Araştırma Makalesi / Research Paper
Bayburt Üniversitesi Fen Bilimleri Dergisi
Bayburt University Journal of Science

dergipark.gov.tr/bufbd
ISSN: 2667-579X

Cilt 7, Sayı 2, Yıl 2024, Sayfa 67-78
Vol 7, Issue 2, Year 2024, Pages 67-78
doi.org/10.55117/bufbd.1483799

Geliş Tarihi / Date of Recieve: 14.05.2024
Revizyon Tarihi / Date of Revision: 30.09.2024
Kabul Tarihi / Date of Acceptance: 22.10.2024

Synthesis, Characterization and Antimicrobial Activity of Mixed-Ligand Metal Complexes of 4,4'-Bipyridine and Aniline-2,5-Disulfonic Acid

Nurgün BÜYÜKKIDAN[1*], Seher KAYA[1], Halil İLKİMEN[1], Aysel GÜLBANDILAR[2]

[1] *Kütahya Dumlupınar University, Department of Chemistry, Faculty of Art and Sciences, Kütahya, Türkiye*
[2] *Eskişehir Osmangazi University, Department of Food Engineering, Faculty of Agriculture, Eskişehir, Türkiye*

Keywords:

4,4'-Bipyridine, Aniline-2,5-disulfonic acid, Metal complex, Antimicrobial activity

Abstract

In this study, we prepared mixed-ligand Co(II) complex{$[Co(ADSA)(BP)]_n.2H_2O$, **1**}, Ni(II) complex {$[Ni(ADSA)(BP)]_n$, **2**}, and Zn(II) complex {$[Zn(ADSA)(BP)(H_2O)_2]_n.3H_2O$, **3**} of 4,4'-bipyridine (BP) with aniline-2,5-disulfonic acid (H_2ADSA). The **1-3** were characterized by elemental analysis, AAS, TGA, IR, UV-Vis, molar conductivity and magnetic susceptibility techniques. Furthermore, the microdilution method was used to explore the antibacterial and antifungal activities of the initial and the synthesized metal complexes against the following bacteria and yeast: *Pseudomonas aeruginosa*, *Escherichia coli*, *Enterococcus faecalis*, *Listeria monocytogenes*, *Staphylococcus aureus*, *Bacillus subtilis and Candida albicans*. Antibacterial and antifungal activity results were compared with antibiotics (Vancomycin, Levofloxacin, Cefepime, Chloramphenicol, Fluconazole and Ketoconazole). Through the examination of the conducted studies, it was noted that the recently created compounds demonstrated efficacy in combating both bacterial and yeast infections.

*e-mail: nurgun.buyukkidan@dpu.edu.tr

Bu makaleye atıf yapmak için:
Nurgün BÜYÜKKIDAN; Seher KAYA; Halil İLKİMEN; Aysel GÜLBANDILAR, "Synthesis, Characterization and Antimicrobial Activity of Mixed-Ligand Metal Complexes of 4,4'-Bipyridine and Aniline-2,5-Disulfonic Acid", Bayburt Üniversitesi Fen Bilimleri Dergisi, C. 7, s 2, ss. 67-78

How to cite this article:
Nurgün BÜYÜKKIDAN; Seher KAYA; Halil İLKİMEN; Aysel GÜLBANDILAR, "Synthesis, Characterization and Antimicrobial Activity of Mixed-Ligand Metal Complexes of 4,4'-Bipyridine and Aniline-2,5-Disulfonic Acid", Bayburt University Journal of Science, vol. 7, no 2, pp. 67-78

1 INTRODUCTION

Interest in the synthesis of metal-organic compounds or coordination polymers is piqued by their wide range of structural variations and possible functional characteristics [1-3]. Research shows that bridging ligands containing two or more donor atoms coordinated to different metals are used in the synthesis of metal-organic compounds [4-8]. Bipyridine contains two pyridine rings connected to each other by a C-C covalent bond. Figure 1 shows the isomers of bipyridine.

The most recognized one of these isomers is 2,2'-bipyridine, which forms chelates by bonding to the metal with two nitrogen atoms. Metal complexes of 2,3-bipyridines [9], 2,4-bipyridines [10,11], 3,3-bipyridines [12,13], and 3,4-bipyridines [14,15] are not very common (Fig. 1). The unsymmetrical 2,4'-bipyridine generally acts as a monodentate ligand, coordinating with the metal with only one nitrogen atom, but it can also bind to two individual metal atoms to form bidentate bridge systems [16]. 4,4'-bipyridine is of particular interest due to the coordination of two nitrogen atoms in its structure. 4,4'-bipyridine is an exo-bidentate ligand that is rigid and linear, has no steric hindrance, no branched chains, and has good bridging effect to form one-, two- and three-dimensional coordination polymer networks [17] and generate complexes with different dimensional spatial configurations with metal ions [18,19]. It can also serve as a terminal ligand or an uncoordinated guest molecule [20,21].

On the other hand, aromatic acids are widely used in the synthesis of coordination polymers. It is important to note that because the carboxylate group possesses a range of bridging modes for the development of extended frameworks, the coordination capacity of aromatic carboxylic acids towards transition metal complexes has drawn a lot of attention [22-25]. It has been reported that many coordination polymers have been synthesized using the hydrothermal method [26-30]. Our recent work has focused on creating coordination polymers under room temperature and hydrothermal conditions using *N*-donor ligands and aromatic acid ligands [31,32].

Sulfonic group compounds have recently attracted much attention due to their less predictable coordination mechanisms and for being softer and more flexible ligands [33,34]. Sulfo groups can speed up the synthesis and crystallization of coordination polimers in water by increasing the solubility of organic ligands. The presence of donor atoms in the NH_2 and SO_3^{2-} groups of the aniline-2,5-disulfonate compound shows that it is a suitable ligand for complexation. However, so far, there have been no reports of coordination polymers containing aniline-2,5-disulfonic acid and 4,4'-bipyridine.

These days, it becomes ineffective because disease-causing microorganisms develop resistance to the medications used to treat them. Thus, novel compounds that may be acquired cheaply and effectively are required to eradicate hazardous microbes for human health. Future research will be aided by the discovery that the chemicals produced in this work exhibit antibacterial action against yeasts and bacteria. It has been demonstrated that co-crystals, salts and metal complexes containing aniline-2,5-disulfonic acid and 4,4'-bipyridine can be used in in vitro and in vivo antibacterial and antifungal experiments.

In the present paper, we prepared and characterized three coordination polymers, Co(II) {$[Co(ADSA)(BP)]_n.2H_2O$, **1**}, Ni(II) {$[Ni(ADSA)(BP)]_n$, **2**}, and Zn(II) {$[Zn(ADSA)(BP)(H_2O)_2]_n.3H_2O$, **3**}, of 4,4'-bipyridine (BP) with aniline-2,5-disulfonic acid (H_2ADSA). In addition, antibacterial and antifungal activities were studied and compared with antibiotics (Vancomycin, Levofloxacin, Cefepime, Chloramphenicol, Fluconazole and Ketoconazole).

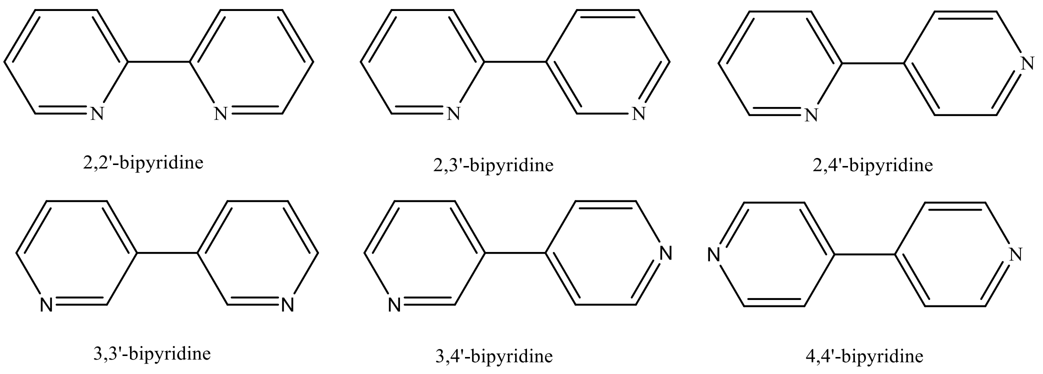


Figure 1. The isomers of bipyridines

2 MATERIALS AND METHODS

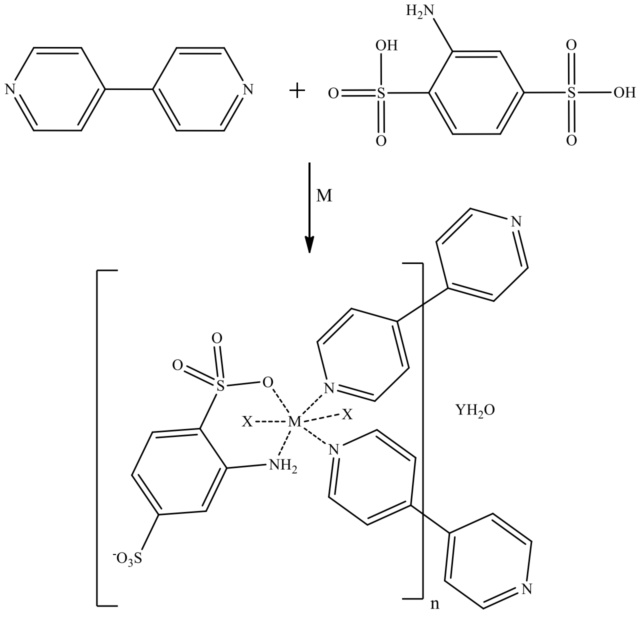
2.1 Methods and materials

All chemicals used were commercially purchased from Aldrich. Perkin Elmer AAS PinAAcle 900T for AAS analyses, Elementar Vario III EL spectrometer for elemental analysis studies, Bruker Optics Vertex 70 FT-IR spectrometer for FT-IR spectra, SHIMADZU UV-2550 spectrometer for UV–Vis spectra, Sherwood Scientific Magway MSB MK1 for magnetic susceptibility measurements and WTW Cond 315i/SET Model conductivity meter for molar conductances were used.

2.2 Synthesis of 1-3

1 mmol (0.253 g) of H_2ADSA, 1 mmol (0.156 g) of BP, 1 mmol metal(II) salt {$Co(CH_3COO)_2$. $4H_2O$ for **1**, $Ni(CH_3COO)_2$. $4H_2O$ for **2** and $Zn(CH_3COO)_2$. $2H_2O$ for **3**} were taken and heated separately in 20 mL of water in a teflon-coated stainless container at 160 °C for three days. The temperature of the reaction vessel was lowered to 120 °C and then to 80 °C. The resulting amorphous solids were filtered and dried (pink, 90% yield for **1**, green, 83% yield for **2**, and white, 83% yield for **3**) (Fig. 2).

The results of elemental analysis and AAS; Anal. Calcd. for **1** {$C_{16}H_{17}CoN_3O_8S_2$, M = 502.39 g/mol}, C, 38.25%; H, 3.41%; N, 8.36%; Co, 11.73%; S, 12.77%. Found: C, 38.27%; H, 3.45%; N, 8.35%; Co, 11.70%; S, 12.80%. for **2** {$C_{16}H_{13}N_3NiO_6S_2$, M = 466.11 g/mol}, C, 41.23%; H, 2.81%; N, 9.01%; Ni, 12.59%; S, 13.76%. Found: C, 41.20%; H, 2.85%; N, 9.00%; Ni, 12.50%; S, 13.70%. for **3** {$C_{16}H_{23}N_3O_{11}S_2Zn$, M = 562.88 g/mol}, C, 34.14%; H, 4.12%; N, 7.47%; S, 11.39%; Zn, 11.39%. Found: C, 34.10%; H, 4.15%; N, 7.45%; S, 11.35%; Zn, 11.70 %.



M = Co(II), X = -, Y = 2 (**1**)
M = Ni(II), X = -, Y = - (**2**)
M = Zn(II), X = H_2O, Y = 2 (**3**)

Figure 2. The structures of compounds **1-3**

2.3 Antimicrobial study

The microbroth dilution method was used to assess the antibacterial and antifungal activities of the initial (BP and H_2ADSA}) and newly synthesized compounds **1-3**. In order to prepare stock solutions for the samples, DMSO was used. Each of the free, synthesized, and antibiotic compounds was weighed at 4 mg, and 2 mL of DMSO was added to dissolve them. A Mueller-Hinton broth medium was used to grow overnight culture suspensions, and cell densities were adjusted to 0.5 McFarland tube turbidity (1×10^8 CFU/mL). Then the microorganism suspension was transferred to the wells. The final well chain devoid of microbes served as the negative control, and sterilized distilled water served as the positive growth control. All plates seeded at 37 °C were incubated for 24 hours, and the first non-turbidity well was determined to be the MIC.

3 RESULTS AND DISCUSSION

3.1 Thermal analyses of 1-3

TG-DTG and DTA curves and values of **1-3** are given in Figs S1-S3, respectively, and Table 1. Compounds **1** and **3** are thermally decomposed in three steps. The endothermic first stage corresponds to the loss of two and five moles of water molecules for compounds **1** and **3**, respectively (DTG_{max} = 66 and 87 °C for **1** and 65, 89 and 155 °C for **3**). The endothermic second stage is consistent with the loss of C_7H_5 and C_8H_6 units for **1** and **3**, respectively (DTG_{max} = 190, 256 and 316 °C for **1** and 253 °C for **3**). The exothermic third stage shows the loss of $C_9H_8N_3O_4S_2$ and $C_8H_4N_3O_6S_2$ units for **1** and **3**, respectively (DTG_{max} = 489 and 675 °C for **1** and 392 and 559 °C for **3**). The final product which is left undecomposed is CoO for 1 and ZnO for 3.

Compound **2** is thermally decomposed in two steps. The endothermic first stage corresponds to the loss of the C_5H_3 unit, and the exothermic second stage corresponds to the loss of the $C_{11}H_9N_3O_6S_2$ unit. The final product which is left undecomposed is NiO.

Table 1. Thermal analyses results of **1-3**

Compound	**Temperature (ºC)**	**DTG_{max} (ºC)**	**Leaving Group**	**Found (%)**	**Calculated (%)**
1	35-91	66, 87	$2H_2O$	7.00	7.17
	91-336	190, 256, 316	C_7H_5	17.60	17.71
	336-900	489, 675	$C_9H_8N_3O_4S_2$	63.70	63.39
	-	-	Co	11.70	11.73
2	35-255	212	C_5H_3	13.50	13.50
	255-900	476	$C_{11}H_9N_3O_6S_2$	74.00	73.99
	-	-	Ni	12.50	12.56
3	35-169	65, 89, 155	$5H_2O$	15.70	15.99
	169-280	253	C_8H_6	18.30	18.12
	280-900	392, 559	$C_8H_4N_3O_6S_2$	54.30	54.27
	-	-	Zn	11.70	11.62

3.2 FT-IR results of all compounds

The IR data for H_2ADSA, BP and **1-3** are given in Table 2 and Figs. S4-S8. There are broad vibration peaks between 3500 and 3200 cm^{-1} attributed to the ν(OH) vibrations of **1** and **3**. Bands appearing at 3479 and 3366 cm^{-1} for **1**, 3480 and 3300 cm^{-1} for **2**, and 3426 and 33371 cm^{-1} for **3** are assigned to NH_2 vibrations [31,35]. The peaks at the range of **1-3**, 3075-3045 cm^{-1}, 1614-1414 cm^{-1}, 1242-1210 cm^{-1}, 1019-1007 cm^{-1}, 815-808 cm^{-1}, 670-665cm^{-1}, 559-557cm^{-1} and 486-462 cm^{-1} are assigned as $\nu(C–H)_{ar.}$, ν(C=N)/ ν(C=C), $\nu(S=O)_{asym}$, $\nu(S=O)_{sym}$, ν(S-O), ν(C-S), ν(M-O) and ν(M-N), respectively. The wave numbers of the compounds are in agreement with studies involving similar ligands found in the literature [31,35].

Table 2. IR data of all compounds (cm^{-1})

	H_2ADSA	BP	**1**	**2**	**3**
ν(O–H)	3501(br)	-	3500-3200(br)	-	3500-3200(br)
ν(N–H)	3480(w)	-	3479(w)	3480(w)	3426(w)
	3435(w)		3366(w)	3300(w)	3371(w)
$\nu(C–H)_{ar.}$	3093(w)	3020(w)	3065(w)	3075(w)	3045(w)
ν(C=N)	1526(s)	1649(s)	1613(s)	1614(s)	1611(s)
ν(C=C)	1579(s)	1597(s)	1561(s)	1562(s)	1563(s)
	1539(s)	1532(s)	1536(s)	1538(s)	1532(s)
	1478v	1486(s)	1491(s)	1491(s)	1481(s)
	1407(s)	1407(s)	1477(s)	1480(s)	1414(s)
			1419(s)	1422(s)	
$\nu(S=O)_{asym}$	1221(s)	-	1214(s)	1210(s)	1242(s)
$\nu(S=O)_{sym}$	1053(s)	-	1007(s)	1007(s)	1019(s)
ν(S-O)	841(s)	-	810(s)	815(s)	808(s)
ν(C-S)	666(s)	-	670(s)	669(s)	665(s)
ν(M–O)	-	-	557(w)	557(w)	559(w)
ν(M–N)	-	-	462(w)	468(w)	486(w)

3.3 UV-vis results of all compounds

UV-Vis spectra of all compounds were taken in DMSO (1x10^{3-} M) between 200-900 nm. The *π-π* and n-π** transitions are seen in the spectra {304 (34020 Lmol^{-1}cm^{-1}) nm for H$_2$ADSA, 299 (36130 Lmol^{-1}cm^{-1}) nm for BP, 312 (38180 Lmol^{-1}cm^{-1}), 317 (39140 Lmol^{-1}cm^{-1}) and 323 (39720 Lmol^{-1}cm^{-1}) nm for **1**, 289 (20370 Lmol^{-1}cm^{-1}) and 311 (25890 Lmol^{-1}cm^{-1}) nm for **2**, and 290(23540 Lmol^{-1}cm^{-1}), 314(38180 Lmol^{-1}cm^{-1}) and 319 (3864 Lmol^{-1}cm^{-1}) nm for **3** (Fig. S9). The d-d transition bands of **1** and **2** are observed at 529(270 Lmol^{-1}cm^{-1}), 866(60 Lmol^{-1}cm^{-1}) and 895(70 Lmol^{-1}cm^{-1}) nm for **1** and 783 (170 Lmol^{-1}cm^{-1}) and 889(240 Lmol^{-1}cm^{-1}) nm for **2** suggesting an octahedral geometry for **1** and tetrahedral geometry for **2** around metal ions [31,36]. The d-d transition for **3** has not been observed due to containing Zn(II) ions (d^{10}).

3.4 Magnetic susceptibilities results of 1-3

Generally, cobalt(II) forms six coordinated octahedral complexes and four coordinated tetrahedral complexes; however, there have also been reported of five coordinated trigonal bipyramidal complexes and a few four coordinated planar complexes. Single unpaired electron Cobalt(II) complexes can be low-spin octahedral or planar, while complexes with three unpaired electrons can be octahedral or tetrahedral. Cobalt(II) complex magnetic moment values are useful in differentiating between octahedral, planar, and tetrahedral forms. The magnetic moments of high-spin octahedral cobalt(II) complexes range from 4.7 to 5.2 B.M. [37]. The magnetic moments of high-spin tetrahedral compounds are independent of temperature and have been reported to range from 4.3 to 4.7 B.M. [38]. The magnetic moment value of the high-spin cobalt(II) complex in the current research measured at room temperature is 3.83 B.M. This value shows that the complex has a four-coordinated tetrahedral geometry and is consistent with the predicted spin-only value of 3.87 B.M. for three unpaired electrons. The magnetic moment of compound **2** at room temperature is 3.22 B.M. Due to two unpaired electrons, there are deviations from the spin-only magnetic moment of 2.83 B.M. that are ascribed to the orbital contribution. This value is consistent with the magnetic moments of tetrahedral Ni(II) complexes containing in the range 3.2–4.1 B.M. [39]. As expected, the magnetic moment is zero for the Zn(II) complex with the d^{10} electron configuration.

3.5 Molar Conductivity results of 1-3

Conductivity measurements of **1-3** (in DMSO) were observed as 5.70 for **1**, 5.50 for **2** and 5.20 μS/cm for **3** and these results are non-ionic for **1-3** [40].

3.6 Antimicrobial results of all compounds

In this work, the antibacterial and antifungal activities of BP, H$_2$ADSA, and **1-3** were tested by the microdilution method. The MIC values of all compounds are given in Table 3. According to MIC values it was observed that all compounds have antibacterial and antifungal activity properties. The observed activity results are similar to BP and ADSA, salt and metal complexes found in the literature [31,32,35].

Against *C. albicans* yeast species, BP and H$_2$ADSA (15.60 μg/mL), **1** and **2** (31.25 μg/mL) showed a higher effect than the control compound Fluconazole and Ketoconazole (62.50 μg/mL) while **1** had similar effects (62.50 μg/mL) with Fluconazole and Ketoconazole.

Table 3. Antimicrobial activity values of compounds (μg/mL)

Compound	*E. coli*	*E. faecalis*	*P. aeruginosa*	*L. monocytogenes*	*S. aureus*	*B. subtilis*	*C. albicans*
Vancomycin	31.25	62.50	62.50	125.00	31.25	250	-
Levofloxacin	31.25	62.50	31.25	31.25	31.25	62.50	-
Cefepime	62.50	31.25	31.25	31.25	62.50	62.50	-
Chloramphenicol	62.50	62.50	125.00	62.50	62.50	62.50	
Fluconazole	-	-	-	-	-	-	62.50
Ketoconazole	-	-	-	-	-	-	62.50
BP	31.25	62.50	62.50	15.60	62.50	62.50	15.60
H$_2$ADSA	7.80	62.50	31.25	62.50	62.50	62.50	15.60
1	62.50	31.25	62.50	62.50	62.50	62.50	62.50
2	62.50	31.25	31.25	62.50	31.25	31.25	31.25
3	31.25	31.25	31.25	31.25	62.50	31.25	31.25

Against *S. aureus* bacteria, BP, H_2ADSA **1** and **3** were determined to have similar effects (62.50 µg/mL) with Cefepime and Chloramphenicol while **2** showed higher activity (31.25 µg/mL) than Cefepime and Chloramphenicol. Compound **2** was determined to have similar effects (31.25 µg/mL) with Vancomycin and Levofloxacin while the other compounds showed less activity (62.50 µg/mL) than Vancomycin and Levofloxacin. Against *E. faecalis* bacteria, **1-3** have similar activity (31.25 µg/mL) with Cefepime and Chloramphenicol while BP and H_2ADSA have similar effects (62.50 µg/mL) with Vancomycin and Levoflaxacin.

Compared to the control compounds, BP exhibited a greater impact (15.60 µg/mL) against *L. monocytogens*. H_2ADSA, **1** and **2** were determined to have similar effects with Chloramphenicol (62.50 µg/mL) while BP (15.60 µg/mL) and **3** (31.25 µg/mL) showed higher activity than Chloramphenicol. **3** showed similar effects with as Levofloxacin and Cefepime while the other compounds showed less activity (62.50 µg/mL) than Levofloxacin and Cefepime. All compounds were found to have higher efficacy against this bacterium than the Vancomycin.

Comparing **2** and **3** to the control compounds, the former had greater potency (31.25 µg/mL) against *B. subtilis* bacteria. The other drugs were shown to be more effective than Vancomycin and to have similar effects to Levofloxacin, Cefepime, and Chloramphenicol (62.50 µg/mL).

Against *P. aeruginoa* bacteria, BP and **1** were determined to have similar effects (62.50 µg/mL) with Vancomycin while H_2ADSA, **2** and **3** showed similar activity (31.25 µg/mL) than Levoflaxacin and Cefepime. All compounds were found to have higher efficacy against this bacterium than the Chloramphenicol.

Against *E. coli* bacteria, H_2ADSA (7.80 µg/mL) had higher activity than Vancomycin, Levofloxacin, Cefepime, and Chloramphenicol. BP and **3** for Vancomycin and Levofloxacin and **1** and **2** for Cefepime and Chloramphenicol have similar effects with control compounds.

The charge and quantity of the metals, the presence of complementary ions, the chelating impact of the ligands, the characteristics of the ligands, and the quantity of donor atoms they contain are some of the variables that may affect the antimicrobial activity of metal complexes. Analyzing the correlations between the structures and activities of the examined compounds reveals that the quantity of chelating ligands and metal ions present in the compounds most likely influences their activities. Their capacity to pass through cell walls or membrane architecture accounts for the variations in the actions of the complexes against bacteria.

4 CONCLUSION

In this work, a hydrothermal reaction was used to create newly three mixed-ligand complexes of Co(II) (**1**), Ni(II) (**2**), and Zn(II) (**3**). Elemental analysis, AAS, TGA, IR, UV-Vis, molar conductivity, and magnetic susceptibility techniques were used to characterize **1-3**. Furthermore, the antimicrobial characteristics of **1-3** and the free ligands (BP, H_2ADSA) were also examined. New substances are now required to eradicate harmful bacteria from human health in an economical and efficient manner. Recently, compounds with antibacterial and antiyeast characteristics have been developed. Comparing **2** and **3** to control compounds, they exhibit good antimicrobial action, particularly against *B. subtilis* and *C. albicans*. The recently created substances shown antibacterial and antiyeast properties. The preliminary biological evaluation suggests that the derivatives of these complexes are valuable for further antibacterial and antifungal in vivo and in vitro tests. Their capacity to pass through cell walls or membrane architecture accounts for the variations in the actions of the complexes against bacteria.

Acknowledgements

This work was supported by the Kütahya Dumlupinar University Research Foundation (Grant No: 2020-07 and 2021-42) and carried out at the Chemistry Department of the same university.

Author Contributions

Nurgün BÜYÜKKIDAN: Conceptualization, Software, Formal analysis, Investigation, Writing - Original Draft, Funding acquisiton
Seher KAYA: Formal analysis, Investigation
Halil İLKİMEN: Formal analysis, Investigation, Writing - Original Draft
Aysel GÜLBANDILAR: Formal analysis, Investigation, Data curation, Writing - Original Draft

All authors read and approved the final manuscript.

Conflict of interest

No conflict of interest was declared by the authors.

References

[1] T.M. Reineke, M. Eddaoudi, D. Moler, M.O’. Keeffe, O.M. Yaghi, “Large free volume in maximally interpenetrating networks: the role of secondary building units exemplified by $Tb_2(ADB)_3[(CH_3)_2SO]_4\cdot 16[(CH_3)_2SO]^1$”. *J. Am. Chem. Soc.*, vol. 122, pp. 4843-4844, 2000.

[2] C.B. Liu, S.S. Tan, Z.S. Wu, H.L. Wen, “Poly[di-μ_3-chloro-μ_2-4,4’-bipyridine-dicopper(I)]”. *Acta Cryst.*, vol. E62, pp. m1496-m1496, 2006.

[3] N. Lah, I. Leban, “Polymeric monovalent and divalent copper sulfates with 4,4'-bipyridine: $[Cu_2(SO_4)(4,4'\text{-bipy})_2.6H_2O]_n$ and $[Cu(SO_4)(4.4'\text{-bipy})(H_2O).0.5H_2O]_n$”. *Inorg. Chem. Commun.*, vol. 9, pp. 42-45, 2006.

[4] K. Biradha, M. Fujita, “Coordination polymers containing square grids of dimension 15 × 15 Å”. *J. Chem. Soc., Dalton Trans.*, pp. 3805-3810, 2000.

[5] S.A. Bourne, J. Lu, B. Moulton, M. J. Zawarokto, “Coexisting covalent and noncovalent nets: parallel interpenetration of a puckered rectangular coordination polymer and aromatic noncovalent nets”. *Chem. Commun.*, pp. 861-862, 2001.

[6] L.J. Moitsheki, S.A. Bourne, L. R. Nassimbeni, “A coordination polymer of thallium(III) nitrate with 4,4’-bipyridine-*N,N*’-dioxide”. *Acta Cryst.*, vol. E62, pp. m542-m544, 2006.

[7] S.J. Dalgarno, M.D. Hardie, J.L. Atwood, J.E. Warren, C.L. Raston, “A complex 3D ‘wavy brick wall’ coordination polymer based on p-sulfonatocalix[8]arene”. *New J. Chem.*, vol. 29, pp. 649-652, 2005.

[8] D.L. Long, A.J. Blake, N.R. Champness, M. Schroder, Constructing terbium co-ordination polymers of 4,4′-bipyridine-*N,N′*-dioxide by means of diffusion solvent mixtures. *Chem.: A Euro. J.*, vol. 8, no. 9, pp. 2026-2033, 2002.

[9] Y. Chen, S. Songsheng, E. Rex, “The effect of zinc(II) on the formation of 2,2′- and 2,3′-bipyridine complexes of $[Ru_2^{II}(ttha)]^{2-}$ ($ttha^{6-}$ = triethylenetetraminehexa-acetate)”. *Trans. Met. Chem.*, vol. 22, pp. 338-346, 1997.

[10] D. Czakis-Sulikowska, J. Radwanska-Doczekalska, M. Markiewicz, “Synthesis and thermal decomposition of mixed 2, 4'-bipyridine-oxalato complexes with Mn(II), Co(II), Ni(II) and Cu(II)”. *J. Ther. Anal. Cal.*, vol. 60, no. 1, pp. 145-151, 2000.

[11] Z. Wang, R.G. Xiong, E. Naggar, B.M. Foxman, W.B. Lin, “Coordination chemistry of 2,4'-bipyridine. synthesis and structures of $Co(2,4'\text{-bipyridine})_2(NO_3)_2(H_2O)$ and $Cd(2,4'\text{-bipyridine})_2(NO_3)_2(H_2O)_2$”. *Inorg. Chim. Acta*, vol. 288, pp. 215-219, 1999.

[12] R.L. LaDuca Jr, C. Brodkin, R.C. Finn, J. Zubieta, “A three dimensional organic–inorganic composite material constructed from cobalt-3,3′-bipyridyl networks linked through tetravanadate clusters: $[\{Co(3,3'\text{-bpy})_2\}_2V_4O_{12}]$”. *Inorg. Chem. Commun.*, vol. 3, no. 5, pp. 248-250, 2000.

[13] R.L. LaDuca Jr., M. Desciak, M. Laskoski, R.S. Rarig Jr., J. Zubieta, “Hydrothermal synthesis of two-dimensional organic-inorganic hybrid materials of the nickel-molybdate family: the structures of $[\{Ni(3,3'\text{-bpy})_2\}_2Mo_4O_{14}]$ and $[Ni(3,3'\text{-Hbpy})Mo_4O_{13}(OH)]$”. *J. Chem. Soc., Dalton Trans.*, pp. 2255-2257, 2000.

[14] X. Cui, A.N. Khlobystov, X. Chen, D.H. Marsh, A.J. Blake, W. Lewis, N.R. Champness, C.J. Roberts and M. Schroeder, “Dynamic equilibria in solvent-mediated anion, cation and ligand exchange in transition-metal coordination polymers: solid-state transfer or recrystallisation?” *Chem. - A Euro. J.*, vol. 15, no. 35, pp. 8861-8873, S8861/1-S8861/32, 2009.

[15] F.F.B.J. Janssen, L.P.J. Veraart, J.M.M, Smits, R. de Gelder, A.E. Rowan, “1. Solvent, linker, and anion effects on the formation, connectivity, and topology of Cu(I)/PPh_3/*N*-Donor ligand coordination polymers”. *Cryst. Grow. Des.*, vol. 11, no. 10, pp. 4313-4325, 2011.

[16] M.L. Tong, X.M. Chen, B.H. Ye, S.W. Ng, “Helical silver(I)−2,4‘-bipyridine chains organized into 2-D networks by metal-counterion or metal-metal bonding. structures of [Ag(2,4‘-bipyridine)]X (X^- = NO_3^- or ClO_4^-)”. *Inorg. Chem.*, vol. 37, no. 20, pp. 5278-5281, 1998.

[17] T.J.J. Kinnunen, M. Haukka, E. Pesonen, T.A. Pakkanen, “Ruthenium complexes with 2,2′, 2,4′- and 4,4′-bipyridine ligands: The role of bipyridine coordination modes and halide ligands”. *J. Organomet. Chem.*, vol. 655, pp. 31-38, 2002, doi: 10.1016/S0022-328X(02)01408-0

[18] X. Xiao, L. Zou, H. Pang, Q. Xu, “Synthesis of micro/nanoscaled metal-organic frameworks and their direct electrochemical applications”. *Chem. Soc. Rev.*, vol. 49, pp. 301-331, 2020.

[19] Y. Zhao, Y. Yuan, X. Du, X. Lin, F. Liao, “Hydrothermal assembly of various dimensional pure-inorganic copper-molybdenum frameworks”, *CrystEngComm*, vol. 18, pp. 521-524, 2016.

[20] Z. Hulvey, B.C. Melot, A.K. Cheetham, “Crystal structure of catena-poly[aqua-(μ^2-hexamethylenetetramine-κ^2N:N')-bis(2,6-difluorobenzoato-κ^2O:O')cadmium(II)] monohydrate, $C_{20}H_{22}CdF_4N_4O_6$”. *Inorg. Chem.*, vol. 49, pp. 4594-4598, 2010.

[21] N. Moliner, J.A. Real, M.C. Muñoz, R. Martínez-Mañez, J.M.C. Juan, “Unprecedented pseudo-trigonal-bipyramidal intermediate-spin iron(III) complex: synthesis, crystal structure and magnetic properties of $[Fe(4,4'\text{-bipy})_2(NCS)_3](CH_3)_2CO$”. *J. Chem. Soc., Dalton Trans.*, pp. 1375-1380, 1999.

[22] S.M.F. Lo, S.S.Y. Chui, L.Y. Shek, Z.Y. Lin, X.X. Zhang, G.H. Wen, I.D. Williams, “Solvothermal synthesis of a stable coordination polymer with copper-I−copper-II dimer units: $[Cu_4\{1,4\text{-}C_6H_4(COO)_2\}_3(4,4'\text{-bipy})_2]_n$”. *J. Am. Chem. Soc.*, vol. 122, pp. 6293-6294, 2000.

[23] H. Zhao, Z.R. Qu, Q. Ye, X.S. Wang, J. Zhang, R.G. Xiong, X.Z. You, “An unusual mixed-valence Cu(I)−Cu(II) 3-D framework”. *Inorg. Chem.*, vol. 43, pp. 1813-1815, 2004.

[24] B. Zhao, P. Cheng, Y. Dai, C. Cheng, W. Shi, D.Z. Liao, D.Z. Liao, S.P. Yan, Jiang, Z.H. “Coordination polymers containing 1D channels as selective luminescent probes”. *J. Am. Chem. Soc.*, vol. 126, no. 47, pp. 15394-15395, 2004.

[25] T.J. Prior, D. Bradshaw, S.J. Teat, M.J. Rosseinsky, “Designed layer assembly: a three-dimensional framework with 74% extra-framework volume by connection of infinite two-dimensional sheets”. *Chem. Commun.*, pp. 500-501, 2003.

[26] J.Y. Lu, “Crystal engineering of Cu-containing metal-organic coordination polymers under hydrothermal conditions”. *Coord. Chem. Rev.*, vol. 246, no. 1-2, pp. 327-347, 2003.

[27] Y.Q. Zheng, J.L. Lin, A. Y. Pan, “A novel adipate bridged supramolecular layer: crystal structure of the cobalt(II) complex $[(\mu\text{-}C_6H_8O_4)_{4/2}Co(\mu\text{-}H_2O)_2Co(H_2O)_4].4H_2O$*”. Zeits. Anorg. Allg. Chem.*, vol. 626, pp. 1718-1720, 2000.

[28] Y.Q. Zheng, Z.P. Kong, “A suberato-pillared Mn(II) coordination Polymer: Hydrothermal synthesis, crystal structure, and magnetic properties of $Mn_2(H_2O)[O_2C(CH_2)_6CO_2]_2$”. *J. Solid State Chem.*, vol. 166, no. 2, pp. 279-284, 2002, doi: 10.1006/jssc.2002.9585

[29] P.M. Forster, A.K. Cheetham, “Open-Framework Nickel Succinate, $[Ni_7(C_4H_4O_4)_6(OH)_2(H_2O)_2].2H_2O$: A New hybrid material with three-dimensional Ni-O-Ni connectivity”. *Ang. Chem. Inter. Ed.*, 41, 457-459, 2002.

[30] E.W. Lee, Y.J. Kim, D.Y. Jung, “A coordination polymer of cobalt(II)-glutarate: Two-dimensional interlocking structure by dicarboxylate ligands with two different conformations”. *Inorg. Chem.*, vol. 41, pp. 501-506, 2002.

[31] N. Büyükkıdan, H. İlkimen, S. Bozyel, M. Sarı, A. Gülbandılar, “The syntheses, structural and biological studies of Co(II) complexes of 1,2-bis(pyridin-4-yl)ethane with 2-aminobenzene-1,4-disulfonic acid and 2,6-pyridinedicarboxylic acid”. *J. Mol. Struct.*, vol. 1275, 134586, 2023.

[32] N. Büyükkıdan, H. İlkimen, S. Bozyel, M. Sarı, A. Gülbandılar, “Two new Cu(II) coordination complexes with 1,2-bis(pyridin-4-yl)ethane bridge-ligand: Synthesis, characterization and antimicrobial activity”. *Polyhedro*n, vol. 223, 115951, 2022.

[33] G.K.H. Shimizu, R. Vaidhyanathan, J.M. Taylor, “Phosphonate and sulfonate metal organic frameworks”. *Chem. Soc. Rev.*, vol. 38, pp. 1430-1449, 2009.

[34] D. Sun, R. Cao, Y. Sun, W. Bi, X. Li, Y. Wang, Q. Shi, X. Li, “Novel silver-containing supramolecular frameworks constructed by combination of coordination bonds and supramolecular interactions”. *Inorg. Chem.*, vol. 42, pp. 7512-7518, 2003.

[35] N. Büyükkıdan, S.B. Turgut, H. İlkimen, M. Sarı, A. Gülbandılar, “Aniline-2,5-disulfonic acid based new proton transfer salt and new Co(II) and Cu(II) coordination polymers: synthesis, structural and antimicrobial studies”. Chem. Papers, vol. 78, pp. 6405-6416, 2024.

[36] H. İlkimen, S.G. Salün, A. Gülbandılar, M. Sarı, “The new salt of 2-amino-3-methylpyridine with dipicolinic acid and its metal complexes: Synthesis, characterization and antimicrobial activity studies”. *J. Mol. Struct.*, vol. 1270, pp. 133961, 2022.

[37] R. Kant, “Magnetic behavior studies on Co (II) complexes with *N*- And *O*- donor sites ligand”. *Inter. J. Sci. Res. Pub.*, vol. 9, no. 3, pp. 728-730, 2019.

[38] N.N. Jha, I.P. Ray, “Magnetic studies on Co(II) and Ni(II) complexes of hydroxamic acid”. *Asian J. Chem.*, vol. 12, no. 3, pp. 703-706, 2000.

[39] A.A. Osowole, G.A. Kolawole, O.E. Fagade, “Synthesis, physicochemical, and biological properties of nickel (II), copper (II), and zinc (II) complexes of an unsymmetrical tetradentate Schiff base and their adducts”. *Synth. Reac. Inorg. Metal-Org. Nano-Metal Chem.* vol. 35, no. 10, pp. 829-836, 2005.

[40] W.J. Geary, “The use of conductivity measurements in organic solvents for the characterisation of coordination compounds”. *Coord. Chem. Rev.*, vol. 7, no. 1, pp. 81-122, 1971.

APPENDICES

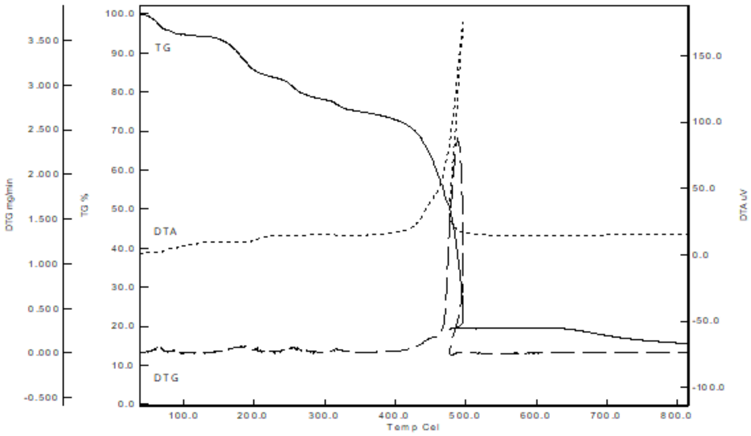


Fig. S1. Thermal analysis results of **1**

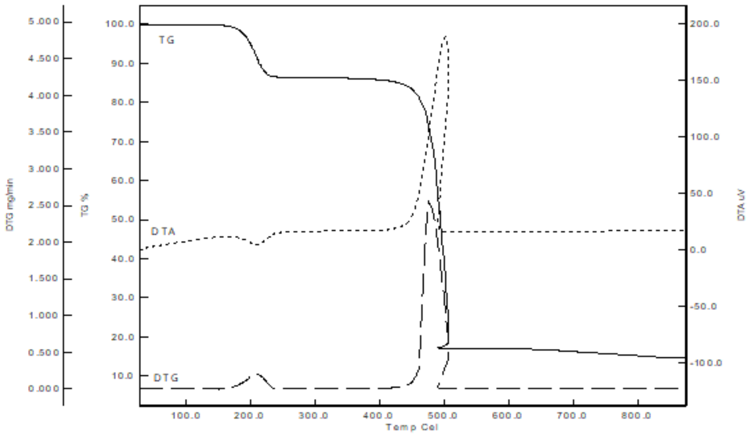


Fig. S2. Thermal analysis results of **2**

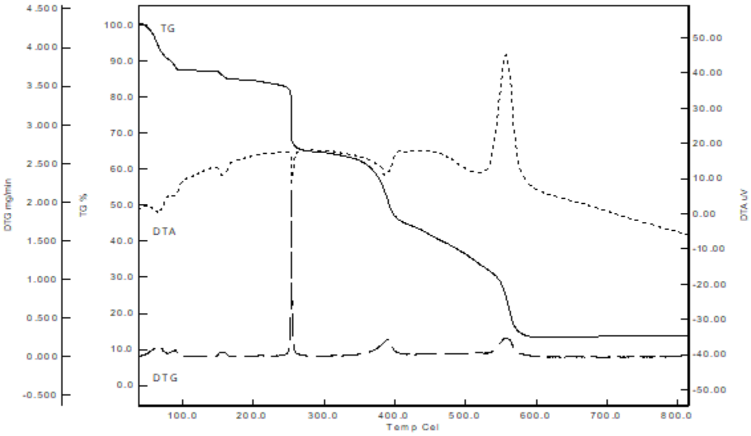


Fig. S3. Thermal analysis results of **3**

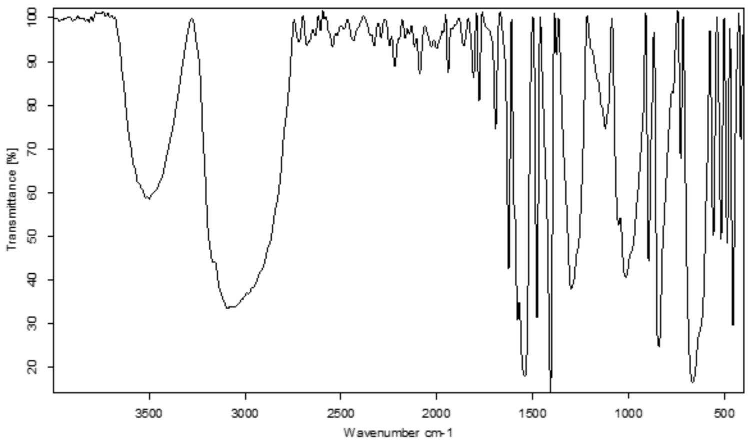


Fig. S4. FT-IR spectrum of H_2ADSA

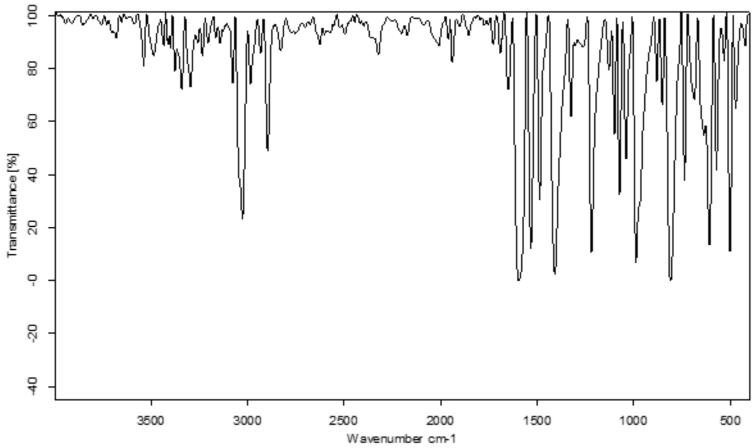


Fig. S5. FT-IR spectrum of BP

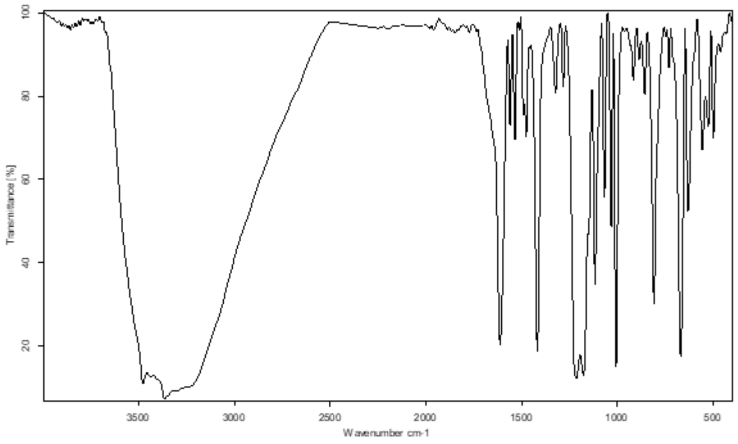


Fig. S6. FT-IR spectrum of **1**

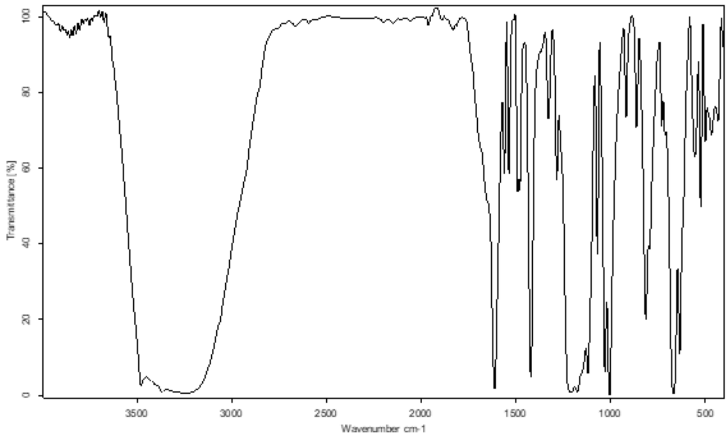


Fig. S7. FT-IR spectrum of **2**

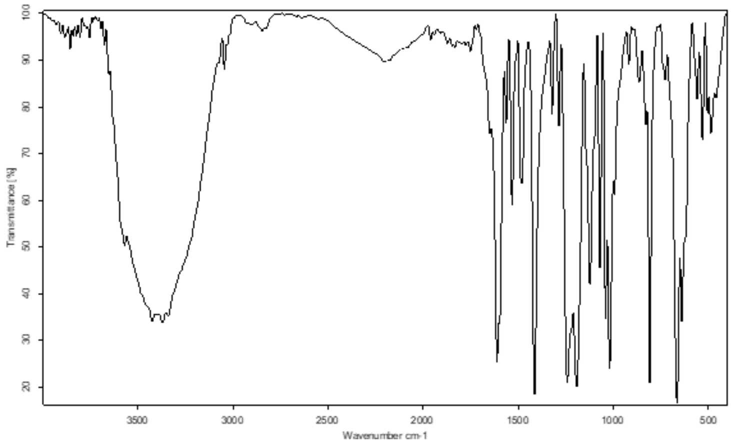


Fig. S8. FT-IR spectrum of **3**

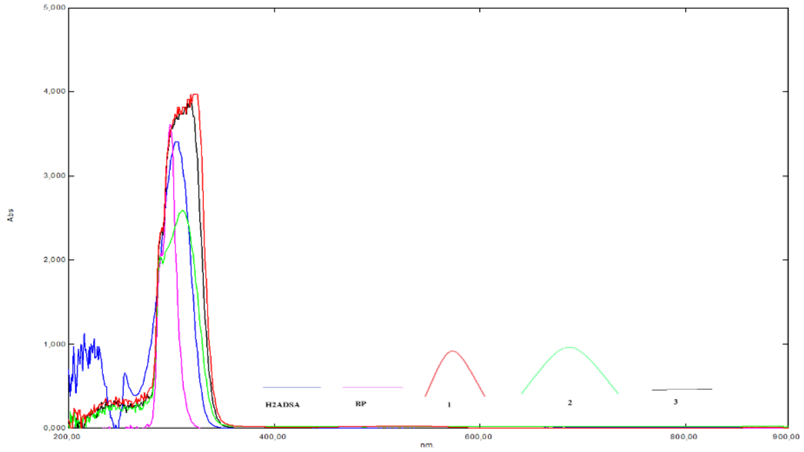


Fig. S9. UV-Vis spectra of all compounds