TEST Engineering & Management

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

Optical properties of the novel ligand (5-ClCPAI) thin films Prepared by spray pyrolysis method

[1]Raheem Abed Jeber, [2]Alaa Hussien Ali, [3]Mustafa Ali Abbas
[1] University of Al-Qadisiyah ,college of Dentistry
[2] University of Al-Qadisiyah, Diwaniya, Iraq
[3] University of Al-Qadisiyah, College of Education, Department of Physics

Article Info
Volume 83
Page Number: 9163 – 9173
Publication Issue:
May - June 2020

Abstract:
This research consist of synthesized of heterocyclic compounds derivatives the novel from imidazole of the ligand: 2-[2-(5-Chloro carboxyl phenyl) azo]-imidazole and the identification of ligand (5-ClCPAI) were identification and analyzed by using Nuclear magnetic resonance (^{1}H-NMR), Mass spectrometry (MS), Ultraviolet visible (UV), Fourier transform infrared (FTIR), X-ray diffraction analysis (XRD) and Scanning electron microscopy-Energy dispersive X-Ray spectroscopy (SEM-EDS). Thin films of ligand prepared of concentration of (0.05, 0.1, 0.3)M membrane pure and doped of 10% hexaferrite ($SrFe_{12}O_{19}$) of concentration (0.05)M was prepared of thin films with thickness (1000 ±10)nm the preparation of membranes by method spray pyrolysis. The study of optical properties of thin films pure and doped study spectral of absorbance and transmittance within the wavelength (200-800)nm the results shows of the transmittance decrease of the molar concentration increase and doped and the absorbance arise with the increase in molar concentration and doped and energy bandgap decline with arise in molar concentration and doping, the study of structure properties of the Thin films prepared through (XRD) where the results show membranes multiple crystallization and preferred trend of growth is (101) particle.

Article History
Article Received*: 19 November 2019*
Revised*: 27 January 2020*
Accepted*: 24 February 2020*
Publication*: 18 May 2020*

Keywords: *Azo imidazole, Spray pyrolysis, Strontium hexaferrite.*

1. Introduction

Azo dyes include minimal one nitrogen-nitrogen twice bond (N=N) constructs which are conceivable,[1] this type of vehicle is characterized by its high stability this is due to the double bond between the two nitrogen atoms of the azo group,[2] 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,[3] azo imidazole compounds are characterized by being heterogeneous compounds and contain nitrogen and carbon catalyst that contribute to the alignment with the transition element,[4] one of the most important uses of azo imidazole compound is use in spectral mapping to estimate the very small quantities of transitional element as such imidazole compounds are use in pharmaceutical preparation,[5] 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,[6] in this study we preparation and spectral correspond of new heterocyclic periodic of new azo dye ligand new 2-[2-(5-Chloro carboxyl phenyl) azo]-imidazole (5-ClCPAI) the present study States on the regulation and spectral description of new azo imidazole ligand (5-ClCPAI) the term thin films is used to describe layer or several layers of atoms of ascertain substance whose thickness less than (1) um thin film application in electronic resistances,[7]

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

transistor and solar cell achieved using spray pyrolysis technique under the optimum conditions like the separation distance between the spraying head and the hot substrate is (30)cm the compaction air pressure was saved at (4.5) Kg/cm^2.
pressure was saved at (4.5) Kg/cm^2 and deposition spray pyrolysis is versatile technique for deposition of ligand (5-ClCPAI) because of its cheapness and process control gives the films.[8]

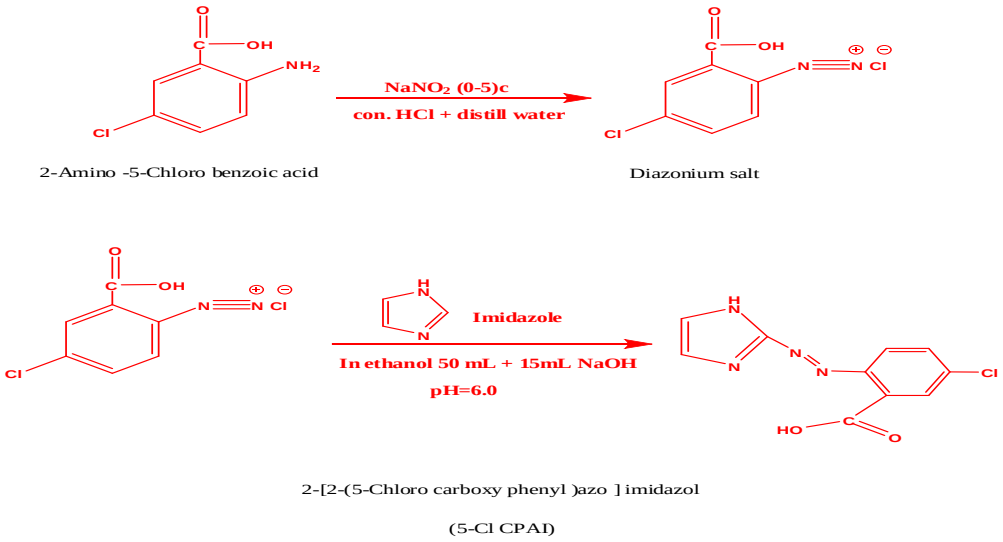
2- Experiment

2-1 Chemicals and method

Chemicals used the work are the 2-amino-5-chloro benzoic acid, imidazole, NaOH, HCl, $NaNO_2$ and Strontium hexaferrite $SrFe_{12}O_{19}$ produced Fluka, Sigma and Aldrich company, furthermore it employ of ethanol and DMSO as a solvent azo dye ligand (5-ClCPAI) distinguished in analytical and numerical data. ^{1}H-NMR spectra were recorded in DMSO-d6 on a Bruker 300 MHZ spectrophotometer by TMS as an internal resource, the mass spectrum was obtained by using Shimadzu Agilent technologies, the Infrared (IR) spectrum for azo dye ligand on record by KBr average in Shimadzu 8400 Fourier transform infrared (FTIR) spectrophotometer in wavenumber at domain (4000-400)cm-^{1}, X-Ray diffraction analysis (XRD) technique using a Shimadzu x-ray diffractometer with CuK_(k=1.5418°)A radiation for 2 theta values in the domain of (10-80°)A, the electronic spectra for ligand and thin-film ligand was registered in a Shimadzu twin-beam Ultraviolet visible (UV) spectrophotometer the domain of (200-1100)nm in a full ethanol solvent, Scanning electron microscopy (SEM) images of azo dye ligand using micrograph Zeiss em 3200, Energy dispersive x-ray spectroscopy (EDS) of azo dye ligand.

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

synthesis of ligand with about 1,2g (0.01)Mol of 2-amino-5-chloro benzoic acid dissolved in a blend of 5ml hydrochloric acid (30)ml distillery water and (5)ml ethanol the blend with persistent flipping and a temperature less (5)°c with confuses (0.9)g Sodium nitrite dissolved to (30)ml distillery water added dropwise at about (0-5)°c continuous flipping for (25)min the added of diazonium salt solution with persistent dropwise with a decrease in temperature arrived about (0-5)°c into 0.9g (0.012)Mol of imidazole was dissolved in blend 50ml ethanol and (10)ml Sodium hydroxide. for conjugation and then stirring persistent 2 hours at (0-5)°c to PH = 6.0 the precipitate.



Scheme (1): Synthesis of azo dye ligand (5-ClCPAI)

TEST Engineering & Management

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

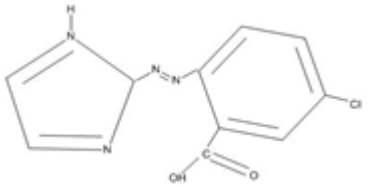
2-3- Preparation of ligand (5-ClCPAI) thin films

Ligand thin films pure from a solution with different molar concentration (0.05, 0.1, 0.3)M in 100ml of deionzed water and thin film distortion of 10% Strontium hexaferrite ($SrFe_{12}O_{19}$) of concentration (0.05)M thin films were prepared by spray pyrolysis, the solution prepared was sprayed with spray average of (1)ml min into heated glass substrate at (130)°c by compacted air as a carrier gas, the distance was of the nozzle to substrate about (45)cm number of bribes (10) and time stop (1)sec.

3- Result and discussion

3-1 ^{1}H-NMR Spectra of ligand (5-ClCPAI)

In the ^{1}H-NMR of azo dye ligand (5-ClCPAI) used solvent DMSO and TMS internal reference the ^{1}H-NMR of ligand shows a signal peak back to solvent DMSO (δ=2.523ppm), singlet due to **H7** into benzene ring (δ=7.427)ppm, singlet due to **H10** into benzene ring (δ=7.561-7.590), signal due to **H9** into benzene ring (δ=7.739-7.747)ppm, signal due to **H5** into imidazole ring (δ=7.767-7.775)ppm signal due to **H4** into imidazole ring (δ=7.837-7.845)ppm, singlet peak due to **H1** into imidazole ring (δ=7.011)ppm, singlet due to OH (δ=13.191)ppm. [9,10]



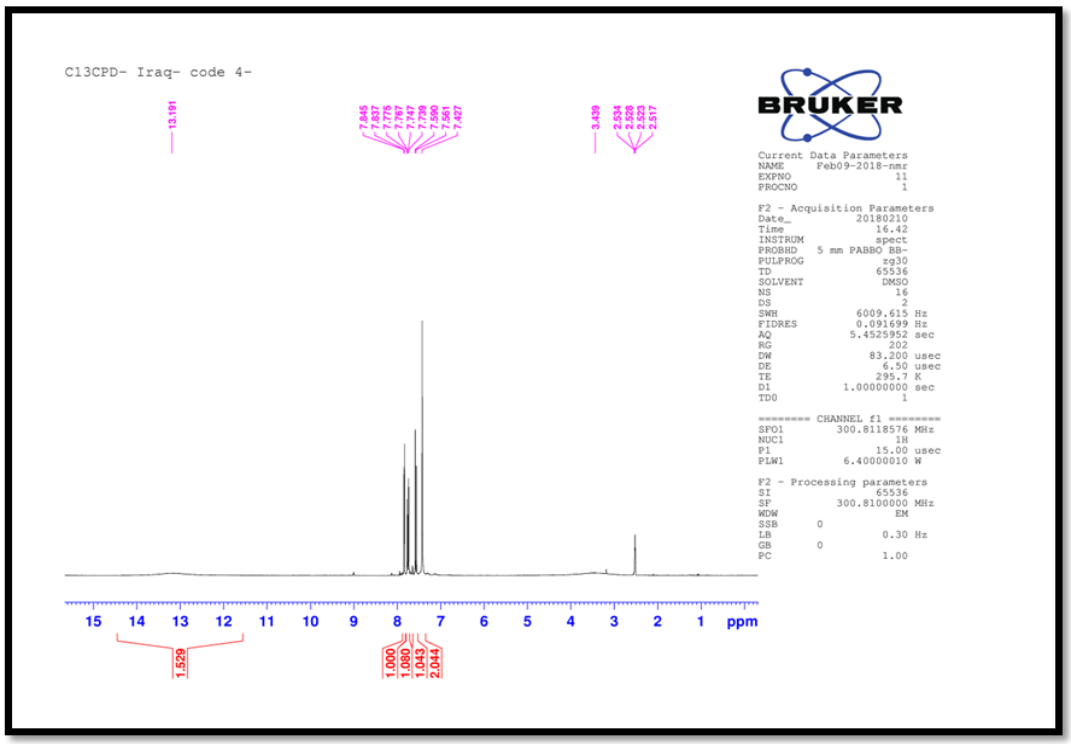


figure (1): ^{1}H-NMR spectrum of azo dye ligand (5-ClCPAI)

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

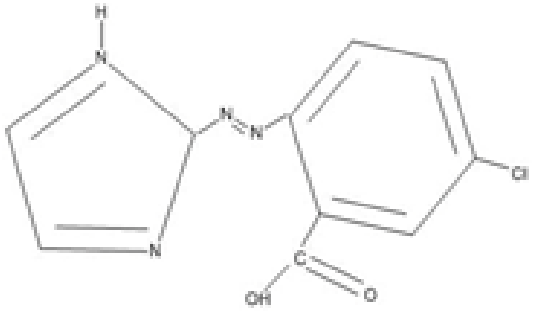
Recorded of the Mass spectrometry (MS) of ligand (5-ClCPAI) and molecular ion peaks the mass spectrometry (MS) of ligand (5-ClCPAI) appeared peaks to the molecular ions m/z$^+$.[11,12]

Fragment	m/z$^+$ Exact mass	Relative Abundance (%)
$[C_{10}H_7N_4O_2Cl]$	**250.9**	**59.4**
$[C_{10}H_5N_4O_2Cl]^+$	**248.8**	**100**

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

[$C_{10}H_5N_2O$ Cl]$^+$	**204.9**	**79.0**
[$C_9H_5N_2$ Cl]$^+$	**176.9**	**84.4**
[C_9H_5 N2]$^+$	**141.0**	**2.0**
[$C_8H_4N_2$]	**127.9**	**6.7**
[C_5H_2]$^+$	**61.9**	**2.8**

Table (1): Ligand State Mass Fragmentation Products (5-ClCPAI)



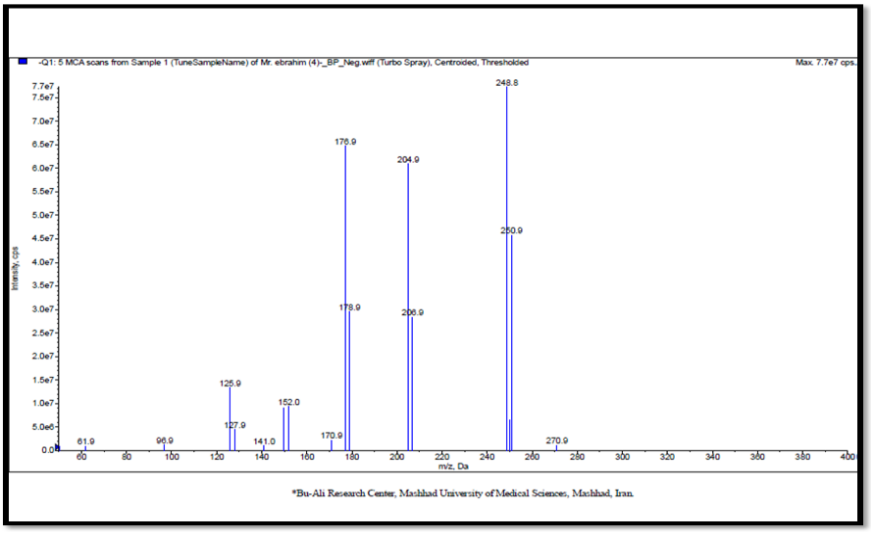


Figure (2): Mass spectrometry (MS) of ligand (5-ClCPAI)

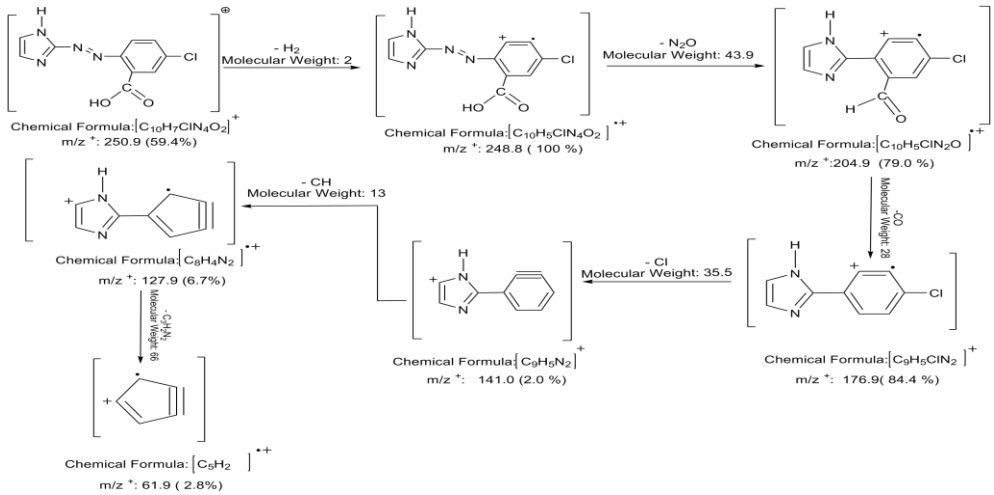


Figure (3): Mass spectrometry (MS) fragmentation of ligand (5-ClCPAI)

3-3 Electronic spectral

The electronic absorption for azo dye ligand (5-ClCPAI) of the ethanol solution (0.0001)M in which at normal temperature the electronic spectrum is described for 3 of absorptions is a chain in Ultraviolet visible (UV) these chains are shown at the posit (256)nm (41508)cm^{-1} (296)nm (30384)cm^{-1} can be referred to as transference at **π→π*** and chain (465)nm (19290)cm^{-1} can be referred to as transference **n→π***.[13,14]

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

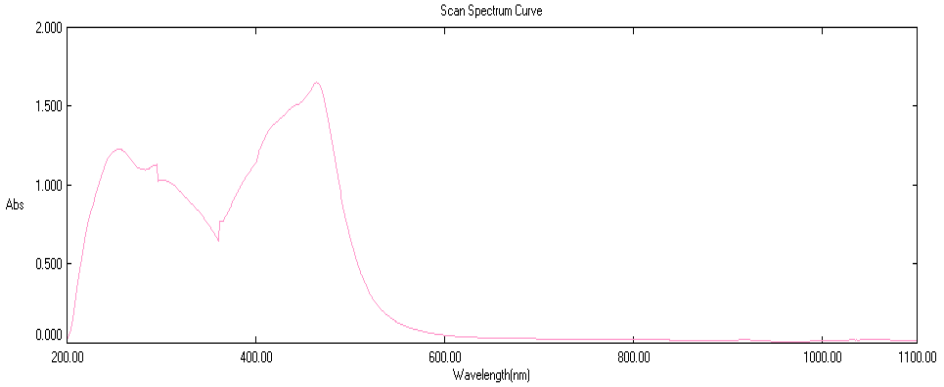
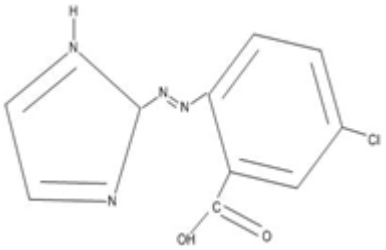


Figure (4): Ultraviolet visible (UV) of azo dye ligand (5-ClCPAI)

3-4 Infrared spectra

Infrared spectral (IR) of the achieved to azo dye ligand (5-ClCPAI), Fourier transform infrared (FTIR) spectrum shows absorption chain in the zone (3132)cm-^{1} for expanding vibration (N-H) imidazole group, vanish 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.[15]



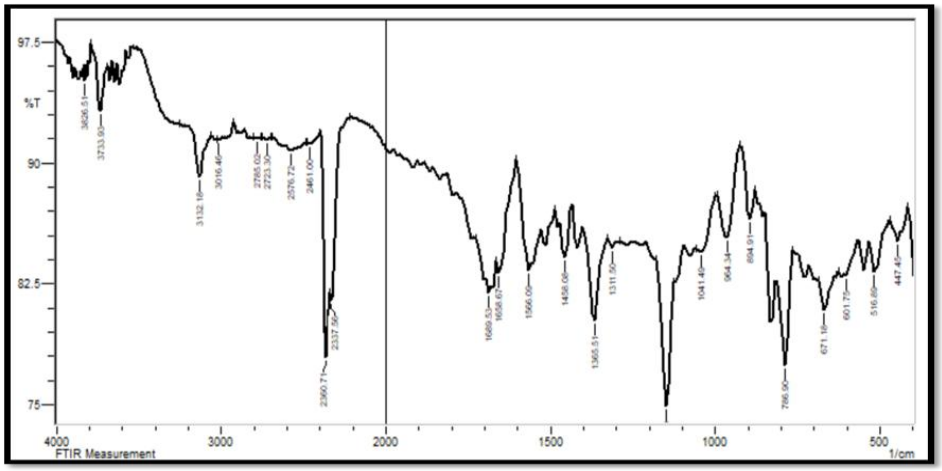


Figure (5): Fourier transform infrared (FTIR) spectrum of azo dye of ligand (5-ClCPAI)

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

For the element analysis or chemical characterized of ligand.[16]

Elements	Wight%
C	39.85
N	38.11
O	18.34
Cl	3.02

Table (2): The element found of ligand (5-ClCPAI)

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

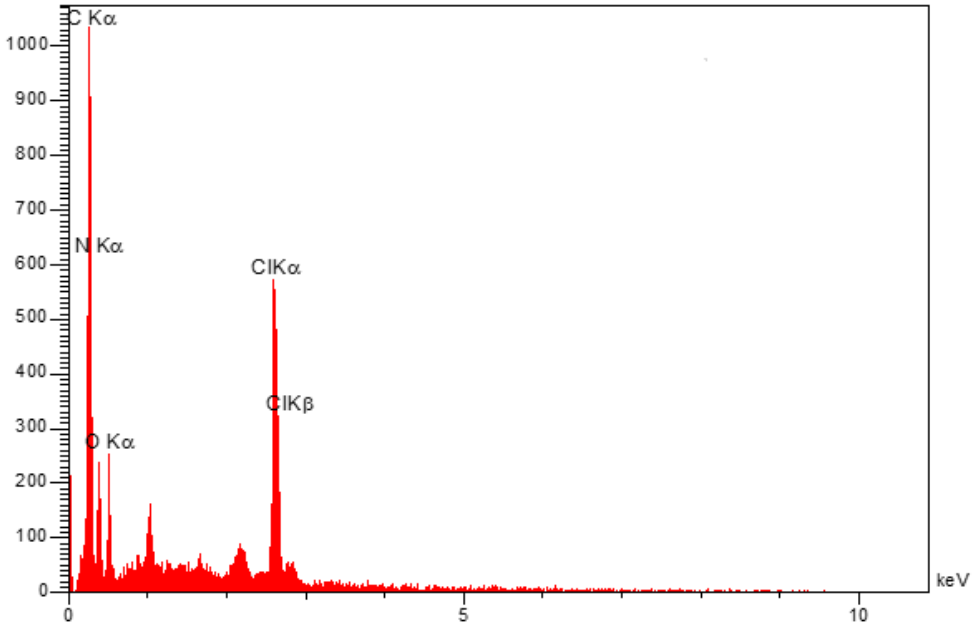


figure (6): Energy dispersive X-Ray spectroscopy (EDS) of azo dye ligand (5-ClCPAI)

3-6 Scanning electron microscopy (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.[17]

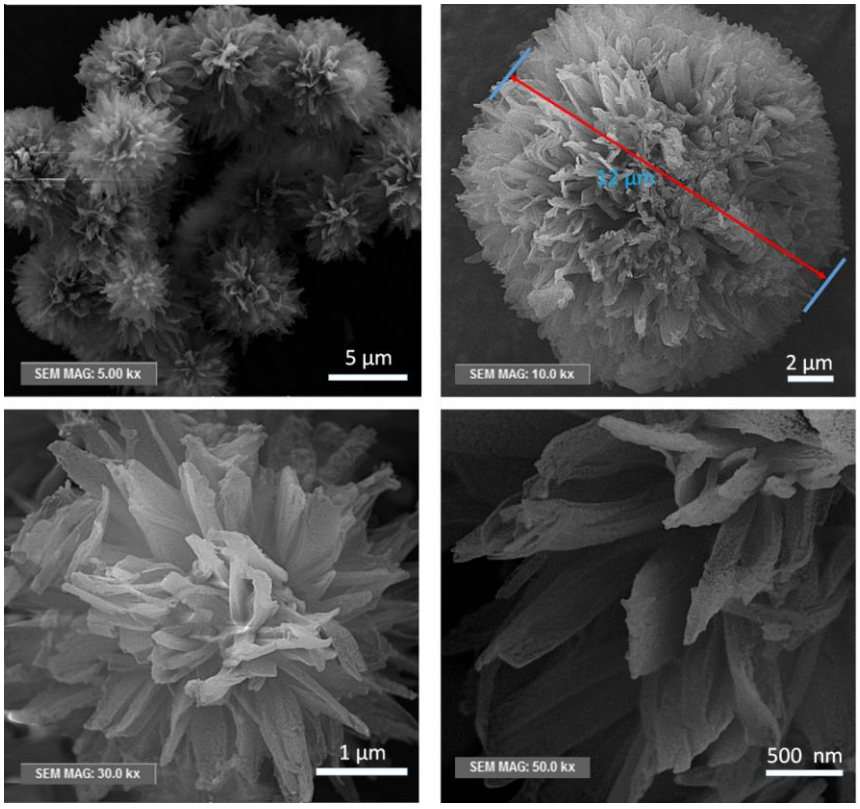


Figure (7): Scanning electron microscopy (SEM) of the ligand (5-ClCPAI)

TEST Engineering & Management

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

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

The diffraction patterns of ligand (5-ClCPAI) films deposited at (0.05, 0.1, 0.3)M and doping 10% hexaferrite of concentration (0.05M) precursor concentration at substrate temperature (130)°c in nature with (101) preferred orientation, (18) the crystallite size (D) of X-ray using Debye – Scherer's:[18]

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

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

Molar Concentration (M)	2 theta (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 Strontium hexaferrite $SrFe_{12}O_{19}$	23.9	0.376	156	101

Table (3): The crystallite size, FWHM, hkl and 2 theta of thin films of ligand (5-ClCPAI)

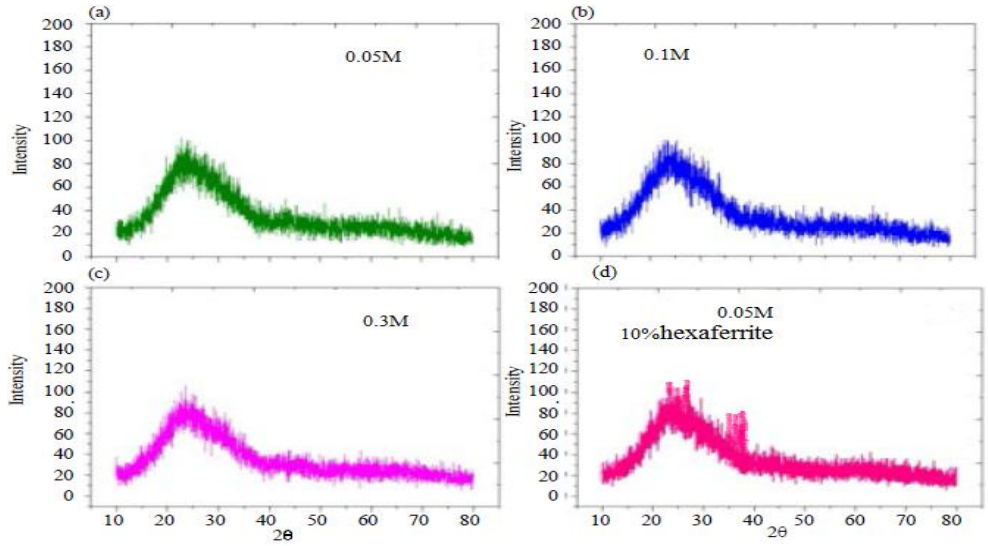


Figure (8): The (XRD) thin films of ligand (5-ClCPAI)

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

Transmission and absorbance curves of ligand (5-ClCPAI) thin films were calculated as a function of wavelength in the domain (200-1100)nm, will reduce the transmission from 90% to 70% when concentration increased from (0.05)M to (0.3)M and doping 10% hexaferrite, all of the films are high absorbance in UV, the reduction of the transmission at high molar concentration may be referred to the arisen scattering of photons by arising of the roughness of the surface morphology.[19]

The optical band gap was determined using equation (2)

$$\alpha h\upsilon = B(h\upsilon - Eg)^{1/2}$$

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

equation (2)
h: Planck's constant
E_g: optical band gap
a: absorption coefficient
B: constant
hv is the photon energy.

The energy band gap decreased with increased molar concentration and doping 10% hexaferrite ,the energy band gap decrease about (3.21-3.821)ev, the band gap decrease with a rise molar concentration and doping because reduce in strain values has been demonstrated earlier the join between the direct bandgap and the compaction stress of the ligand thin films.[20]

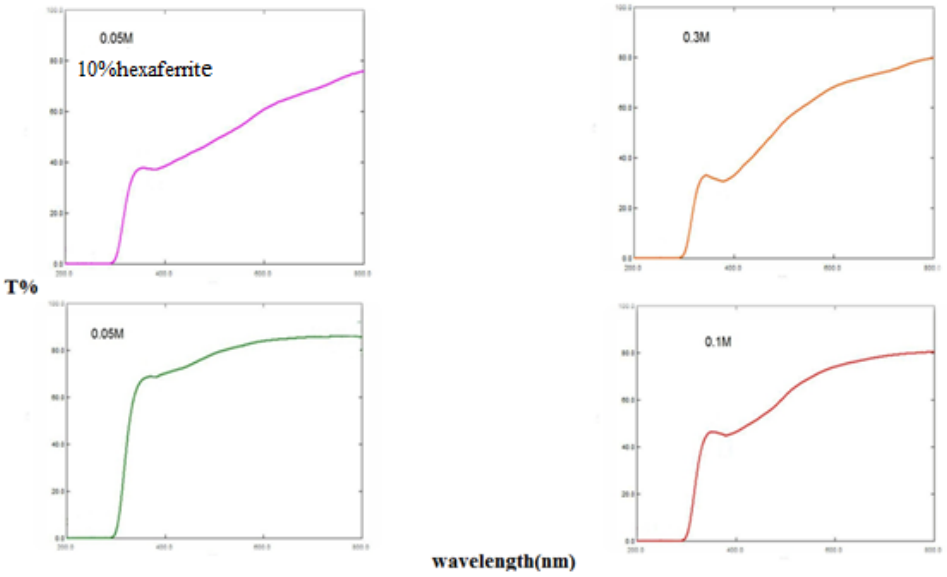


Figure (9): The transmission spectral thin films of ligand

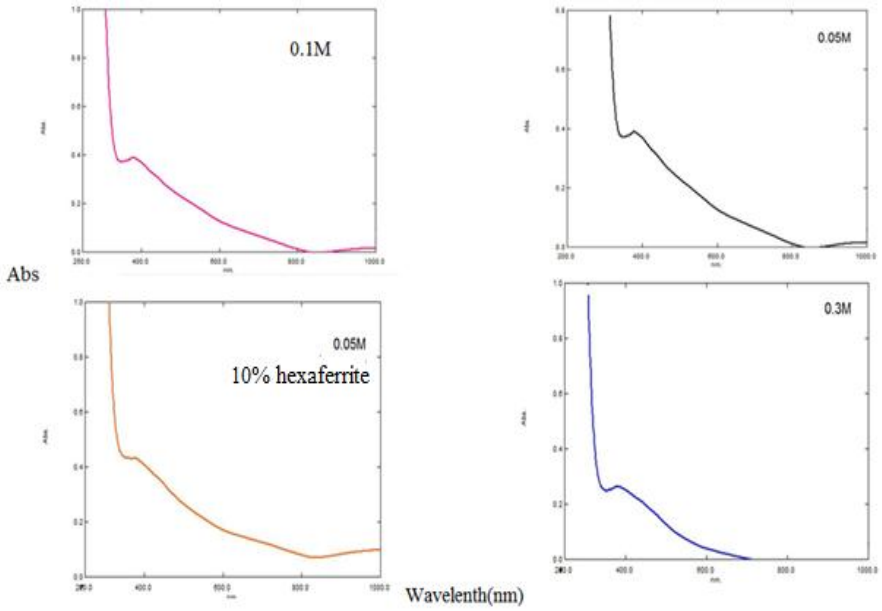


Figure (10): The absorbance spectral thin films of ligand

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

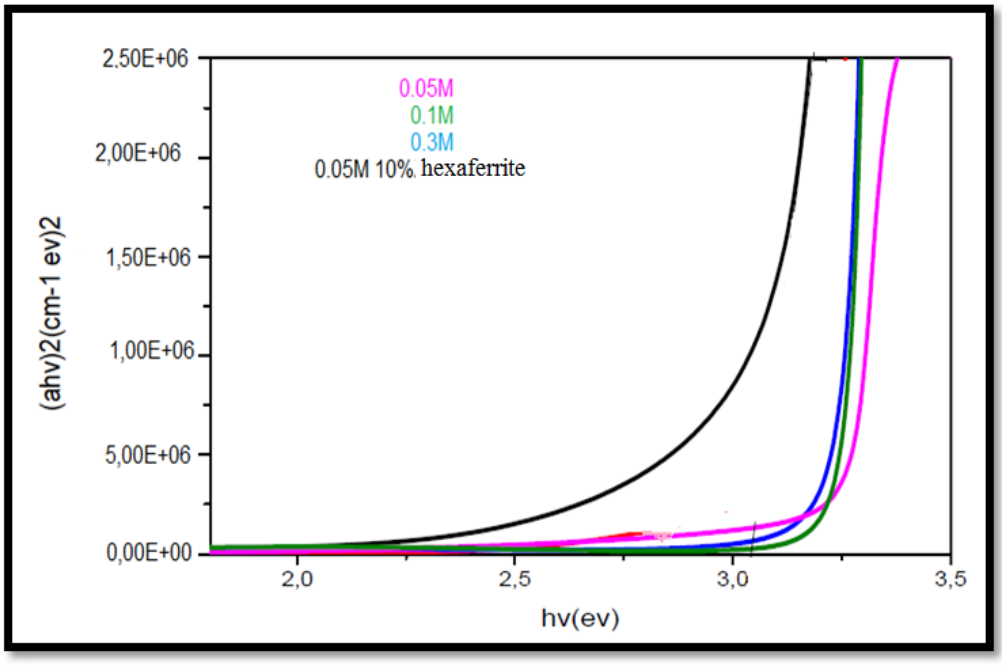


Figure (11): The energy band gap thin films of ligand

Concentration (M)	Eg (ev)
0.05M	3.218
0.1M	3.194
0.3M	3.125
0.05M 10% hexaferrite doped	3.087

Table (4): Energy band gap with different molar concentration and doping

4- Conclusion

A synthetic and spectral correspondence of fresh azo dye ligand ligand (5-ClCPAI) derived from imidazole and the spectroscopy of ligand by analytical data. Mass spectrometry (MS), ^{1}H-NMR, Fourier transform infrared (FTIR), electronic spectra and Scanning electron microscopy-Energy dispersive X-Ray spectroscopy (SEM-EDS), the ligand (5-ClCPAI) thin films were deposited using easy and low-cost method spray pyrolysis.

The X-ray diffraction analysis (XRD) appeared that films Contain a polycrystalline formation in orientation the (101), The optical measurements appear a reduction in the transformation T with an arise for the molar concentration due to the surface roughness, SEM image shows the morphology thin films of ligand (5-ClCPAI) seems relatively homogeneous. The bandgap values were reduced about (3.24-3.815) ev as the molarity of arising about (0.05-0.3)M and doping 10% the decreased bandgap is due to the impurity levels that are inserted into the bandgap.

References

1. Khammas, Z. A., Ibrahim, Z. T., Al-adilee, K. J. **(2015).** Two-Steps Cloud Point Extraction-Spectrophotomtric Method for Separation, Pre-concentration and Determination of V (IV) and V (V) Ions in Real Samples Using Laboratory-Made Organic Reagents. *International Research Journal of Pure and Applied Chemistry*, *8*(1), 33-48.
2. Pellei, M., Gandin, V., Marzano, C., Marinelli, M., Del Bello, F., Santini, C. **(2018)**. The first water-soluble copper (I) complexes bearing sulfonated imidazole-and benzimidazole-derived N-heterocyclic carbenes: Synthesis and anticancer

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

studies. *Applied Organometallic Chemistry*, *32*(3), e4185.

3. Samal, S., Aradhyula, B. P. R., Venkatasubbaiah, K. **(2018)**. Effect of methyl at the 1-phenyl of tetraaryl substituted imidazole boron difluoride complexes: synthesis, characterization, photophysical and electrochemical studies. *Journal of Chemical Sciences*, *130*(7), 95.
4. Al-adely, K. J. **(2017)**. Preparation And Spectral Characterization of New Azo imidazole Ligand 2-[1-(2, 4-Dichoro phenyl) Azo]-α-Amino-1H-imidazole-4-Propionic Acid And Its Complexes With Co (II), Ni (II), Cu (II), Pd (II) And Ag (I) Ions. *Al-Qadisiyah Journal Of Pure Science*, *16*(2), 50-64
5. Patel, P., Patel, P. S. **(2018).** Synthesis, characterization, and antimicrobial activity of heterocyclic azo dye derivatives. *World Scientific News*, *95*, 265-272.
6. Hunger, K., Mischke, P., Rieper, W., Raue, R., Kunde, K., Engel, A. (2005). Azo Dyes in Ullmann's Encyclopedia of Industrial Chemistry.
7. Chung, K. T. **(2016)**. Azo dyes and human health: A review. *Journal of Environmental Science and Health, Part C*, *34*(4), 233-261.
8. Al-Hamdani, A. A. S., Hasan, Z. A. A. H. **(2016)**. Spectroscopic Studies and Thermal Analysis of New Azo Dyes Ligands and their Complexes with some Transition of Metal Ions. *Baghdad Science Journal*, *13*(3), 511-523
9. Habiban, A. M., Mahmoud, W. A., Kareem, T. A. **(2015)**. Preparation and Characterization of Some Metal Complexes with Heterocyclic Azo Ligand (4-SuBAI). *Baghdad Science Journal*, *12*(3), 503-515.
10. Emwanta, D. O., Ngochindo, R. I., Odokuma, L. O., Eruteya, O. C. **(2018)**. Syntheses And Antimicrobial Evaluation Of Brominated Imidazole And Its Co (II), Cu (II), Mn (II), Ni (II), and Zn (II) Complexes. *EPH-International Journal of Biological & Pharmaceutical Science (ISSN: 2208-2166)*, *4*(3), 07-13.
11. Di Santo, A., Echeverría, G. A., Piro, O. E., Pérez, H., Altabef, A. B., Gil, D. M. **(2017).** Supramolecular architectures in luminescent Zn (II) and Cd (II) complexes containing imidazole derivatives: Crystal structures, vibrational and thermal properties, Hirshfeld surface analysis and electrostatic potentials. *Journal of Molecular Structure*, *1134*, 492-503.
12. Al-Adilee, K., Kyhoiesh, H. A. **(2017)**. Preparation and identification of some metal complexes with new heterocyclic azo dye ligand 2-[2−-(1-Hydroxy-4-Chloro phenyl) azo]-imidazole and their spectral and thermal studies. *Journal of Molecular Structure*, *1137*, 160-178.
13. Orojloo, M., Nourian, F., Arabahmadi, R., Amani, S. **(2015)**. Ni (II), Cu (II), AND Zn (II) Complexes derived from a new Schiff base 2-((Z)-(3-methylpyridin-2-yleimino) methyl) phenol and synthesis of nano sized metal oxide particles from these compounds. *Química Nova*, *38*(9), 1187-1191
14. Al-Adilee, K. J., Abedalrazaq, K. A., Al-Hamdiny, Z. M. **(2013)**. Synthesis and Spectroscopic Properties of Some Transition Metal Complexes with New Azo-Dyes Derived From Thiazole and Imidazole. *Asian Journal of Chemistry*, *25*(18).
15. Mostafa, A., El-Ghossein, N., Cieslinski, G. B., Bazzi, H. S. **(2013).** UV–Vis, IR spectra and thermal studies of charge transfer complexes formed in the reaction of 4-benzylpiperidine with σ-and π-electron acceptors. *Journal of Molecular Structure*, *1054*, 199-208

May-June 2020
ISSN: 0193-4120 Page No. 9163 - 9173

16. Khan, I. M., Shakya, S., Singh, N. **(2018)**. Preparation, single-crystal investigation and spectrophotometric studies of proton transfer complex of 2, 6-diaminopyridine with oxalic acid in various polar solvents. *Journal of Molecular Liquids*, *250*, 150-161.
17. Zhang, L. M., Li, H. Y., Li, H. X., Young, D. J., Wang, Y., Lang, J. P. **(2017)**. Palladium (II) Chloride Complexes of N, N′-Disubstituted Imidazole-2-thiones: Syntheses, Structures, and Catalytic Performances in Suzuki–Miyaura and Sonogashira Coupling Reactions. *Inorganic chemistry*, *56*(18), 11230-11243.
18. Direm, A., Abdelbaky, M. S., Sayın, K., Cornia, A., Abosede, O., García-Granda, S. **(2018)**. Sev and pcu topological nets in one-pot newly synthesized mixed-ligand imidazole-containing Cu (II) coordination frameworks: Crystal structure, intermolecular interactions, theoretical calculations, magnetic behavior and biological activity. *Inorganica Chimica Acta*, *478*, 59-70
19. Miecznikowski, J., Lynn, M., Jasinski, J., Reinheimer, E. **(2018**), March). Synthetic, spectroscopic, and computational study of SNS copper (I) pincer complexes based on bis-imidazole and bis-triazole precursors: Impact of ligand design and solvent coordination on conformer interconversion. In *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY* (Vol. 255). 1155 16TH ST, NW, WASHINGTON, DC 20036 USA: AMER CHEMICAL SOC.
20. Jasim, I. K., Ibrahim, I. M., Alyas, M. K. **(2018).** In2O3-ZnO pyramids like structure prepared by Spray-pyrolysis Technique for gas Sensing Applications. *Iraqi Journal of Science*, *59*(1A), 67-74