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METAL COMPLEX-BASED CHEMOSENSORS FOR SELECTIVE SENSING OF BIOLOGICALLY AND ENVIRONMENTALLY SIGNIFICANTIONS

Dr. Meenakshi Ghosh [1]

[1] Department of Chemistry, Vidyasagar College for Women, India

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ABSTRACT

Chemosensors based on metal complexes are advanced analytical tools designed to detect and quantify specific ions or molecules in various environments. Among the various types, metal complex-based chemosensors have garnered considerable attention due to their high sensitivity, selectivity, and versatility. These chemosensors employ metal complexes as the core sensing units, taking advantage of their unique coordination chemistry and photophysical properties to achieve selective sensing of biologically and environmentally significantions.

1. INTRODUCTION

Chemosensors based on metal complexes are advanced analytical tools designed to detect and quantify specific ions or molecules in various environments. Among the various types, metal complex-based chemosensors have garnered considerable attention due to their high sensitivity, selectivity, and versatility. These chemosensors employ metal complexes as the core sensing units, taking advantage of their unique coordination chemistry and photophysical properties to achieve selective sensing of biologically and environmentally significant ions.

The metal center typically interacts with the analyte, causing a measurable change in the sensor's physical or chemical properties, such as fluorescence, color, or electrical conductivity. This interaction results in high selectivity and sensitivity, making metal complex-based chemosensors ideal for applications in environmental monitoring, biomedical diagnostics, and industrial process control. Their versatility, coupled with the ability to tailor the metal-ligand coordination chemistry, enables precise detection of biologically and environmentally significant ions, contributing to advancements in both scientific research and practical applications.

2. MECHANISMS OF METAL COMPLEX-BASED CHEMOSENSORS

The design and function of metal complex-based chemosensors hinge on the interaction between the metal ion and the target specific analytes, often leading to a measurable signal such as fluorescence, color change, or electrochemical changes etc.

3. THE MECHANISMS OF THE SENSORS CAN BE BROADLY CLASSIFIED INTO FOLLOWING TYPES

Coordination Interaction is one of the main intriguing sites: Metal complexes are excellent coordinators for various ions, such as anions and cations. The interaction typically involves the binding of the target ion to the metal center, altering the electronic or structural properties of the complex. This change can be monitored using spectroscopic or electrochemical techniques.

Photoinduced Electron Transfer (PET) is one of the key solution maker: In PET-based chemosensors, the interaction of the target ion with the metal complex perturbs the electron transfer process, leading to changes in fluorescence or absorbance. These changes are often highly selective, as they depend on the electronic properties of both the metal complex and the target ions.

Fluorescence Resonance Energy Transfer (FRET) is another portfolio of sensing/recognition event: FRET-based sensing relies on energy transfer between two fluorophores, with the metal complex often serving as the donor or acceptor. Binding of the target ion modifies the energy transfer efficiency, producing a measurable change in fluorescence.

Luminescence Enhancement or Quenching: Some metal complexes exhibit luminescence properties that are either enhanced or quenched upon interaction with specific ions. For instance, lanthanide complexes often display sharp and intense emission lines, which are highly responsive to changes in their coordination environment.

4. BIOLOGICALLY SIGNIFICANT IONS

Biological systems rely on a delicate balance of various ions for physiological processes. Metal complex-based chemosensors play a crucial role in monitoring these ions, as deviations from their normal concentrations can indicate pathological conditions.

- Calcium (Ca^{2+}) is critical for cellular signaling, muscle contraction, and neurotransmission. Metal complex-based chemosensors for calcium often employ the decisive role such as calmodulin or synthetic derivatives to achieve high selectivity. For instance, Eu(III) and Tb(III) complexes have been used to detect calcium due to their prolific luminescence properties.
- Zinc (Zn^{2+}) is essential for enzymatic activity and protein stabilization. Zn^{2+}-selective chemosensors often employ coordination complexes of Schiff bases or polyamines. Changes in fluorescence intensity or color upon zinc binding provide a straightforward bio-benign detection approaches.
- Sodium (Na^{+}) and Potassium (K^{+}) are vital for maintaining osmotic balance and electrical signaling in cells. Metal complexes based on crown ethers or cryptands are frequently used as chemosensors for Na^{+} and K^{+}, exploiting their ability to form stable complexes with alkali metals.
- Copper (Cu^{2+}) play a pivotal role in redox reactions and are a cofactor in several enzymatic activities. Chemosensors for Cu^{2+} often involve complexes with nitrogen- or sulfur-containing ligands, which undergo changes in optical or electrochemical properties upon copper binding.
- Iron (Fe^{3+} and Fe^{2+}) is crucial for oxygen transport and electron transfer. Metal complex-based chemosensors of iron often exploit the ability of Fe^{3+} to quench fluorescence through electron transfer, enabling sensitive detection process path.

5. ENVIRONMENTALLY SIGNIFICANT IONS

Environmental monitoring often focuses on detecting potentially toxic and hazardous ions that can have detrimental effects on ecosystems and human health. Metal complex-based chemosensors provide a reliable means of detecting these ions in trace amounts.

1) Mercury (Hg^{2+}) is a highly toxic heavy metal, and its detection is critical for environmental safety. Metal complex-based chemosensors for Hg^{2+} often utilize thiol-containing ligands, as Hg^{2+} forms strong complexes with sulfur. Measurement of change in fluorescence or colorimetric responses are common detection methods.
2) Lead (Pb^{2+}) contamination is a significant concern due to its neurotoxicity. Pb^{2+}-selective chemosensors often use crown ethers or calixarene type derivatives. Coordination with Pb^{2+} induces optical or electrochemical changes, enabling sensitive detection.
3) Arsenic (As^{3}+) is a toxic metalloid found in contaminated water. Chemosensors for discerning detection of arsenic often involve metal complexes with high affinity for arsenate ions, producing detectable optical or electrochemical signals upon binding.
4) Cyanide (CN^{-}) is a potent environmental toxin. Chemosensors for low level of CN^{-} often employ transition metal complexes that form stable complexes with cyanide ions, leading to distinct changes in luminescence or color.
5) Nitrate and Phosphate (NO_3^{-} and PO_4^{3-}) are critical in environmental monitoring due to their role in eutrophication. Metal complexes with high affinity for oxygen-containing anions, such as zirconium or lanthanum complexes, are frequently employed as chemosensors.
6) Fluoride (F^{-}) ions are significant in both biological and environmental contexts. While fluoride is essential in small amounts for dental health, excessive fluoride can cause health issues such as skeletal fluorosis. Metal complex-based chemosensors for fluoride often utilize boron or aluminum complexes, which exhibit changes in fluorescence or color upon fluoride binding. These sensors are particularly useful for monitoring fluoride levels in drinking water.

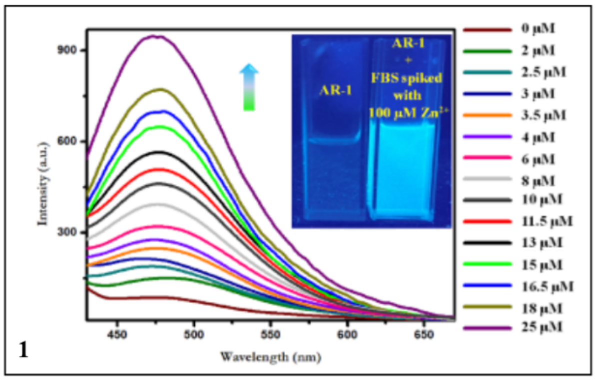
6. ADVANTAGES OF METAL COMPLEX-BASED CHEMOSENSORS

- Metal complex-based chemosensors offer several advantages that make them highly effective for detecting biologically and environmentally significant ions in very low level (PPM to PPB level):
- High Sensitivity of target specific Metal complexes can exhibit strong interactions with targetted ions, resulting in significant changes in their physical or chemical properties, which enhance the sensitivity of detection.
- Selectivity is a prime issue, by carefully choosing metal centers and ligands, chemosensors can be designed to selectively bind specific ions, reducing interference from other substances and ensuring accurate measurements.
- Versatility of Metal complexes can be tailored for various detection mechanisms, such as fluorescence, colorimetric changes, or electrochemical signals, providing flexibility for different applications.
- Fast Response is a very crucial factor to be taken care. These chemosensors often provide rapid responses to changes in ion concentrations, enabling real-time monitoring and quick decision-making in critical situations.
- Robustness of Metal complex-based sensors are generally stable under a range of environmental conditions, making them suitable for use in diverse and challenging environments, including biological systems and industrial processes.
- Miniaturization is the ability to design small and portable chemosensors allows for their use in field applications, on-site testing, and point-of-care diagnostics.

7. CHALLENGES AND LIMITATIONS

Metal complex-based chemosensors, while advantageous in many aspects, also face several challenges and limitations that need to be addressed for broader and more effective use:

Despite high selectivity, metal complex-based chemosensors can sometimes suffer from cross-reactivity with similar ions, leading to false positives or inaccurate readings. The chemical and physical stability of these sensors can be compromised in harsh conditions, such as extreme pH levels, high temperatures, or the presence of interfering substances, which can degrade the metal complexes. The design and synthesis of metal complexes with precise properties can be complex and time-consuming, requiring specialized knowledge and techniques. This can limit the scalability and widespread adoption of such sensors. The use of precious or rare metals, along with complex ligand synthesis, can limit widespread application. In some cases, the response time of metal complex-based chemosensors may not be fast enough for real-time monitoring, especially in dynamic environments where rapid changes have every possibility to be occured. Ensuring that the sensors can return to their original state after detecting ions and can be reused multiple times without losing sensitivity or selectivity remains a significant challenge and there are several GAPs till date in existing scenarios. The disposal of sensors containing heavy or toxic metals can pose environmental threat/concerns, requiring careful consideration of their life cycle and impact. Achieving extremely low detection limits(LOD) for certain ions can be difficult, especially in complex matrices like biological fluids or contaminated water sources where multiple interfering substances are present.



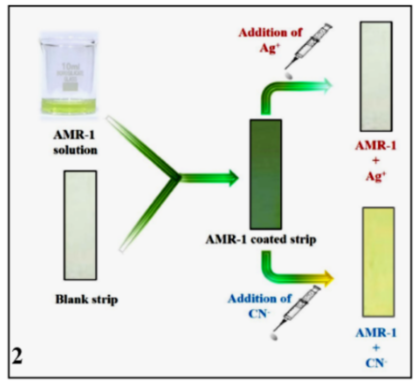


Fig. 1: One representative selective ion sensing event following spectrofluorimetric pathway

Fig. 2: A paper strip based sensing event: the real day application

8. FUTURE PERSPECTIVES

The field of metal complex-based chemosensors continues to evolve, driven by advances in materials science, synthetic chemistry, and analytical techniques. Development of Multi-Analyte Sensors: Designing chemosensors capable of detecting multiple ions simultaneously and precisely to improve efficiency. Integration with Nanomaterials, wherein the fused metal complexes into nanostructures enhance sensitivity and enable new detection modalities. Biocompatible Sensors: Developing non-toxic and biocompatible metal complexes for in vivo applications. Portable Devices is the ultimate goal, wherein Integrating metal complex-based chemosensors with portable analytical devices for field applications is of prima-facie interest.

Sustainable Design: Employing earth-abundant and environmentally friendly metals to reduce cost and ecological impact is also of today's demand.

9. CONCLUSION

Functional organic ligand/Metal complex-based chemosensors represent a powerful tool for the selective sensing of biologically and environmentally significant ions. Their high sensitivity, selectivity, and adaptability make them invaluable in diverse applications, from clinical diagnostics to environmental monitoring. Despite challenges, ongoing research and technological advancements promise to expand their utility, paving the way for innovative solutions to pressing analytical challenges.

CONFLICT OF INTERESTS

None.

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REFERENCES

N. Roohani, R. Hurrell, R. Kelishadi, R. Schulin J. Res. Med. Sci., 18 (2013), pp. 144-157

K. Kaur, R. Gupta, S.A. Saraf, S.K. Saraf Compr.Rev. Food. Sci. F, 13 (2014), pp. 358-376

K.J. Barnham, A.I. Bush Chem. Soc. Rev., 43 (2014), pp. 6727-6749

M.P. Cuajungco, M.S. Ramirez, M.E. Tolmasky Biomedicines, 9 (2021), pp. 208-232

V.R. Djordjevic, D.R. Wallace, A. Schweitzer, N. Boricic, D. Knezevic, S. Matic, N. Grubor, M. Kerkez, D. Radenkovic, Z. Bula t, B. Antonijevic Environ. Int., 128 (2019), pp. 353-361

Z. Gao, G.G. Liu, H. Ye, R. Rauschendorfer, D. Tang, X. Xia, Anal. Chem. 89 (2017) 3622–3629.

J. An, R.B. Chen, M.Z. Chen, Y.Q. Hu, Y. Lyu, Y.F. Liu, Sens. Actuators B Chem. 329 (2021), 129097.

Z. Xu, X. Chen, H.N. Kim, J. Yoon, Chem. Soc. Rev. 39 (2010) 127–137.

J.J. Lee, Z. Xu, X. Chen, H.N. Kim, J. Yoon, Chem. Soc. Rev. 39 (2010) 127–137.

J.J. Lee, S.Y. Lee, K.H. Bok, C. Kim, J. Fluoresc. 25 (2015) 1449–1459.

1. B. L. Vallee and K. H. Falchuk, The biochemical basis of zinc physiology, Physiol. Rev.73 (1993) 79–118.

2. D. Martin, M. Rouffet and S. M. Cohen, Illuminating metal ion sensors-benzimidazole sulfonamide metal complexes Inorg. Chem. 49 (2010) 10226–10228

3.D. Plantone, G.Primiano, R.Renna, D. Restuccia, R. Iorio, K.A. Patanella, M. N. Ferilli, and S. Servidei, Copper deficiency myelopathy: A report of two cases, J Spinal Cord Med. 38(4) (2015) 559–562.

D. Martin, M. Rouffet and S. M. Cohen, Illuminating metal ion sensors-benzimidazole sulfonamide metal complexes Inorg. Chem. 49 (2010) 10226–10228.

D. Plantone, G.Primiano, R.Renna, D. Restuccia, R. Iorio, K.A. Patanella, M. N. Ferilli, and S. Servidei, Copper deficiency myelopathy: A report of two cases, J Spinal Cord Med. 38(4) (2015) 559–562.

L. K. Kirk, Biochemistry of the Halogens and Inorganic Halides, Plenum Press: New York, 1991.

D. Briancon, Fluoride and osteoporosis: an overview, Rev. Rhum. Engl Ed. 64 (1997) 78-8

P.G. Sutariya, N.R. Modi, A. Pandya, B.K. Joshi, K.V. Joshia, S.K. Menon, An ICT based turn on/off quinoline armed calix[4] arene fluoroionophore: its sensing efficiency towards fluoride from waste water and Zn2+ from blood serum, Analyst 137 (2012) 5491–5494.

C.R. Li, S.L. Li, G.G. Wang, Z.Y. Yang, Spectroscopic properties of a chromone-fluorescein conjugate as Mg2+ “turn on” fluorescent probe, J. Photochem. Photobiol. A: Chem. 356 (2016) 700–707.