chemistry proceedings

MDPI

Proceeding Paper

Pyridine Derivatives as Fluorescent Sensors for Cations †

Ikram Baba-Ahmed [1,2,*], Zahira Kibou [1,2], Julio A. Seijas [3], Ridha Hassaine [1], Fatiha Nouali [1], M. Pilar Vázquez-Tato [3] and Noureddine Choukchou-Braham [1]

[1] Laboratoire de Catalyse et Synthèse en Chimie Organique, Faculté des Sciences, Université de Tlemcen, B.P. 119, 13000 Tlemcen, Algeria; email1@email.com (Z.K.); email1@email.com (R.H.); email1@email.com (F.N.); email1@email.com (N.C.-B.)
[2] Faculté des Sciences, Université Belhadj Bouchaib de Ain Témouchent, B.P. 284, 46000 Ain Témouchent, Alegria
[3] Departamento de Química Orgánica, Facultad de Ciencias, Universidad of Santiago de Compostela, Campus Terra, Alfonso X el Sabio, 27002 Lugo, Spain; email1@email.com (J.A.S.); email1@email.com (M.P.V.-T.)
* Correspondence: i_babaahmed@yahoo.com

† Presented at the 27th International Electronic Conference on Synthetic Organic Chemistry (ECSOC-27), 15–30 November 2023; Available online: https://ecsoc-27.sciforum.net/.

Abstract: A fluorescence grating sensor based on a pyridine derivative was synthesized. Results showed that it can rapidly identify and detect toxic heavy metal ions, such as Cr^{2+}, Hg^{2+}, Ni^{2+} and Co^{2+}. When these toxic heavy metal ions were added to the fluorescence array sensor, different fluorescent responses were produced due to the different binding capacities of the metal ion complex. These toxic heavy metal ions present in environmental water were identified using the fluorescence grating sensor. This sensor provides a fast and convenient method for monitoring toxic heavy metal ions in wastewater.

Keywords: 2-amino-pyridine; synthesis of chemosensors; toxic cations; fluorescence

Citation: Baba-Ahmed, I.; Kibou, Z.; Seijas, J.A.; Hassaine, R.; Nouali, F.; Vázquez-Tato, M.P.; Choukchou-Braham, N. Pyridine Derivatives as Fluorescent Sensors for Cations. *Chem. Proc.* **2023**, *14*, x. https://doi.org/10.3390/xxxxx

Academic Editor: Firstname Lastname

Published: 15 November 2023

1. Introduction

Environmental pollution is one of the main concerns of contemporary research.

The content of all metal ions becomes toxic when it exceeds the acceptable threshold.

Recognition of toxic metal ions is receiving particular attention, as they cause serious damage to human health and the environment [1,2].

Over the last few decades, several small-molecule-based fluorescence chemosensors have been developed [3].

There is a wide range of highly electronegative fluorescent heteroaromatics (nitrogen, oxygen, etc.) [4]. In addition, pyridine ring molecules are used as nonlinear optical materials, electrical materials and chelating agents in metal ligand chemistry [5].

From the literature, it's clear that among the fluorescent sensors developed for cation detection, those sensitive to mercury, lead, chromium, nickel, cobalt and thallium are of crucial interest due to their high toxicity [1,3,6–8].

In the present work, we report on the synthesis of chemosensors containing the pyrinidic moiety as the fluorophore unit, so we have studied their influence on the detection of toxic cations, including chromium, iron, cobalt, nickel and copper in acetonitrile/water (1:1) mixtures given the importance of developing water-soluble probes for metal detection in biological and environmental systems.

2. Materials and Methods

These fluorimetric chemosensors were analyzed at room temperature. The fluorescence excitation wavelength was set at 432 nm. All ligand was prepared in acetonitrile, maintaining a concentration of 10^{-6} M. Metal salt solutions were prepared by diluting the solutions with distilled water. The samples to be analyzed were prepared from a mixture of acetonitrile/water (1:1) at a concentration of 1 × 10^{-6} M for compound **2**, and at a concentration of 1 × 10^{-4} M for the ions studied.

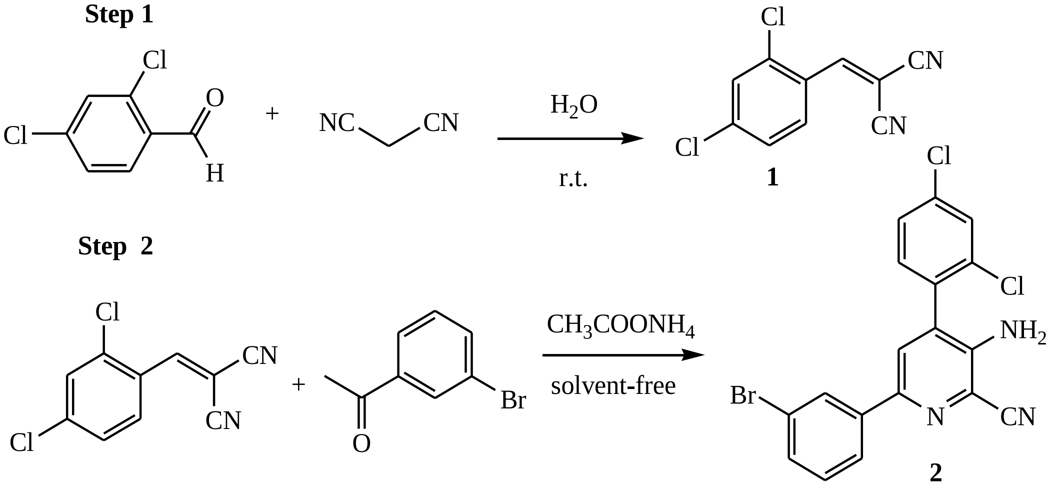
Salts used:

- $CrCl_2·6H_2O$, $CoCl_2·6H_2O$, $CuCl_2$, $AlCl_3·6H_2O$, $NiCl_2$, $FeCl_2$, $FeCl_2·4H_2O$, $CaCl_2$, $ZnCl_2$, $FeCl_3$, $HgCl_2$, $BaCl_2·2H_2O$.
- $Fe_2(SO_4)_3·9H_2O$, $CuSO_4$, $CuSO_4·5H_2O$, $MnSO_4$, $BaSO_4$, $ZnSO_4$, $NiSO_4$, $MgSO_4·H_2O$, $HgSO_4$

3. Results and Discussion

3.1. Synthesis of 2-Amino-3-cyanopyridine Derivatives from Alkenes

The first route involves the preparation of alkene **1** from Knoevenagel condensation between aromatic aldehyde and malononitrile in water at room temperature. Next, 2-amino-3-cyanopyridine derivative **2** was obtained by reacting alkene, acetophenone derivative and ammonium acetate. The reaction took place by conventional solvent-free heating (Scheme 1). The reaction mixtures was subsequently washed with diethyl ether and a small amount of ethanol. The crude product was purified by recrystallization in ethanol to give the product in good yield.



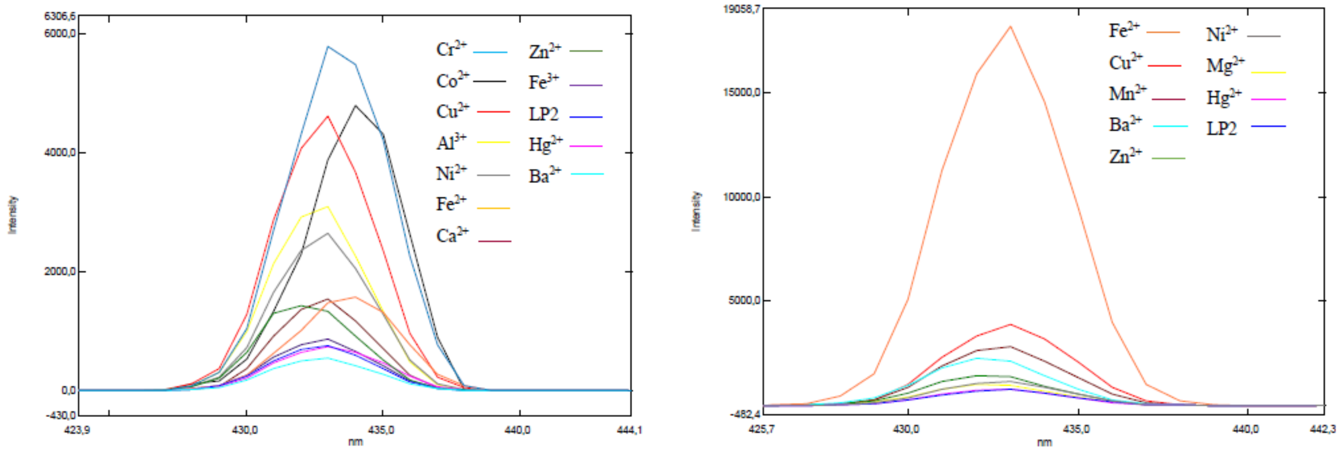
Scheme 1. Synthesis of 2-amino-3-cyanopyridine **2** from alkene **1**.

The compounds **2** was evaluated as fluorometric chemosensor evaluated the sensitivity and selectivity in the presence of several metals Hg^{2+}, Mg^{2+}, Ba^{2+}, Ca^{2+}, Mn^{2+}, Cu^{2+}, Cr^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Fe^{2+}, Fe^{3+} and Al^{3+}.

3.2. Fluorometry Analysis

The results obtained imply that compound **2** does indeed act as a chemoselective agent for Cr^{2+} ions in the presence of chloride ion Figure 1a. As expected, our chemosensors had different fluorometric responses towards the different cations studied: compound **2** interacted with Cr^{2+}, Co^{2+} and Cu^{2+} revealing remarkable fluorescence intensity at 5796.4, 4626.2 and 4324.4 a.u., respectively, while compound **2** interacting with Ba^{2+} revealed fluorescence quenching (Figure 1a). In addition, we studied the fluorescence behavior associated with the detection of iron with different degrees of oxidation (Fe(II) and Fe(III)). Similarly, compound **2** revealed sensitivity and selectivity for these two ions, with fluorescence intensity of 1578.7 a.u. for Fe^{2+} and 862.5 a.u. for Fe^{3+} in the presence of chloride ion (Figure 1a). In contrast, for the same compound, the addition of Fe^{3+} resulted in a significant deviation reaching 18,208 a.u. in the presence of sulfate as counter ion (Figure 1b). Compound **2** in the presence of cations such as Cu^{2+}, Mn^{2+}, Ba^{2+}, Zn^{2+}, Ni^{2+} and Mg^{2+}

showed an increase in fluorescence intensity compared to the ligand. No decrease in fluorescence intensity was observed in the presence of sulfate ions (Figure 1b).



(**a**) (**b**)

Figure 1. (**a**) Effect of metals on the fluorescence intensity of product **2** in the presence of chloride ions; (**b**) Effect of metals on the fluorescence intensity of product **2** in the presence of sulfate ions.

4. Conclusions

Compound **2** revealed good selectivity and sensitivity for the detection of Cr^{2+}, Co^{2+} and Cu^{2+} compared with the other metals studied, this ligand has chelating power with Fe^{3+}, it gave rise to a significant deviation in fluorescence intensity with sulfate as counterion. From this study, we conclude that product **2** can be considered as an original fluoroionophore, due to its good selectivity and sensitivity to the cations studied as well as to their appropriate counterions.

Relevant fluorometric responses of compound **2** were observed for the detection of transition metals in acetonitrile/water (1:1) mixtures. However, given the importance of water-soluble probes, the development of this selective sensor will enable many real challenges in the recognition of toxic trace metals in different biological and environmental samples to be solved quickly and easily.

Binding to metal ions is probably attributed to the nitrogen atoms of pyridine moieties as donors. The size and charge of metal ions also affect fluorescence absorption.

Enhancing or reducing fluorescence absorption makes it easier to detect a particular metal ion than many others.

Author Contributions: Conceptualization; methodology; formal analysis, I.B.-A.; software, F.N.; R.H. and I.B.-A.; validation, I.B.-A., R.H. and F.N.; data curation, I.B.-A. and R.H.; writing—original draft preparation, I.B.-A.; writing—review and editing, I.B.-A.; visualization; supervision, Z.K.; N.C.-B., J.A.S. and M.P.V.-T.; project administration, N.C.-B., Z.K. and I.B.-A. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Informed Consent Statement: Not applicable for studies not involving humans.

Data Availability Statement: Not applicable here.

Acknowledgments: The authors wish to thank Directorate General for Scientific Research and Technological Development (DGRSDT), the University of Tlemcen and University of Ain-Témouchent for the financial support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Dutta, M.; Das, D. Recent developments in fluorescent sensors for trace-level determination of toxic-metal ions. *Trends Anal. Chem.* **2012**, *32*, 113–132. https://doi.org/10.1016/j.trac.2011.08.010.
2. Poomalai, S.; Kannan, A.; Sivaraj, P.; Selvan, T.; Mosae, G.; Paulraj, S. A simply synthesized biphenyl substituted piperidin-4-one for the fluorescence chemosensing of Cd^{2+}. *Luminescence* **2017**, *32*, 1405–1410.
3. Koner, R.R.; Sinha, S.; Kumar, S.; Nandi, C.K.; Ghosh, S. 2-Aminopyridine derivative as fluorescence "On-Off" molecular switch for selective detection of Fe^{3+}/Hg^{2+}. *Tetrahedron Lett.* **2012**, *53*, 2302–2307.
4. Cheon, J.D.; Mutai, T.; Araki, K. Tuning of fluorescence properties of aminoterpyridine fluorophores by *N*-substitution. *Org. Biomol. Chem.* **2007**, *5*, 2762–2766.
5. Khalifeh, R.; Ghamari, M. A Multicomponent Synthesis of 2-Amino-3-cyanopyridine Derivatives Catalyzed by Heterogeneous and Recyclable Copper Nanoparticles on Charcoal. *J. Braz. Chem. Soc.* **2016**, *27*, 759–768.
6. Wu, D.; Chen, L.; Lee, W.; Ko, G.; Yin, J.; Yoon, J. Recent progress in the development of organic dye based near-infrared fluorescence probes for metal ions. *Coord. Chem. Rev.* **2017**, *354*, 74–97.
7. Rasheed, T.; Bilal, M.; Nabeel, F.; Iqbal, M.N.; Li, C.; Zhou, Y. Science of the Total Environment Fluorescent sensor based models for the detection of environmentally-related toxic heavy metals. *Sci. Total Environ.* **2018**, *615*, 476–485.
8. Prabpal, J.; Vilaivan, T.; Praneenararat, T. Paper-Based Heavy Metal Sensors from the Concise Synthesis of an Anionic Porphyrin: A Practical Application of Organic Synthesis to Environmental Chemistry. *J. Chem. Educ.* **2017**, *94*, 1137–1142.