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Chemosensing Study of 1,4-Benzothiazine Generated from Acetylacetone

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ABSTRACT
Investigated the chemosensing property of already reported benzothiazine molecule. Electronic spectroscopy has been used for the detection of cations in solution. The cations Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} exhibited different colours with 1,4-benzothiazine derivative due to the absorption in the visible region.
Keywords: 2-aminobenzothiazole, Acetylacetone, Benzothiazine, Chemosensor, Absorption spectra

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1. INTRODUCTION

Because colorimetric chemosensors are less expensive and require less complicated assays than other sensing techniques, this field is rapidly expanding (Bansod, Kumar, Thakur, Rana & Singh 2017) [1]. Clinical toxicology, environmental, bioorganic chemistry, bioremediation and waste management are among the fields that heavily rely on sensing devices for the study of toxic or heavy metal ions (Formica, Fusi, Giorgi, Micheloni, 2012) [2]. Thus, over the past ten years, there has been a lot of research focused on the creation of small molecule-based colorimetric chemosensors that require one-pot synthesis and isolation techniques. Chromogenic and fluorescence properties of functionalized benzothiazine were evaluated (Fateh, Yildirim, A., Bhatti & Yilmaz, 2021) [3]. A novel photochromic diarylethene derivative containing a benzothiazine unit has been synthesized. Its photochromism and fluorescent selectivity to metal ions were studied in detail (Wang, Cui, Qiu & Pu, 2018) [4]. Distinct methods for the multi-component synthesis of heterocyclic derivatives of benzothiazines reported (Shafia, Ayas and Ahmad, 2020) [5]. Moreover, benzothiazine derivatives have a broad range of biological applications, including anti-microbial, anti-malarial, anti-cancer, anti-viral, ant-oxidant, and anti-inflammatory properties, they are of great interest to scientists in a variety of domains. Recent trends focus toward the synthesis of benzothiazines and their derivatives (Furqan, Matloob, Afshan, Sana & Ameer, 2021; Lystsova, Dmitriev, Maslivets & Khrastsova, 2023; Mlakic et al., 2023, Rai, Singh, Raj & Saha, 2018) [6, 7,8, 9]. This work presents chemosensing analysis of the 1,4-benzothiazine derived from acetyl acetone.

2. EXPERIMENTAL

2.1 General

2-aminothiophenol and acetyl acetone were became available through Sigma-Aldrich and were used without further purification. Organic solvents were used as received. Electronic spectrum in acetonitrile in the range 200-800 nm was taken using the UV-Vis spectrophotometer Cary 5000, version 1.09.

2.2 Synthesis of ATP-AC

The well-known standard procedure outlined in the literature was followed to synthesize the 1,4-benzothiazine under investigation, ATP-AC (Shajeelammal, Minitha, Reena Ravindran, 2018) [10]. 2-Acetylacetone and 2-aminothiophenol were in 1:1 ratio and dissolved in methanol separately. After that, they mixed, stirred well and set aside for two days. ATP-AC recrystallized from ethanol as orange-red in colour was filtered, washed with ethanol and dried (Minitha & Shajeelammal, 2021) [11].

3. RESULTS AND DISCUSSION

3.1 Synthesis

Acetylacetone and 2-aminothiophenol underwent an oxidative cyclisation process to yield 1,4-benzothiazine, ATP-AC. Using the slow evaporation approach, compound ATP-AC was isolated from ethanol to form orange-red crystals (Figure 1).

Figure 1: Crystals of ATP-AC

3.2 CHEMOSENSING STUDY OF ATP-AC

Due to their significant functions in biological, chemical and environmental systems, the design and synthesis of chemosensors have drawn a considerable focus in the supramolecular chemistry discipline (Busschaert, Caltagirone, Rossom & Gale, 2015) [12]. By using UV–Vis spectroscopy, the compound ATP-AC with the different cations (Ba^{2+}, Ca^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}) has been subjected to a spectrophotometric analysis. In order to make the determination, solutions of ATP-AC (10^{-3}M) and the cations under study (10^{-3}M) were prepared in acetonitrile (as chloride salts for Ba^{2+}, Ca^{2+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}). Then, equivalents of cations were added one at a time to the benzothiazine derivative solution and absorbance spectra were obtained in a quartz cuvette with a 10 mm route length. The results showed that Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions cause a discernible colour shift in the ATP-AC's spectrum responses when different cations are added (Scheme 1 and Figure 2).

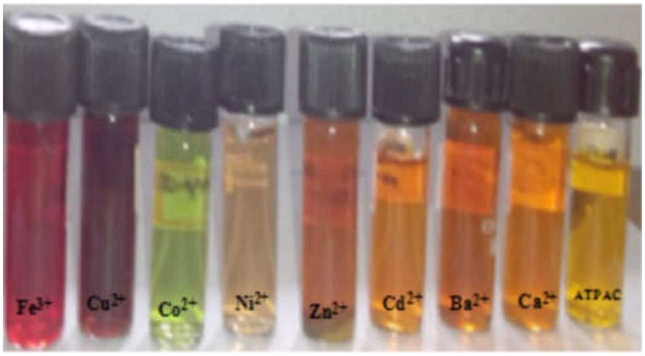
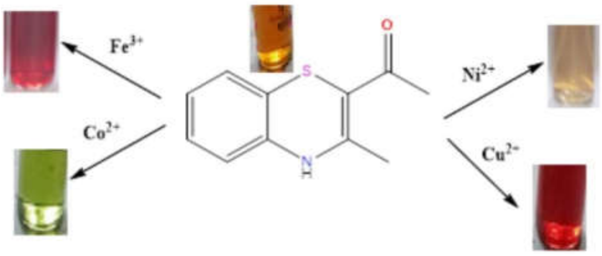


Figure 2: The ATP-AC absorbance in CH_3CN with the addition of cations



Scheme 1: Diagrammatic representation of the chemosensor ATP-AC's selective detection of cations

An intense absorption band at 250 and 300nm, is perhaps attributed to the absorbance of thiazine and carbonyl moiety, respectively, was discovered from the ATP-AC absorption spectra in CH_3CN. The absorption intensity of ATP-AC at 300nm progressively drops as the concentration of Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+} increases sequentially. Additionally, a new absorption peak in the visible range of the ATPAC–Fe^{3+}, ATP-AC–Co^{2+}, ATP-AC–Ni^{2+} and ATP-AC–Cu^{2+} systems arise at 500nm. The coordination of ATPAC with cations is most likely the cause of this absorption peak. It is observed that the color of ATP-AC solution changes, plainly visible to the unaided eye, from orange to pink for Fe^{3+}, green for Co^{2+}, brown for Ni^{2+}, and red for Cu^{2+}.

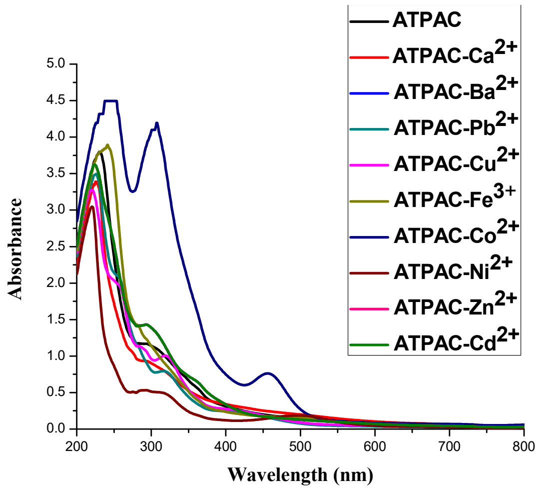


Figure 3(a): ATP-AC-different cations in the range 200 nm to 800 nm

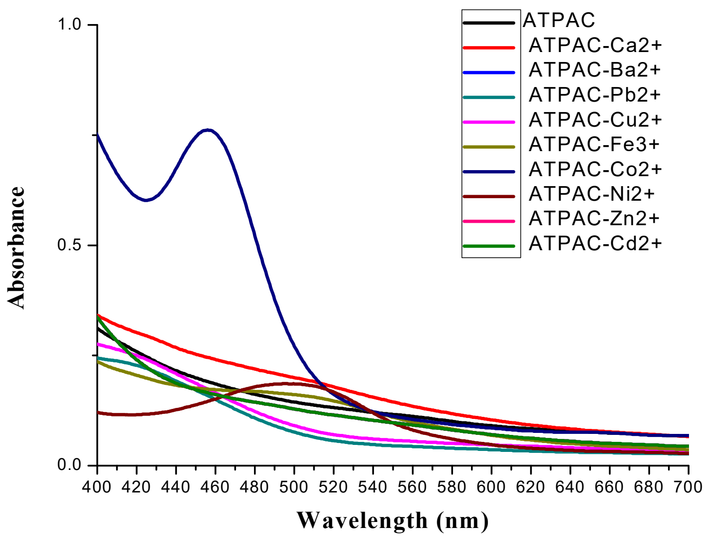


Figure 3(b): ATP-AC-different cations in the range 400 nm to 700 nm

In order to confirm whether ATP-AC may function as a colorimetric probe for Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}, we have investigated how different cations additions affect ATP-AC's spectrum characteristics. Figure 3.3(a) and (b) depicts the variation in ATP-AC's absorption spectra with the addition of different cations, including Ba^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} metal cations. The incorporation of cations Ba^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} does not appear to alter the absorption maximum in any noticeable way. The solution's colour changed as a result of the addition of Fe^{3+}, Co^{2+}, Cu^{2+} and Ni^{2+}, which were detected at 450 and 500 nm, respectively. This suggests that these cations have the ability to coordinate with ATP-AC. A variety of donor atoms, including the neutral O and S in the ATP-AC, can combine with metal ions to form coordination complexes. The Figure 3.4 describes the chemical synthesis of the ATP-AC-metal complex under selective ion sensing conditions.

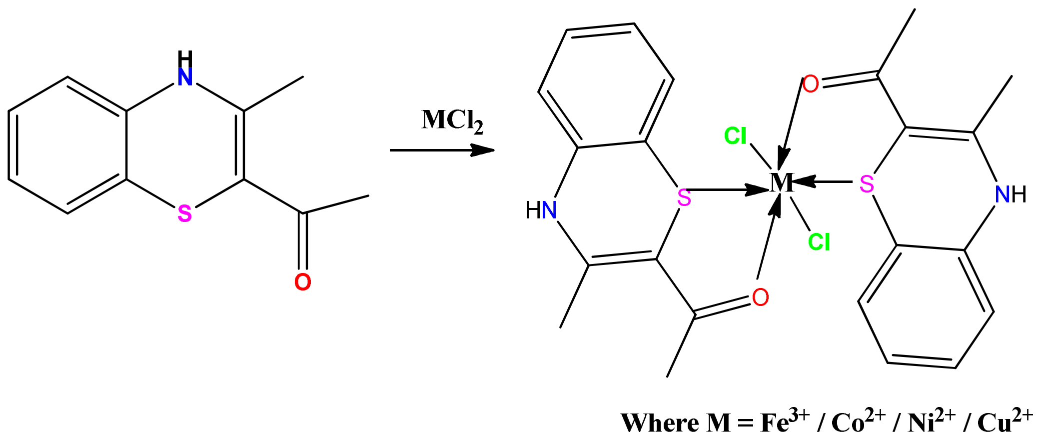


Figure 4: ATP-AC binding mechanism with metal ions proposed

4. CONCLUSIONS

Using an oxidative cyclization procedure, a derivative of 1,4-benzothiazine was created from 2-aminothiophenol and acetylacetone. We have demonstrated a single phenothiazine chemosensor based on multiple metal ions sensing. Since benzothiazine absorbs light in the visible spectrum, it takes on distinct colors when combined with Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+}. The benzothiazine derivative can be used to identify these cations. Benzothiazine also forms chelation with other ions, although no discernible color change is seen. Therefore, the straightforward UV-Vis spectroscopy approach is unable to detect them. Thus, a straightforward framework for creating multiple metal ions detecting chemosensor was made available by the acetylacetone-based benzothiazine.

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REFERENCES

1. Bansod, B.K., Kumar, T., Thakur, R., Rana , S., Singh, I. (2017). A review on various electrochemical techniques for heavy metal ions detection with different sensing platforms. *Biosens. Bioelectron*, 94(15), 443–455.
2. Formica, M., Fusi, V., Giorgi, L., Micheloni, M. (2012). New fluorescent chemosensors for metal ions in solution. *Coord. Chem. Rev.*, 256, 170–192.
3. Fateh, F., Yildirim, A., Bhatti, A.A., Yilmaz M. (2021). New Benzothiazin-functionalized Calix [4]arene-based Fluorescent Chemosensor for the Selective Detection of Co^{2+} Ion. *J. Fluoresc.*, 31, 1075–1083.
4. Wang, Z., Cui, S., Qiu, S., Pu, S. (2018). A new fluorescence probe based on diarylethene with a benzothiazine unit for selective detection of Cd^{2+}. *Tetrahedron* 74(52), 7431–7437
5. Shafia, M., D., Ayaz M., Ahmad D.B. (2020). Synthetic Strategies of Benzothiazines: A Mini Review. *Mini-Rev. Org. Chem.*, 17, 148–157.
6. Furqan, A.S., Matloob, A., Afshan, K., Sana, A., Ameer, F.Z. (2021). Recent trends toward the synthesis of fused-benzothiazines and their derivatives. *Synth. Commun.*, 51, 351-378.
7. Lystsova, E.A., Dmitriev, M.V., Maslivets, A.N., Khrastsova, E.E. (2023). Nucleophile-induced ring contraction in pyrrolo[2,1-

c][1,4]benzothiazines: access to pyrrolo[2,1-b][1,3]benzothiazoles. *Beilstein J. Org. Chem.*, 19, 646–657.

8. Mlakic, M., Cipor, I., Kovacec, P., Goran Kragol, G., Ratkovic, A., Kovacevic, T., Zadravec, R., Milasinovic, V., Molcanov, K., Piantanida, I., Skoric, I. (2023). The Benzothiazine Core as a Novel Motif for DNA-Binding Small Molecules. *Molecules*, 28(11), 4499.

9. Rai, A., Singh, A.K., Raj, V., Saha, S. (2018). 1,4-Benzothiazines-A Biologically Attractive Scaffold. *Mini Rev. Med. Chem.*, 18, 42–57.

10. Shajeelammal, Minitha, R., Reena Ravindran (2018). One pot synthesis of 1–(3–methyl–4H–benzo [1,4] thiazin–2–yl) ethanone and its antimicrobial properties. *Bull. Pure and Appl. Sci. Sec. C*, 37(1), 143–147.

11. Minitha, R., Shajeelammal, J. (2021). CCDC 2079931, Experimental Crystal Structure Determination. DOI: 10.5517/ccdc.csd.cc27tbkz, *CSD Communication.*

12. Busschaert, N., Caltagirone, C., Rossom, W.V., Gale P.A., (2015). Applications of supramolecular anion recognition. *Chem. Rev.*, 115 8038–8155.

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