

Synthesis, Characterization, DFT Calculation, Photochromic, Antimicrobial and Antifungal Properties of Co(II), Ni(II), Zn(II), Ag(I) Complexes with Azo Dye of 2-Aminopyrimidine

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Abstract

A New azo dye 3-(2-pyrimidinylazo)-4-dimethylbenzaldehyde (PADB) consisting 2-aminopyrimidine was synthesized by coupling reaction of diazonium salt and 4-dimethylaminobenzaldehyde. The PADB was further utilized to synthesis of its complexes with Ni (II), Co (II), Zn (II) and Ag (I). All the synthesized complexes were characterized by different techniques (infrared, UV-VIS and mass spectroscopies and elemental analysis). The complexes of Co (II) and Ni (II) were found to be octahedral and nonelectrolytic with general formulas $[M (PADB)_2 Cl_2]$. The complexes of Zn (II) and Ag (I) were tetrahedral and electrolytic with general formulas $[Zn (PADB) Cl_2]$ and $[Ag (PADB) (H_2O)] NO_3$ which is electrolytic. The PADB and its complexes exhibited potent antimicrobial activities against two types of bacterial strains, *Staph-aureus* (positive gram) and *E-coli* (negative gram) and two types of fungies: *Aspergillus niger* and *Pinicillium-Sp*. The PADB dye exhibited good photochromic and solvachromic properties.

Keywords: Pyrimidine, Photoisomerization, Pyrimidinylazo, Biological activity, Inorganic chemistry.

Introduction

Azo compounds exhibit wide range of applications such as antibiotic (prontosil), antifungal, dyes for fiber, sensors, optical storage, ink-jet printers [1, 5]. Organic components bond to inorganic components to form inorganic-organic hybrid materials which have features of both of organic and inorganic materials are of great importance [6, 8]. The silver (I) sulfazine is well known for its applications to prevent the burns from bacterial infections [9]. The Chlorhexidine-silver sulfadiazine complex is used to treat catheter infections in vivo [10]. The silver (I) complexes having N-heterocyclic carbene

ligands exhibited anticancer activity towards HL 60 cells [11]. Silver complexes are well known having broad spectrum against gram positive and gram negative bacteria, fungi and yeast at low concentrations [11,14]. The appropriate light induces isomerization in azo dyes from trans isomer to cis isomer around the azo chromophore which depicted in Figure 1. The suitable light determines depending on the electronic transitions of the azo dye. The conversion process is a reversible and the cis isomer can be back to trans isomer via photoirradiation or thermally [15, 17].

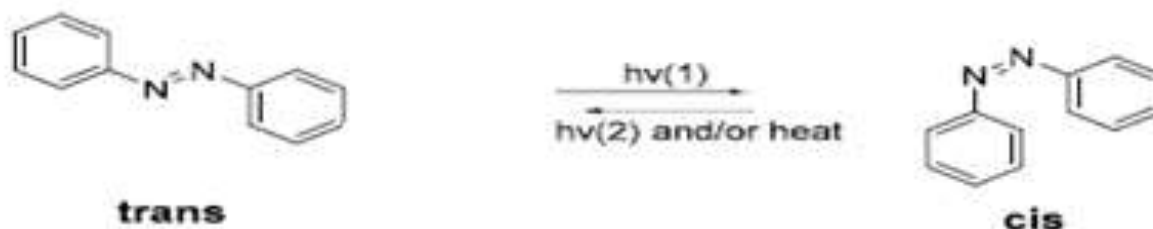


Figure 1: Photochromic behavior of the azo dye

Azo dyes can be exhibited photoisomerization behavior when it incorporates in sol-gel systems, solutions, liquid crystals, monolayer film and polymers which lead to presence large field of potential applications [18, 19]. The imine ligands having azobenzene as side groups were incorporated in metal transition complexes where the complexes undergo photoisomerization regarding to azobenzene chromophres [8].

Photochromism indicates to the reversible changes in the color and structure of the molecule upon irradiation [20]. Therefore we are interested in biological activities and photochromic properties of azo dyes of pyrimidine and their complexes.

In this study we reported the synthesis, characterization, DFT calculation, photochromic and biological properties of new azo ligand of 2-aminopyrimidine which is 3-(2-pyrimidinylazo)-4-dimethylbenzaldehyde (PADB) and its complexes with Co (II), Ni (II), Zn (II) and Ag (I) ions.

Experimental Part

Materials and Methods

The used solvent in the research were reagent grade. The chemical materials were supplied from different companies: 2-aminopyrimidine, dimethyl sulfoxide, hydrochloric acid from (BDH), para-dimethylaminobenzaldehyde (Sigma Aldrich), Co (II).6H₂O, NiCl₂.6H₂O, ZnCl₂, AgNO₃, NaNO₂ (Merck). Elemental analyses were performed by Euro Ea 300 C.H.N Element Analysis 2012. The molar conductance was measured for the synthesized complexes by Cond.720 (WTW).

The infrared spectra were measured between 4000 -400 cm⁻¹, by using KBr pellet on Shimadzu FT-IR 8400S spectrophotometer. The electronic spectra of synthesized complexes on UV-1650 PC UV-Visible spectrophotometer Shimadzu NMR spectra were done by Bruker 500 MHz spectrophotometer at 298 K in DMSO d₆.

The surface morphology of PADB dye and complex Ag(I) were checked by field-emission scanning electron microscope technique (FESEM) using TESCAN BRONO-Mira3 LMU. DFT calculation was done via Gaussain 9 with B3LYP functional using (LanL2DZ) basis set [21].

Synthesis of PADB Dye

5 mL of hydrochloric acid was added to solution of 0.63 g, (0.006 mol) of 2-aminopyrimidine in 10 mL distilled water. Resulting solution was put under cooling at 0 °C in ice bath. In another flask a solution of 3 g of sodium acetate in 8 mL water was added to 10 mL ethanolic solution 1g 4-dimethylaminobenzaldehyde followed by cooling it at 0° C.

Then a solution of 0.5 g of sodium nitrite (NaNO₂) in water was added to it. Then the acidic solution of 2-aminopyrimidine was added drop wise to 4-dimethylaminobenzaldehyde solution [22]. Resulting mixture was stirred at 0 °C for one hr, and then it was kept overnight. Resulting solution was filtrated off and the precipitate was re-crystallized in ethanol. The yield was 51% for green dye of 2-aminopyrimidine.

Synthesis of Complexes of PADB

A solution of 0.5 g (0.0021 mol) of PADB ligand in 20 mL ethanol was added slowly to solution of CoCl₂.6H₂O (0.03 g, 0.001 mol) in 10 mL water at 60 °C under stirring for 30 minutes. The red precipitate formed was filtrated off and washed by distilled water and dried under vacuum. Yield 70 %.

The complex Ni (II) was synthesized by same procedure of Co (II) complex excepting the heating period of reaction mixture was 2 hours.

The complexes of Zn (II) and Ag (I) were synthesized by same procedure of Ni (II) complex with mole ratio Ligand: metal (1:1).

PADB dye: green, yield 51%. FTIR (KBr, cm⁻¹): ν (C-H aromatic) 3186, ν (C-H aliphatic) 2908, ν (C-H aldehyde) 2792, ν (C=O) 1700, ν (C=N) 1666, ν (N=N) 1610, ν (C=C) 1590, ν (C-H bending of aromatic) 810. ¹HNMR (ppm, DMSO-d₆): 10(s, 1H), 8.9(d, 2H), 8(t, 1H), 7.8(d, 1H), 7.5(s, 1H), 7.2(d, 1H), 3(s, 6H). Anal. Calc. for C₁₃H₁₃N₅O: C, 61.17; H, 5.13; N, 27.44%. Found C, 61.24; H, 5.22; N, 27.38%. *M/Z*: 256.8

Complex Co (II): clear red, yield 70%. FTIR (KBr, cm⁻¹): ν (C-H aromatic) 3047, ν (C-H aliphatic) 2931, ν (C-H aldehyde) 2715, ν (C=O) 1690, ν (C=N) 1600, ν (N=N) 1542, ν (C=C) 1400, ν (C-H bending of aromatic) 817. Anal. Calc. for C₂₆H₂₆N₁₀OCoCl₂: C, 47.58; H,

3.99; N, 21.34 %. Found C, 47.50; H, 4.13; N, 21.29 %. M/Z : 640.9

Complex Ni (II): dark red, 65%. FTIR (KBr, cm^{-1}): $\nu(\text{C-H aromatic})$ 3050, $\nu(\text{C-H aliphatic})$ 2920, $\nu(\text{C-H aldehyde})$ 2731, $\nu(\text{C=O})$ 1695, $\nu(\text{C=N})$ 1604, $\nu(\text{N=N})$ 1542, $\nu(\text{C=C})$ 1400, $\nu(\text{C-H bending of aromatic})$ 817. Anal. Calc. for $\text{C}_{26}\text{H}_{26}\text{N}_{10}\text{O}_2\text{NiCl}_2$: C, 48.78; H, 4.09; N, 21.88 %. Found C, 48.72; H, 4.15; N, 21.83%. M/Z : 640.8

Complex Zn (II): maroon, yield 75%. PADB dye: FTIR (KBr, cm^{-1}): $\nu(\text{C-H aromatic})$ 3110, $\nu(\text{C-H aliphatic})$ 2916, $\nu(\text{C-H aldehyde})$ 2710, $\nu(\text{C=O})$ 1650, $\nu(\text{C=N})$ 1597, $\nu(\text{N=N})$ 1527, $\nu(\text{C=C})$ 1450, $\nu(\text{C-H bending of aromatic})$ 817, 732. Anal. Calc. for $\text{C}_{13}\text{H}_{13}\text{N}_5\text{OZnCl}_2$: C, 39.88; H, 3.35; N, 17.89 %. Found C, 39.92; H, 3.39; N, 17.92%. M/Z : 391.6

Complex Ag (I): bright green, yield 73% FTIR (KBr, cm^{-1}): $\nu(\text{C-H aromatic})$ 3085, $\nu(\text{C-H aliphatic})$ 2903, $\nu(\text{C-H aldehyde})$ 2707, $\nu(\text{C=O})$ 1705, $\nu(\text{C=N})$ 1656, $\nu(\text{N=N})$ 1600, $\nu(\text{C=C})$ 1590, $\nu(\text{C-H bending of aromatic})$ 810. Anal. Calc. for $\text{C}_{13}\text{H}_{15}\text{N}_6\text{O}_5\text{Ag}$: C, 35.23; H, 3.41; N, 18.96%. Found C, 35.30; H, 3.49; N, 19.10%. 381.8

Biological Activity

To test the anti-microbiology activity of synthesized complexes in our study, diffusion method in the agar by holes was used. We did four holes in the Muler-Hinton agar and the ethanol was used solvent. Each hole was of 5 mm size which was made by cork porer. Three different concentrations for each of the

PADB and its complexes (50, 75 and 100 mg/mL) were prepared. Each hole was added with 0.2 mL of synthesized material and before that we spread 0.1 mL of Bacteria or fungi suspension by spreader. The plates were let in the refrigerator for 24 hours for diffusion the synthesis material in the culture media. Then plates were kept for 28 h at 37 °C. We used three concentrations in the dish with bacteria while we use one concentration in the dish with fungi. Inhibition diameter for the fungi is equal to growth diameter–dish diameter.

Results and Discussion

The azo dye of PADB was synthesized by reaction of 2-aminopyrimidine and 4-dimethylaminobenzaldehyde. During synthesis it was observed that the diazonium ion of 2-aminopyrimidine was very unstable. Therefore we added acidic solution of 2-aminopyrimidine to the mixture of 4-dimethylaminobenzaldehyde and sodium nitrite in basic medium to generate the diazoinium ion and coupling reaction in situ.

In this method, the diazonum salt will immediately react with the coupling compound to form the azo dye. The synthesized dye was green, yield: 53%. Mass spectrum of PADB exhibited a molecular ion peak at M/Z : 256.8 $[\text{M}+\text{H}]^+$, which is corresponding to predict structure of PADB.

The optimization structure of PADB (Figure 2) was found via DFT calculation which packing by Gaussain 9 with B3LYP functional using (LanL2DZ) basis set.

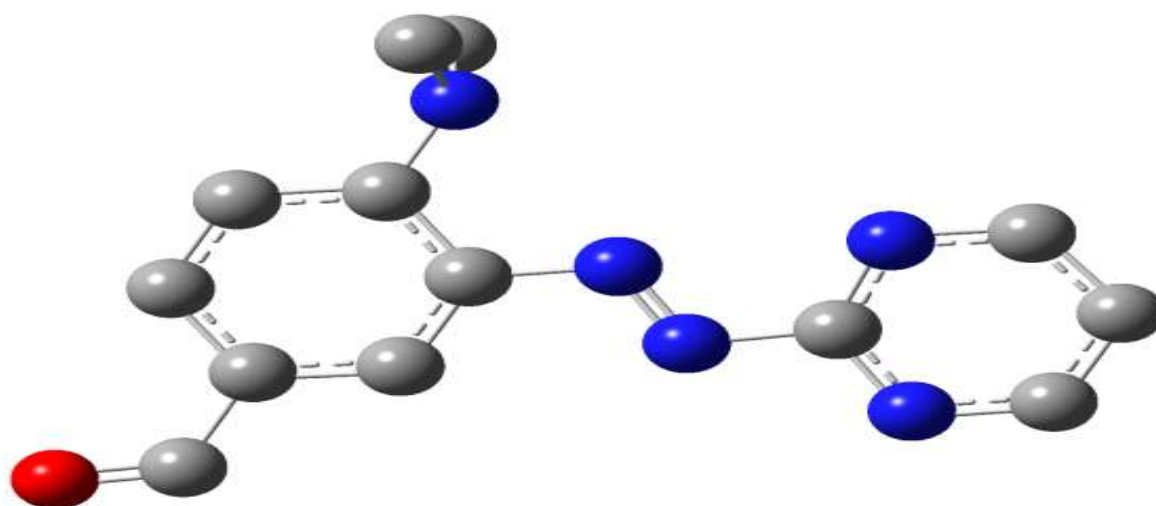


Figure 2: Optimization geometry of PADB dye

The PADB dye exhibited photochromic behavior in ethanol under irradiation with light of 405 nm for 30 minutes (Figure 3) which was followed by changes in absorption spectra in ethanol.

When we remove the source of light of irradiation, the spectrum of PADB returned to original spectrum before irradiation which supports the real chromic behavior for PADB [15, 23, 24].

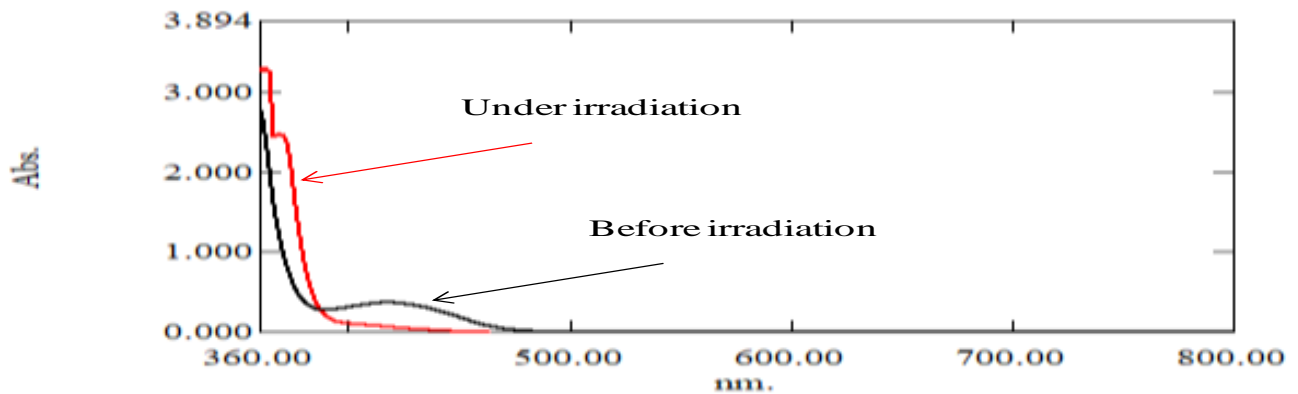


Figure 3: Photochromic behavior of PADB dye in ethanol by UV-Visible spectra under irradiation with light of 405 nm

Many azo dyes are based on acid-base indicators such as methyl orange. The color of PADB converted from green at base medium to clear yellow in acidic medium.

The acidity leads to decrease the electron density which leads to blue shift and decrease the intensity of peaks [25]. This effect depicted in Figure 4.

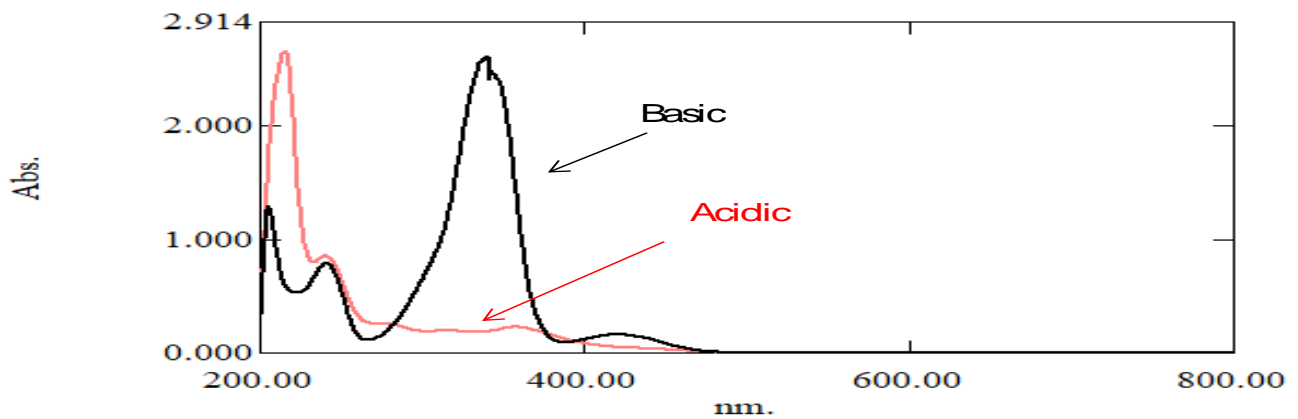


Figure 4: Sensitivity of PADB dye for acidity and basicity medium

To test solvatochromic behavior of PADB, the electronic absorption spectra of PADB dye were done in organic solvents having different polarities. UV-VIS spectra of PADB dye are depicted in Figure 5 which exhibited

bathochromic shift in polar solvent. The possible explanation for this fact can be the excited state of PADB is more polar than ground state which leads to blue shift in nonpolar solvent.

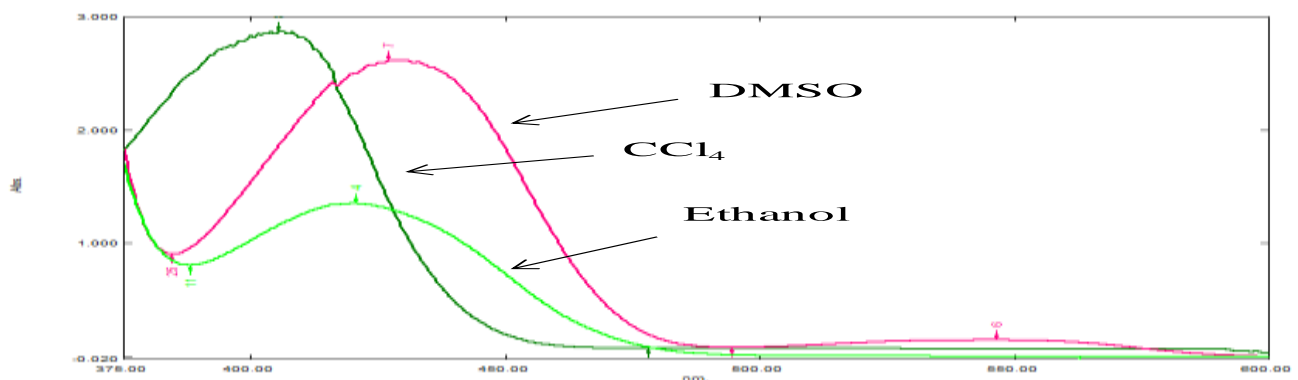


Figure 5: Solvent effect on the chromic behavior of PADB dye

The synthesized complexes Ni(II), Co(II), Zn(II) and Ag(I) for PADB dye were characterized by elemental analysis, molar conductivity, mass, FT-IR, UV-Vis, spectroscopies, as well as by FESEM technique. Depending on the data of elemental analysis CHN and mass spectra of synthesized complexes, we predicted that the ratio of metal-ligand was 1:1 for complexes of Zn (II) and Ag(I) while it was 1:2 for complexes of Co(II) and Ni(II).

The conductivity values of Ag(I) was $40 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ indicating that the complex is electrolytic while complexes of Zn(II), Co(II) and Ni(II) exhibited 12, 10 and $15 \text{ ohm}^{-1} \cdot \text{cm}^{-1}$ indicating nonelectrolytic [26]. The PADB dye exhibited two bands at 340 nm, and another band at 420 nm, which assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively.

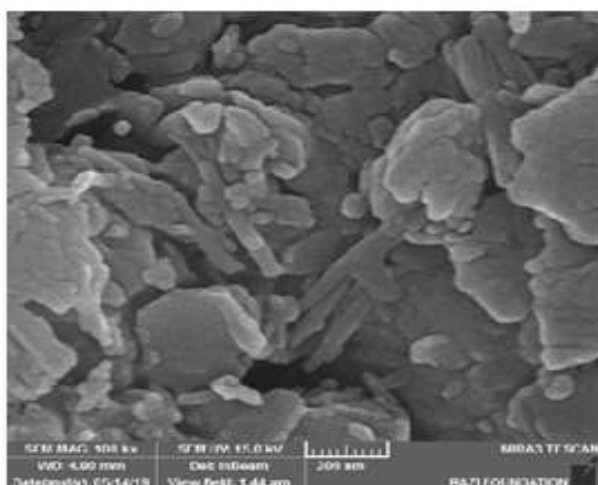
The complex Co(II) exhibited two bands, the first band at 650 nm and the second band at 510 nm may be due to ${}^4T_{1g} \rightarrow {}^4A_2$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ respectively, which is agreement with octahedral shape around the cobalt (II) ion [27]. The complex Ni(II) exhibited two bands in the visible region at 730 nm and 805 nm which are assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ respectively, in agreement with octahedral geometry around

nickel (II) ion [28]. The complexes of Zn (II) and Ag (I) exhibited red shift for the $\pi \rightarrow \pi^*$ transition and vanish the $n \rightarrow \pi^*$ transition. The data of elemental analysis, molar conductivity, mass, FT-IR, UV-Vis spectroscopies confirm that synthesized complexes Zn (II) and Ag(I) are tetrahedral and Co(II) and Ni(II) complexes are octahedral which is in agreement with conclusions of electronic transitions of UV-VIS spectra.

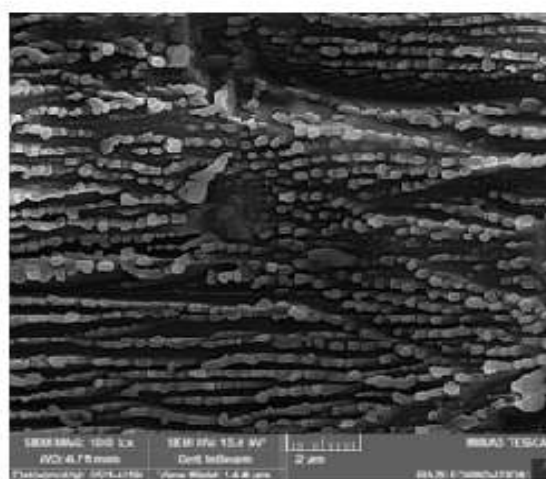
Infrared Spectra

The infrared spectrum of PADB dye exhibited some characteristic stretches like C-H aromatic, aliphatic and aldehyde, C=O, C=N, N=N which were noticed in the spectra of complexes of PADB [29]. It is interesting point, that stretching vibration of C=N and N=N were noticed decreasing to lower frequency 66-10 and $68-10 \text{ cm}^{-1}$ respectively.

That means that nitrogen atoms coordinate to metal ion in the synthesized complexes and electron density transfers from C=N and azo group to metal ion. On the other hand, the images of the FESEM technique show that PADB ligand and complex Ag (I) are nanoparticles and the FESEM images of PADB ligand and complex Ag (I) depicted in Figure 6.



PADB dye



Ag(I) complex

Figure 6: FESEM images of PADB dye and complex Ag(I) of PADB dye

Biological Activities

Antimicrobial activity

Azo dyes having hetrocyclic rings and their complexes exhibited a high growth inhibition against many of patient bacteria and fungi [29,30], therefore were interested in known the effect of the PADB dye and its complexes

(Co(II), Ni(II), Zn(II), Ag(I)) on two type of bacteria, *Staphylococcus aureus* (positive gram) and *E-coli* (negative gram) and two type of fungi: *Aspergillus niger* and *Pinicillium-Sp*. The antimicrobial activity of PADB ligand and its complexes against *Staph-aureus* and *E-coli* bacteria are listed in Table 1.

The PADB ligand exhibited high growth inhibition zone against *staph-aureus*, it was 3 cm at 100 mg/mL.

The antibiological activity of Co, Zn, Ni, Ag complexes against *staph-aureus* arranged from high to moderate (3, 2.5, 1.5, and 1 cm at 100 mg/mL respectively). The Co, Zn, Ag complexes exhibited high biological activity against *E-coli*; it was 2.5 cm at 100 mg/mL except Ni complex which exhibited low biological activity (0.5 cm). The PADB ligand exhibited moderate biological activity which was 1 cm at 100 mg/mL. It looks that inhibition of bacteria growth increase with increasing the concentration of the dye and its synthesized complexes.

Antifungal Activity

The PADB dye and its complexes exhibited excellent antifungal activity against *Aspergillus niger* and *Pinicillium-Sp*. The antifungal activity arranged among 8 to 5 cm except Ni (II) complex which exhibited negative test. The complexes exhibited 8 cm inhibition that means causing complete inhibition of growth of *Aspergillus niger* and *Pinicillium-Sp*. The antifungal activity of PADB ligand and its complexes against *Aspergillus niger* and *Pinicillium-Sp* was listed in Table 2.



Figure 7: Biological activity of [Co (PADB)₂ Cl₂] complex against *Staph-aureus* (left image) and fungi activity of [Zn(PADB)Cl]Cl against *Aspergillus niger* (right image)

Table1: Anti biological data of PADB and its complexes against E-coli and Staph-aureus bacteria

Bacteria	The diameter inhibition zone (cm)					
	Concentration mg/ml	PADB	Co	Ni	Zn	Ag
<i>E - coli</i> (Gram-negative)	100	1	2.5	0.5	2.5	2.5
	75	0.5	1.5	0.5	1.5	1
	50	1	1	-	1	-
<i>Staph-aureus</i> (Gram-positive)	100	3	3	1.5	2.5	1
	75	1.5	1	0.3	1	1
	50	2	0.5	0.2	0.5	0.5

Table 2: Antifungal data of PADB and its complexes against *Aspergillus Niger* and *Pinicillium.sp*

Fungi	The diameter inhibition zone (cm) =(dish diameter –growth diameter)					
	Concentration mg/ml	PADB	Co	Ni	Zn	Ag
<i>Aspergillus Niger</i>	100	3.5	8	-	8	5
	75	7	6.5	-	8	-
	50	-	5	-	3	5
<i>Pinicillium.sp</i>	100	7	8	-	6.5	8
	75	8	8	-	6	2.5
	50	8	8	-	-	8

Conclusion

In this study, we conclude that we have synthesized and characterized PADB ligand which is tridentate with Ag(I) ion while bidentate with Zn(II), Co(II) and Ni(II) ions.

The PADB and its complexes were synthesized, characterized and found to possess antimicrobial properties. The FESEM technique shows that the PADB dye and complex of Ag (I) are nanoparticles. The PADB dye exhibited good chromic properties under irradiation, solvent effect and acidity effect. The PADB ligand and its complexes

shows antimicrobial activity against two types of bacteria, *Staph-aureus* and *E-coli* and two type of fungi: *Aspergillus niger* and *Pinicillium-Sp*.

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