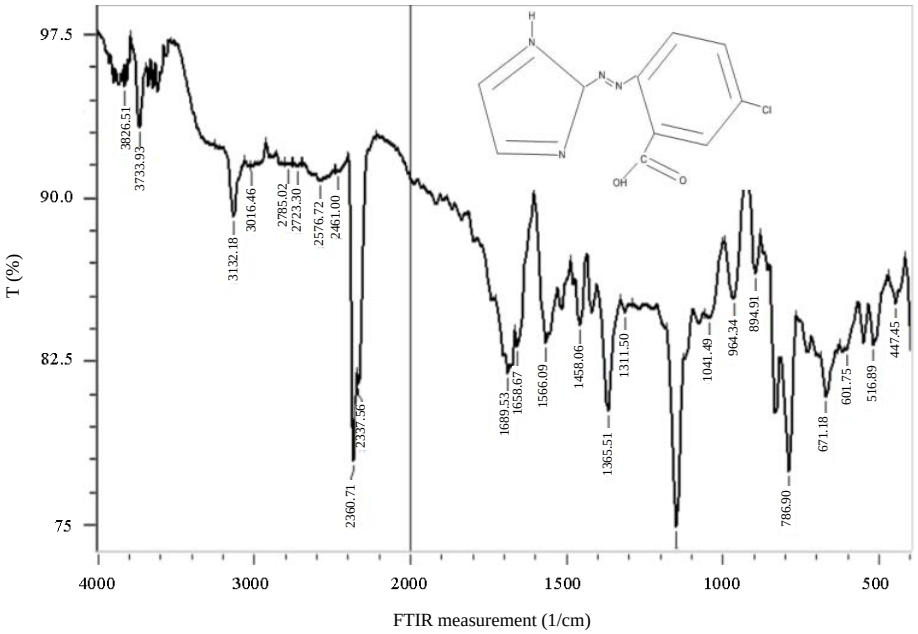

Fig. 6: IR spectrum of azo dye of ligand (5-ClCPAI)

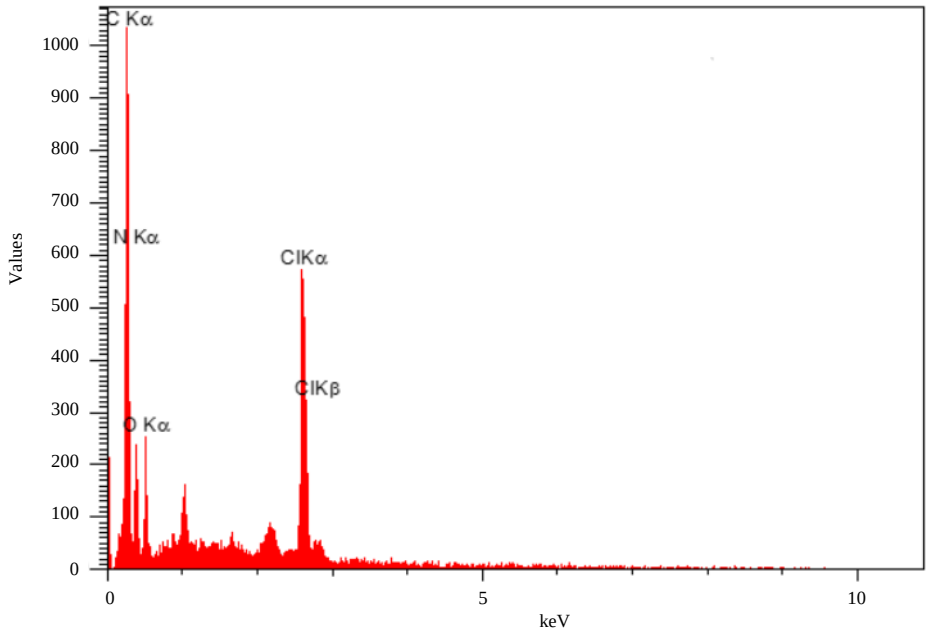

Fig. 7: EDX of azo dye ligand (5-ClCPAI)

Infrared spectra 3-4: 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 (Zhang *et al*., 2017; Al-Adilee and Fanfon, 2012) (Fig. 6 and 7, Table 1).

Table 1: The element found of ligand (5-ClCPAI)

Elements	Weight (%)
C	39.85
N	38.11
O	18.34
Cl	3.02

Energy dispersive-X-ray spectroscopy of ligand (5-ClCPAI) 3-5: For the element analysis or chemical characterized of ligand (Direm *et al*., 2018).

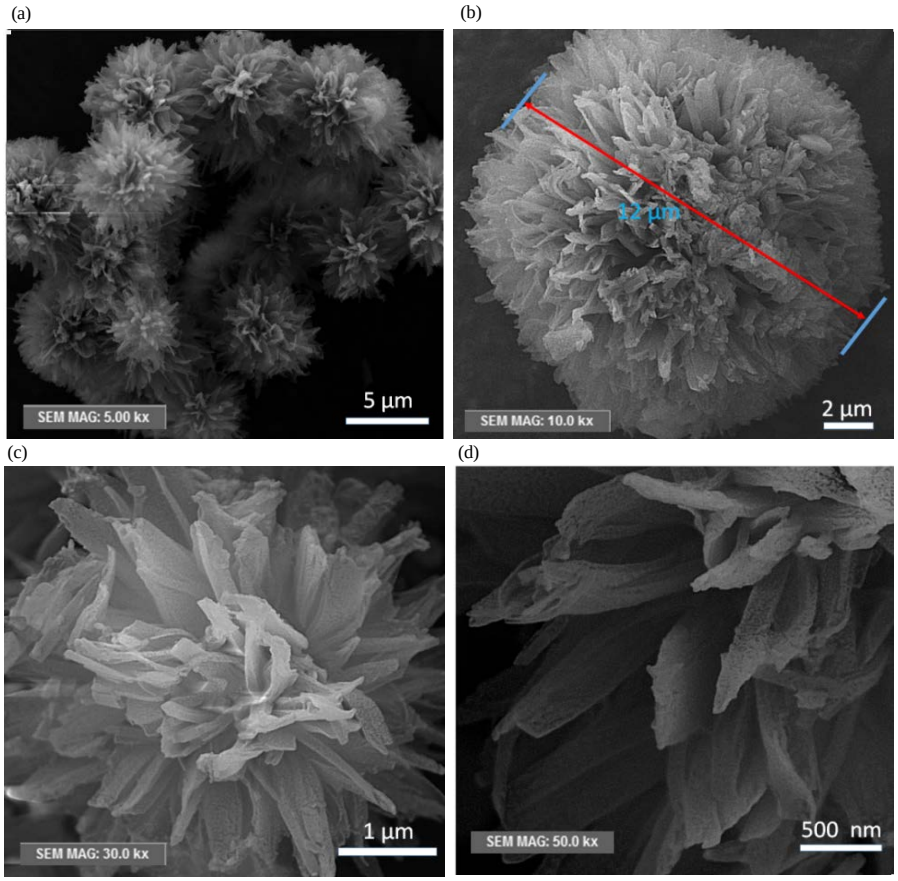

Fig. 8a-d): SEM of the ligand (5-CICPAI)

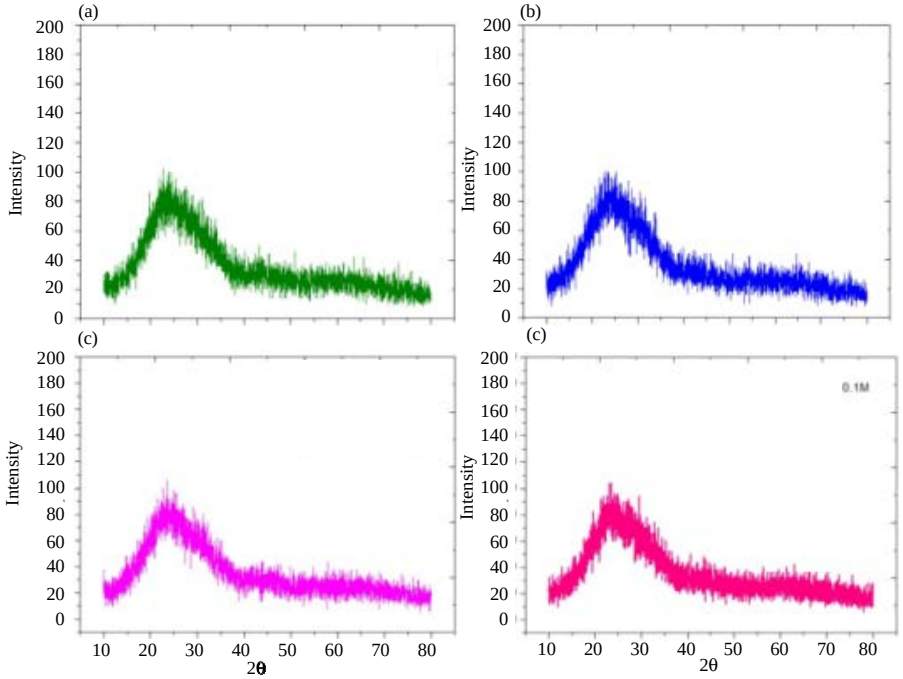

Fig. 9: The (XRD) thin films of ligand (5-ClCPAI); a) 0.3 M; b) 0.05 M; c) 0.05 M (10% ZnO) and d) 0.1 M

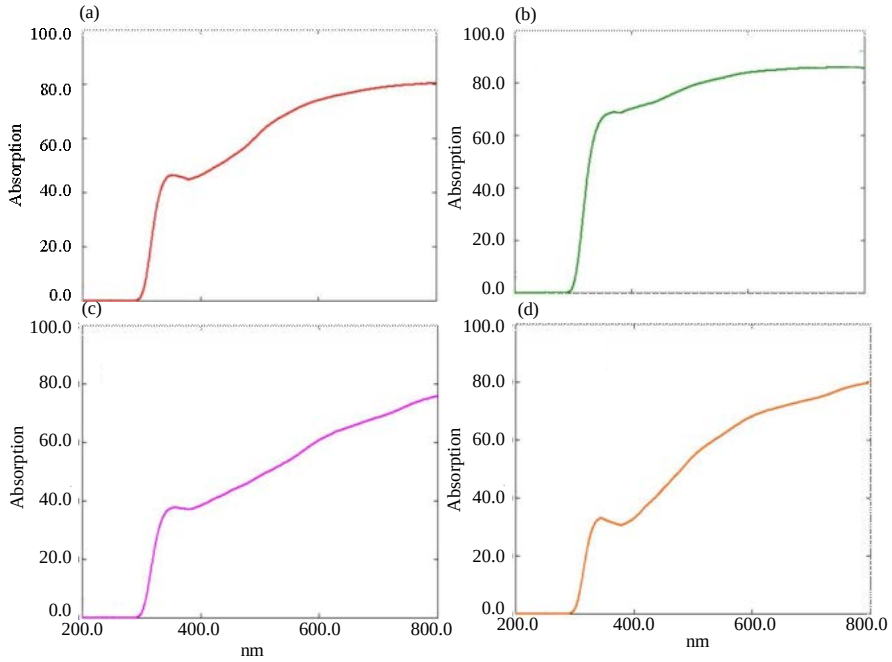

Fig. 10: The transmission spectral thin films of ligand: a) 0.1 M; b) 0.05 M; c) 0.05 M (10% ZnO) and d) 0.3 M

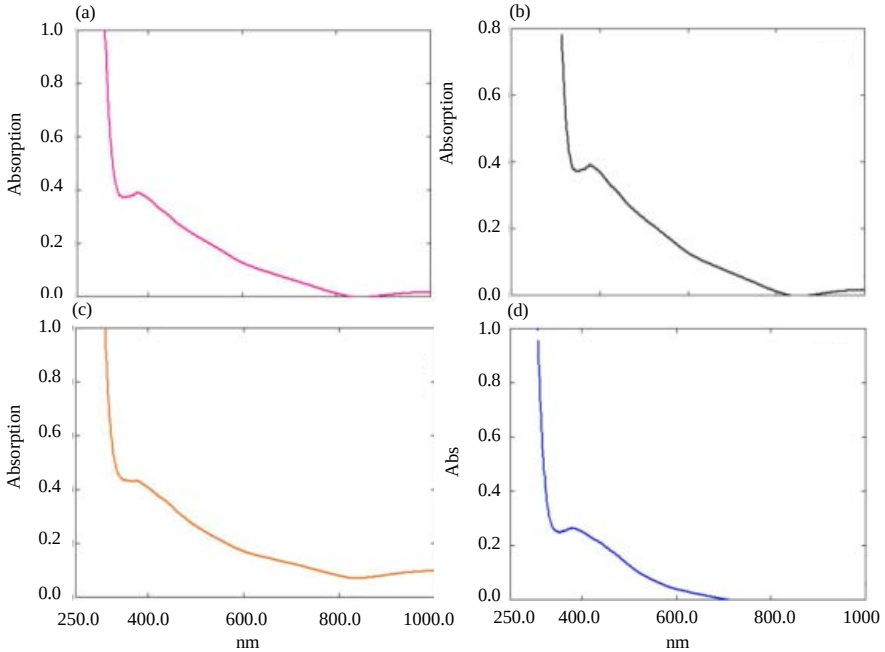

Fig. 11: The absorbance spectral thin films of ligand: a) 0.1 M; b) 0.05 M; c) 0.05 M (10% ZnO) and d) 0.3 M

Strcture properties of thin films of ligand (5-ClCPAI) 3-7: The diffraction patterns of ligand (5-ClCPAI) films deposited at 0.05, 0.1, 0.3 M and 10% ZnO of concentration 0.05 M precursor concentration at substrate temperature 130°C in nature with (101) preferred orientation (Wang *et al*., 2017), the crystallite size (D) of X-ray using Debye-scherrer formula Eq. 1 (Fig. 8-11 and Table 2):

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

Molar concentration (M)	2θ (°)	FWHM (°)	Crystallite size D (nm)	hkl
0.05	25.3	0.394	112	101
0.1	24.3	0.358	132	101
0.3	26.2	0.325	143	101
0.05 Doping ZnO	23.9	0.376	146	101

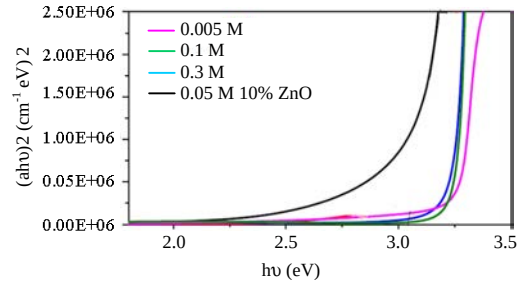

Fig. 12: The energy band gap thin films of ligand

Table 3: Energy band gap with different molar concentration and doping

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

$$D = \left|\frac{k\lambda}{\beta\cos\theta}\right| \quad (1)$$

Where:

D = Grain size in a particular orientation
λ = X-ray wavelength
θ = Diffraction angle corresponding to the particular orientation
$\beta\cos$ = Width at Half Maximum intensity (FWHM)

Optical properties of thin films of ligand (5-ClCPAI) 3-8: 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 90-70% when concentration increased from 0.05-0.3 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 (Mostafa *et al*., 2018). The optical band gap was determine using Eq. 2 (Fig. 12 and Table 3):

$$(ah)^2 = C(h\text{-}E_g) \quad (2)$$

Where:

C = A constant
h = The photon energy
E_g = 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 gaps decrease from 3.21-3.021 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 (Moon *et al*., 2018).

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 4-3.01 5 eV as molarity of increased for 0.05-0.3 M and doping.

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