East European Journal of Physics. 3. 523-528 (2025)
DOI:10.26565/2312-4334-2025-3-58 ISSN 2312-4334

FLUORESCENT DETECTION OF HEAVY METAL IONS USING BENZANTHRONE DYE

U. Malovytsia[a]*, O. Zhytniakivska[a], K. Yeltsov[a], K. Vus[a], V. Trusova[a], E. Kirilova[b], G. Gorbenko[a]

[a]*Department of Medical Physics and Biomedical Nanotechnologies, V.N. Karazin Kharkiv National University 4 Svobody Sq., Kharkiv, 61022, Ukraine*
[b]*Department of Applied Chemistry, Institute of Life Sciences and Technology, Daugavpils University, LV-5401 Daugavpils, Latvia*
**Corresponding Author E-mail: uliana.tarabara@karazin.ua*
Received June 3, 2025; revised July 16, 2025; accepted August 21, 2025

The development of sensitive, low-cost, and biocompatible sensors for detecting toxic heavy metals remains a pressing challenge in environmental monitoring. Protein-based nanostructures present unique opportunities in this regard. Coupling amyloid fibrils with amyloid-sensitive fluorescent dyes, which exhibit distinct spectral responses upon binding to amyloid structures and in the presence of metal ions, may lead to a promising sensing platform. In this study, the benzanthrone derivative ABM was examined as a fluorescent probe for detecting heavy metal ions in aqueous solutions and in the presence of β- β-lactoglobulin amyloid fibrils (β-lgf). In water, benzanthrone dye shows a broad emission spectrum dominated by a band at 690 nm. Binding to β- lgf produces a substantial increase in fluorescence intensity and a ~65 nm hypsochromic shift, indicating dye partitioning into the fibrillar hydrophobic environment. In aqueous solutions, ABM responds to heavy metals with characteristic spectral changes: Pb^{2+} and Ni^{2+} decrease the 690 nm emission band and generate a 560 nm band, while Cu^{2+} and Zn^{2+} cause complete quenching of the 690 nm emission with the appearance of a prominent 560 nm maximum, consistent with the formation of metal–ligand charge–transfer complexes. In the fibrillar environment, ABM displays a dominant emission at 560 nm; addition of heavy metals modulates the intensity and shape of this band in an ion-specific manner. Deconvolution of the emission spectra revealed two spectral components, whose amplitudes and shape descriptors were selectively altered by Ni^{2+} and Cu^{2+}, while Zn^{2+} and Pb^{2+} had lesser effects. These findings demonstrate that ABM fluorescence reports sensitively on the strength and specificity of heavy metal interactions with amyloid fibrils, supporting its potential as an optical sensor for probing protein–metal systems.
Keywords: *Benzanthrone dyes; Metal detection; Heavy metals*
PACS: 87.14.Cc, 87.16.Dg

Heavy metal ion contamination poses a significant environmental and public health challenge, as ions such as mercury (Hg^{2+}), lead (Pb^{2+}), cadmium (Cd^{2+}), and copper (Cu^{2+}) are highly toxic even at trace levels, persist in ecosystems, and readily bioaccumulate, with strong links to cancer and neurodegenerative disorders [1–3]. Accurate detection of these ions remains a critical priority for environmental monitoring and disease prevention related to heavy metals. Despite the high sensitivity and reliability of conventional analytical techniques, including atomic absorption spectroscopy (AAS) [4], inductively coupled plasma mass spectrometry (ICP-MS) [5], and electrochemical assays [6,7], their applications are limited by high costs, extensive sample preparation, and limited field portability. These constraints highlight the urgent need for novel sensing strategies, particularly for detecting water contamination. Recently, fluorescence-based sensing has emerged as an attractive alternative due to its high sensitivity, selectivity, and potential for real-time applications [8-11]. Numerous studies have documented advances in fluorescent sensors incorporating aptamers [8,9], quantum dots [10,11], and organic dyes [12-15] for detecting heavy metals in environmental matrices. Specifically, small-molecule fluorescent probes offer rapid response and high affinity through selective coordination with metal ions, enabling precise fluorescence modulation [8, 16].

Concurrently, protein-based nanomaterials are emerging as highly effective nanoscaffolds for heavy metal removal due to their diverse amino acid functional groups and ability to self-assemble into tunable supramolecular structures such as fibrils, gels, and spherical condensates. Recent advances in protein- and peptide-derived adsorbents demonstrate outstanding metal-binding efficiencies. For example, soy protein hydrogels efficiently captured Cu(II) even in the presence of competing ions [17], while a BSA/graphene oxide hybrid membrane achieved 90.4% mercury removal [18]. Additionally, elastin-like polypeptides with histidine clusters proved effective for Cd(II) [19]. Particularly, hybrid membranes combining activated carbon with amyloid fibrils from proteins such as β-lactoglobulin or soy protein removed over 99% of various metals, including gold, mercury, lead, palladium, arsenic, chromium, and nickel, in both model and real wastewater systems [20-22]. Despite the structural stability, high surface area, and abundant binding sites of amyloid fibrils—making them well-suited for functionalisation with optical reporters in biosensing applications—the convergence of amyloid fibril scaffolding and fluorescent dyes for heavy metal ion detection remains largely unexplored. This hybrid sensing approach could utilise the structural and binding capacity of amyloid frameworks with the optical sensitivity of fluorescent reporters, potentially enabling portable, low-cost detection systems with enhanced sensitivity and selectivity.

In this study, we present a feasibility investigation into the development of a sensor platform comprising β-lactoglobulin amyloid fibrils with the benzanthrone fluorescent dyes ABM for the detection of Cu^{2+}, Zn^{2+}, Ni^{2+}, and

Cite as: U. Malovytsia, O. Zhytniakivska, K. Yeltsov, K. Vus, V. Trusova, E. Kirilova, G. Gorbenko, East Eur. J. Phys. 3, 523 (2025), https://doi.org/10.26565/2312-4334-2025-3-58

Pb^{2+}, heavy metal ions. More specifically, the aim of our study was to assess the ABM sensitivity to heavy metals and metal-β-lactoglobulin fibril interactions.

EXPERIMENTAL SECTION

Materials

Bovine β-lactoglobulin (βlg), copper(II) chloride dihydrate, nickel(II) chloride, lead(II) nitrate, zinc chloride and thioflavin T (ThT) were purchased from Sigma, USA. Benzanthrone dye ABM [23] was synthesized in the Daugavpils University. All other reagents were of analytical grade and used without the further purification.

Preparation of working solutions

The β-lactoglobulin stock solutions 10 mg/ml (βlgF) was prepared in distilled water with HCl (pH 2.0). The reaction of the protein (stock solutions) fibrillization was conducted at 90 °C for 2 days. The kinetics of amyloid formation was monitored using the Thioflavin T assay [24], revealing the dye fluorescence intensity increase at 480 nm *ca.* 7 times (data not shown). The working solutions of protein were prepared by dissolving a stock solution of the fibrillar β-lactoglobulin in distilled water (pH 6.07).The ABM stock solutions were prepared in ethanol, while ThT was dissolved in 10 mM Tris buffer (pH 7.4). The fluorimetric measurements were carried out in distilled water (pH 6.07).

Spectroscopic measurements

The absorption spectra of the examined dyes were recorded with the spectrophotometer Shimadzu UV-2600 (Japan) at 25ºC. The dye concentrations were determined spectrophotometrically using the extinction coefficients $\varepsilon_{444}^{EtOH} = 9.3 \cdot 10^3$ $M^{-1}cm^{-1}$ and $\varepsilon_{412}^{water} = 3.6 \cdot 10^4$ $M^{-1}cm^{-1}$ for ABM and ThT, respectively. Steady-state fluorescence spectra were recorded with an RF-6000 spectrofluorimeter (Shimadzu, Japan). Fluorescence measurements were performed at 25°C using 10 mm pathlength quartz cuvettes. Fluorescence spectra were recorded within the range of 480–800 nm, with an excitation wavelength of 460 nm. The excitation and emission slit widths were set at 10 nm**.**

Fluorescence spectra analysis

The deconvolution of the dye absorption spectra was performed with Origin 9.0 (OriginLab Corporation, Northampton, USA) using the log-normal asymmetric function (LN) [25]:

$$I = I_{\max} \exp\left[-\frac{ln2}{\ln^2(\rho)} \ln^2\left(\frac{a-\lambda}{a-\lambda_c} \right) \right], \tag{1}$$

where I is the fluorescence intensity, $I_{\max}$ is the emission maximum, λ is the wavelength, λ_c is the position of the peak, ρ is the asymmetry of the function defined as:

$$\rho = \frac{\lambda_c - \lambda_{\min}}{\lambda_{\max} - \lambda_c} \tag{2}$$

where $\lambda_{\min}$ and $\lambda_{\max}$ denote the wavelength values at half-emission. The parameter a designates the limiting wavelength:

$$a = \lambda_c + \frac{(\lambda_{\max} - \lambda_{\min}) \cdot \rho}{\rho^2 - 1} \tag{3}$$

Binding model

Quantitative characteristics of the dye-protein binding were determined in terms of the Langmuir adsorption model by analyzing protein-induced changes in the probe fluorescence intensity at the wavelengths, corresponding to emission maximum for ABM (624 nm was selected for non-deconvoluted spectra). Assuming that the ABM fluorescence response is proportional to the amount of the protein-bound fluorophore B, the β-lgF-induced change in the probe fluorescence intensity ΔI at the fluorescence maximum can be written as:

$$\Delta I = I - I_0 = \left[\alpha_{bound} B + \alpha_{free} (Z - B) \right] - \alpha_{free} Z = (\alpha_{bound} - \alpha_{free}) B = F_{mol} B \tag{4}$$

where I_0 and I – fluorescence intensities of the dye in a buffer solution and in the presence of protein, respectively; F_{mol} is a coefficient proportional to the difference of the dye quantum yields in buffer and when bound to the macromolecule; α_{bound} and α_{free} – molar fluorescence of the bound and free dye, respectively, Z is the total concentration of the probe. If one protein molecule contains n dye binding sites, the association constant (K_a) is given by:

$$K_a = \frac{B}{(Z - B)(P \cdot n - B)} \tag{5}$$

where P is total protein concentration.

The F_{mol} parameter was calculated form the fluorimetric titration of the dye by the fibrillar β-lactoglobulin. Specifically, at high protein concentrations, when $P/n >> B$, from the combination of the Eqs. (4) and (5) one obtains:

$$\frac{1}{\Delta I} = \frac{1}{BF_{mol}} = \frac{1}{K_a PnZF_{mol}} + \frac{1}{ZF_{mol}} \tag{6}$$

$$F_{mol} = 1/aZ \tag{7}$$

where a – the y-intercept of the linear fit of the plot $1/\Delta I = 1/P$.
Next, Eqs. (4) and (5) can be rearranged to give:

$$\Delta I = \frac{1}{2} F_{mol} \left[Z + nP + 1/K_a - \sqrt{(Z + nP + 1/K_a)^2 - 4nPZ} \right] \tag{8}$$

The approximation of the experimental dependencies ΔI (fluorescence intensity increase) on P (total protein concentration) by Eq. 8 allowed us to determine the other dye-protein binding parameters – association constant (K_a) and binding stoichiometry (n).

RESULTS AND DISCUSSION

In the initial phase of our study, we assessed the binding of ABM with β- lactoglobulin amyloid fibrils. As can be seen from Figure 1, a free dye in an aqueous environment is characterized by an emission maximum at 690 nm. The emission maximum of ABM shifts from 538 nm in nonpolar benzene to 650 nm in polar ethanol, arising from intramolecular charge transfer between the amine substituent and the carbonyl group, which increases the excited-state dipole moment and induces solvent relaxation [26]. The addition of fibrillar β-lactoglobulin to ABM in water caused a marked increase in fluorescence intensity, accompanied by a ~ 65 nm hypsochromic shift in the emission maximum, indicating dye transfer into a non-polar environment. To quantitatively evaluate the ABM binding, the fluorescence enhancement at 625 nm (ΔI) as a function of the protein concentration was fitted using the Langmuir adsorption model (Eq. 8), yielding the association constant $K_a = 1.9 \times 10^3$ M^{-1} and the number of binding sites $n = 7.5 \pm 0.3$ mol/mol.

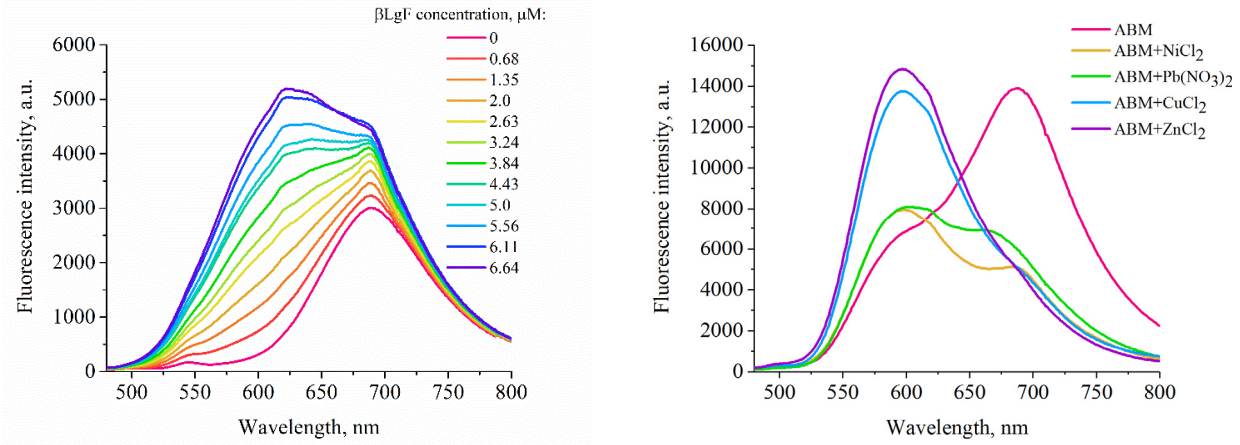

Figure 1. Emission spectra of ABM in the presence of β- lactoglobulin amyloid fibrils (A) and heavy metal ions (B). ABM concentration was 1 μM and 10 μM for ABM-β-lgF and ABM-β-lgF-heavy metal systems, respectively

Next, we evaluated ABM's ability to detect heavy metal ions in aqueous solution (Figure 1B). In water, the benzanthrone dye ABM displays a broad emission spectrum with a prominent peak at 690 nm and a shoulder at approximately 560 nm. When it binds to heavy metals, the 690 nm band diminishes, while emission at around 560 nm increases, with the extent of these changes depending on the specific ion. Particularly, binding with Ni^{2+} and Pb^{2+} results in about a 1.8-fold reduction in fluorescence intensity at 690 nm, a 20 nm blue shift of the emission maximum, and the emergence of a distinct band at 560 nm. Notably, ABM shows an even higher affinity for Cu^{2+} and Zn^{2+}, demonstrated by complete quenching of the 690 nm band and the appearance of a highly intense emission maximum at 560 nm. It is well known that the interaction between fluorescent dyes and heavy metal ions is mainly controlled by the presence of functional donor groups in their molecular structure (such as carbonyl, amine, nitrogen, hydroxyl, etc.), which act as coordination sites for metal binding [8]. The shift in emission peaks for ABM with metal ions likely arises from the formation of metal–ligand charge–transfer complexes involving electron transfer from molecular orbitals in the metal to those in the ligand. Our results indicate that Pb^{2+} and Ni^{2+}, probably, exhibit weaker metal–ligand charge–transfer complex. The strong quenching of the 690 nm maximum and the blue shift at around 560 nm can be explained by the formation of a metal-ligand charge transfer complex involving the amino and carbonyl groups of ABM, as numerous

studies indicate Cu^{2+} preference for these structural groups [8,27]. Conversely, Zn^{2+} tends to form stable coordination complexes mainly through the carbonyl oxygen [8,27], which is also present in the ABM structure. When interacting with the carbonyl group of ABM, Zn^{2+} likely stabilizes the dye's excited state, reducing non-radiative decay and leading to the emergence of a highly emissive band at 560 nm.

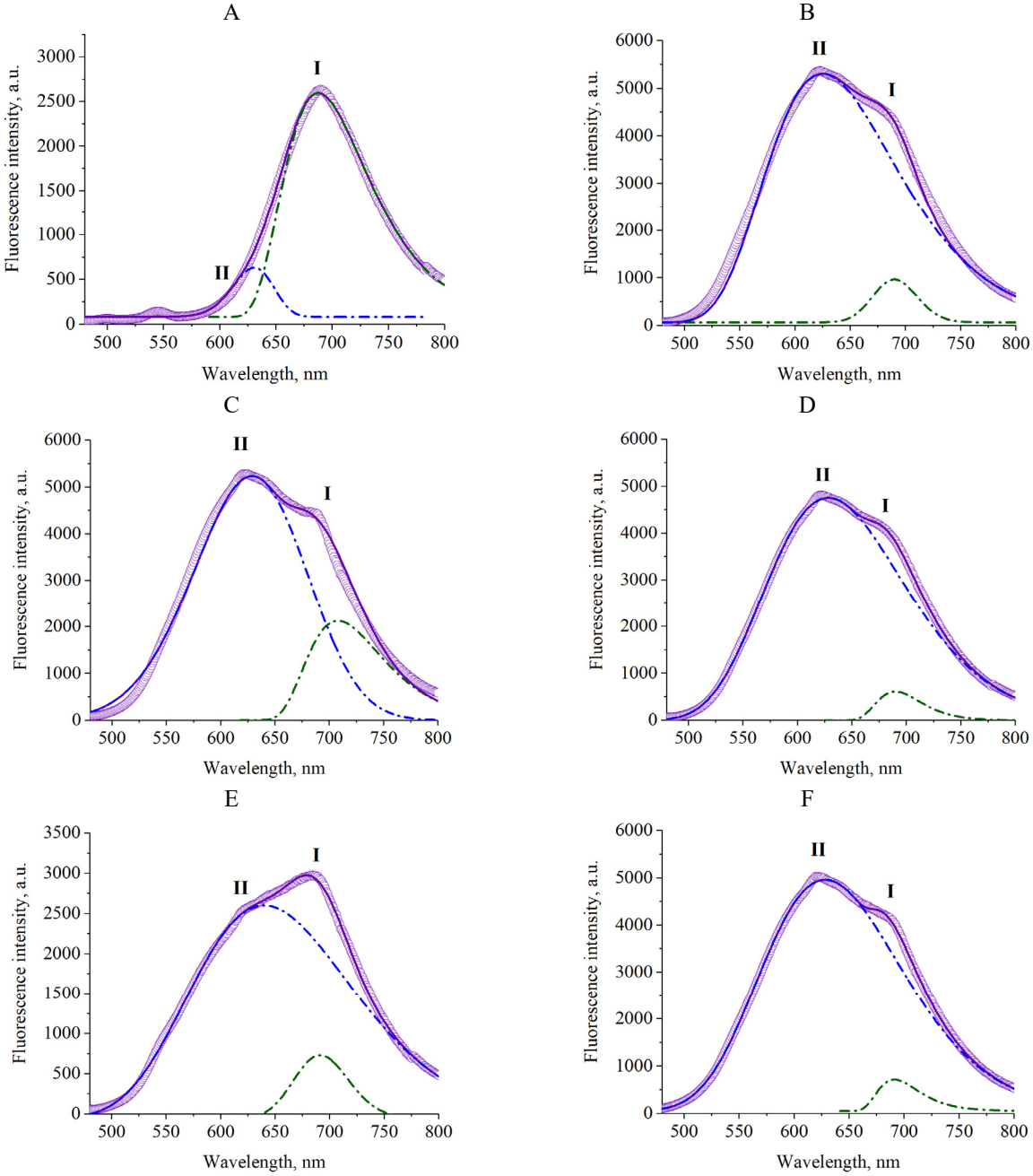

Figure 2. Deconvolution of ABM absorption spectra into two components in water (A), in the presence of 6.64 μM β-lgF (B), ABM-β-lgF-Ni system (C), ABM-β-lgF-Pb system (D), ABM-β-lgF-Cu system (E), ABM-β-lgF-Zn system (F). Heavy metal concentration was 423 μM. Empty circles represent raw data. The solid line demonstrates the fitting of the experimental data by the asymmetric log-normal function

In the next phase of our study, we investigated the sensitivity of ABM to heavy metal ions in the presence of amyloid fibrils. Figure 2 illustrates the emission spectra of ABM in systems containing β-lgF and heavy metals. When only β-lgF is present, ABM shows a prominent emission peak at 560 nm along with a weaker shoulder around 690 nm. The addition of heavy metal ions altered the relative intensities of these bands in a metal-dependent manner. Specifically, the addition of Zn^{2+}, Ni^{2+}, and Pb^{2+} did not significantly change the overall shape of the emission spectra, whereas in the presence of Cu^{2+}, the 690 nm peak became dominant. To analyze the spectral behaviour of ABM in the combined amyloid–heavy metal systems, the dye's fluorescence spectra were decomposed using the log-normal (LN) function, which is well-suited for resolving asymmetric spectra [25]. It was found that the fluorescence spectra of ABM in water, in the presence of β-lactoglobulin amyloid fibrils, and in the ABM–β-lgF–heavy metal systems could be represented as a sum of two distinct

bands corresponding to short-wavelength and long-wavelength spectral components. From the deconvolution data, a set of parameters was obtained, including the amplitude and three shape descriptors: (i) the peak position, which reflects the polarity of the environment; (ii) the full width at half-maximum (FWHM); and (iii) the asymmetry parameter of the peak.

Table 1. Spectral characteristics of ABM in aqueous solution, β-lactoglobulin fibrils and β-lgF–metal systems

System	Band	A_{max}	λ_c, cm^{-1}	FWHM, cm^{-1}	ρ, cm^{-1}	R^2
ABM	I	2514.9	687.7	92.1	0.633	0.996
	II	551.7	630.8	43.3	1.152	
ABM_bLgF	I	903.5	690	47.2	0.950	0.999
	II	5240	625	142.3	0.708	
ABM_bLgF_Ni	I	2120	708	85	0.635	0.993
	II	5231.0	629	122.8	1.082	
ABM_bLgF_Pb	I	613.5	689.9	49.7	0.692	0.999
	II	4755.7	628.4	150.5	0.781	
ABM_bLgF_Cu	I	783.3	691.3	59.2	0.915	0.999
	II	2653.9	639.8	175.7	0.795	
ABM_bLgF_Zn_	I	665.1	691.2	46.0	0.638	0.999
	II	4908.8	628.2	152.1	0.80	

As summarised in Table 1, the bathochromic band I (690 nm) dominates over the hypsochromic band II (630 nm) in aqueous ABM, whereas band II prevails in both ABM–β-lgF and ABM–β-lgF–metal systems. Upon addition of heavy metals, several characteristic changes were observed compared to ABM–β-lgF: (i) an increase in band I amplitude in the presence of Ni^{2+} and Cu^{2+}, more pronounced for Ni^{2+}; (ii) a slight decrease in band II amplitude for Zn^{2+} and Pb^{2+}; and (iii) a 1.9-fold decrease in band II fluorescence intensity in the ABM–β-lgF–Cu^{2+} system. These spectral alterations were accompanied by broadening of band I (Ni^{2+} and Cu^{2+}) and band II (Cu^{2+}), as reflected in increased FWHM values, along with a rise in the asymmetry parameter of band II in the Cu^{2+} complex. The presence of heavy metals did not affect the position of the peaks, except for the band I of ABM_bLgF_Ni, where a slight long-wavelength shift was observed.

Overall, the results in Table 1 indicate that the addition of Ni^{2+} and Cu^{2+} influences the fluorescence response of fibril-bound ABM more strongly than other tested heavy metal ions. Given the highest fluorescence response of ABM in aqueous solution with Cu^{2+} and Zn^{2+}, these findings suggest that both the dye's sensitivity to heavy metals and the interaction strength between heavy metals and amyloid fibrils are key factors in the spectral behaviour of the fibril-bound dye. Little is known about the mechanism of heavy metal ion interaction with β-lactoglobulin amyloid fibrils. However, Peydayesh et al. [21] demonstrated that adsorption of chromium, nickel, silver, and platinum to β-lactoglobulin amyloid fibrils is a highly exothermic and ion-specific process. Assuming that the accessibility of metal-binding sites for different ions in β-lgF varies, stronger binding of Cu^{2+} and Ni^{2+} to the fibrils can perturb the local environment of ABM, amplifying spectral shifts and intensity changes compared to Zn^{2+} and Pb^{2+}. However, further studies are needed to elucidate the molecular mechanisms of metal–fibril binding and quantitatively assess binding affinities.

CONCLUSIONS

This study demonstrates the feasibility of using β-lactoglobulin amyloid fibrils in combination with the benzanthrone-based fluorescent dye ABM as a sensing platform for heavy metal ions, including Cu^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+}. The results show that ABM exhibits distinct, metal-specific fluorescence responses in both aqueous solutions and fibril-bound environments. In particular, ABM undergoes pronounced spectral changes in aqueous solution upon binding Cu^{2+}, Zn^{2+}, Ni^{2+}, and Pb^{2+}, with Cu^{2+} and Zn^{2+} producing the most potent effects due to their preferential coordination to amino and carbonyl donor groups. The incorporation of ABM into β-lactoglobulin fibrils enhances dye fluorescence. It enables the selective modulation of emission signals upon metal binding, with Ni^{2+} and Cu^{2+} causing the most significant changes in spectral characteristics. Collectively, these results indicate that the fluorescence response of ABM reflects not only direct dye–metal binding but also the strength of metal interactions with amyloid fibrils. This dual sensitivity positions ABM as a promising optical probe for studying metal–protein interactions and for developing supramolecular platforms for heavy-metal sensing. Further studies are warranted to characterize the dye-fibril-metal complexation and expand its application to additional metal ions.

Acknowledgements

This work was supported by the Ministry of Education and Science of Ukraine (the project "Development of economically affordable nanosystems for rapid identification and purification of water from heavy metal ions based on carbon nanoallotropes and amyloids from organic waste" No. 0124U000968).

ORCID

Olga Zhytniakivska, https://orcid.org/0000-0002-2068-5823; **Uliana Malovytsia,** https://orcid.org/0000-0002-7677-0779
Kateryna Vus, https://orcid.org/0000-0003-4738-4016; **Valeriya Trusova,** https://orcid.org/0000-0002-7087-071X
Elena Kirilova, https://orcid.org/0000-0002-9577-5612; **Galyna Gorbenko,** https://orcid.org/0000-0002-0954-5053

REFERENCES

[1] L. Järup, Br. Med. Bull. **68**, 167 (2003). https://doi.org/10.1093/bmb/ldg032
[2] P. Zhang, M. Yang, J. Lan, Y. Huang, J. Zhang, *et al*. Toxics, **11**, 828 (2023). https://doi.org/10.3390/toxics11100828
[3] J. Huff, R. Lunn, M. Waalkes, L. Tomatis, and P. Infante. Int. J. Occup. Environ. Health, **13**, 202 (2007). https://doi.org/10.1179/oeh.2007.13.2.202
[4] F. Barbosa, F. Krug, and E.C. Lima. Spectrochimica Acta Part B: Atomic Spectroscopy, **54**(8), 1155 (1999). https://doi.org/10.1016/S0584-8547(99)00055-5
[5] E.L. Silva, P. dos Santos Roldan, M.F. Giné. Journal of Hazardous Materials, **171**(1–3), 1133 (2009). https://doi.org/10.1016/j.jhazmat.2009.06.127
[6] S. Fouziya Sulthana, U. Mohammed Iqbal, S.B. Suseela, *et al*., ACS Omega, **9**(24), 25493 (2024). https://doi.org/10.1021/acsomega.4c00933
[7] R. Ding, Y.H. Cheong, A. Ahamed, G. Lisak. Anal. Chem. **93,** 4, 1880–1888 (2020) https://doi.org/10.1021/acs.analchem.0c04247
[8] N. De Acha, C. Elosúa, J.M. Corres, and F.J. Arregui, Sensors, **19**, 599 (2019). https://doi.org/10.3390/s19030599
[9] Y. Wen, F. Xing, S. He, S. Song, and L. Wang, Chem. Commun. **46**, 2596 (2010). https://doi.org/10.1039/B924832C
[10] M. Zhou, J. Guo, and C. Yang, Sens. Actuators B Chem. **264,** 52 (2018). https://doi.org/10.1016/j.snb.2018.02.119
[11] B. Rezaei, M. Shahshahanipour, A.A. Ensafi, and H. Farrokhpour, Sens. Actuators B Chem. **247**, 400 (2017). https://doi.org/10.1016/j.snb.2017.03.082
[12] W.-B. Huang, W. Gu, H.-X. Huang, *et al*., Dye Pigment, **143**, 427 (2017). https://doi.org/10.1016/j.dyepig.2017.05.001
[13] M. Saleem, and K.-H. Lee, J. Lumin. **145**, 843 2014). https://doi.org/10.1016/j.jlumin.2013.08.044
[14] X. Yang, W. Zeng, L. Wang, *et al*., RSC Adv. **4,** 22613 (2014). https://doi.org/10.1039/C4RA02738H
[15] Y. Han, C. Yang, K. Wu, and Y. Chen. RSC Adv**. 5**, 16723 (2015). https://doi.org/10.1039/C4RA16479B
[16] A. Majhi, K. Venkateswarlu, and P. Sasikumar, J. Fluoresc. **34**, 1453 (2024). https://doi.org/10.1007/s10895-023-03372-3
[17] J. Liu, D. Su, J. Yao, Y. Huang, J. Shao, and X. Chen, J. Mater. Chem. A, **5**, 4163 (2017). https://doi.org/10.1039/C6TA10814H
[18] X. Yu, W. Liu, X. Deng, S. Yan, and Z. Su, Chemical Engineering Journal, **335,** 176 (2017). https://doi.org/10.1016/j.cej.2017.10.148
[19] J. Kostal, A. Mulchandani, and W. Chen, Macromolecules, **34**(7), 2257 (2001). https://doi.org/10.1021/ma001973m
[20] S. Bolisetty, and R. Mezzenga, Nat. Nanotechnol. **11**, 365 (2016). https://doi.org/10.1038/nnano.2015.310
[21] M. Peydayesh, S. Bolisetty, T. Mohammadi, and R. Mezzenga, Langmuir, **35**, 4161 (2019). https://doi.org/10.1021/acs.langmuir.8b04234
[22] L.C. Ramírez-Rodríguez, L.E. Díaz Barrera, M.X. Quintanilla-Carvajal, *et al*., Membranes, **10,** 386 (2020). https://doi.org/10.3390/membranes10120386
[23] E.M. Kirilova, I. Kalnina, G.K. Kirilov, and I. Meirovics, J. Fluoresc. **18**, 645 (2008). https://doi.org/10.1007/s10895-008-0340-3
[24] M. Groenning, J. Chem. Biol. **3**, 1 (2010), https://doi.org/10.1007/s12154-009-0027-5
[25] M. Bacalum, B. Zorila, and M. Radu. Anal Biochem. **440**, 123 (2013). https://doi.org/10.1016/j.ab.2013.05.031
[26] G. Gorbenko, V. Trusova, E. Kirilova, *et al*., Chem. Phys. Lett. **495**, 275 (2010). https://doi.org/10.1016/j.cplett.2010.07.005
[27] Z. Yan, Y. Cai, J. Zhang, Y. Zhao, *et al*., Measurements, **187**, 110355 (2022). https://doi.org/10.1016/j.measurement.2021.110355

ФЛУОРЕСЦЕНТНЕ ДЕТЕКТУВАННЯ ІОНІВ ВАЖКИХ МЕТАЛІВ ЗА ДОПОМОГОЮ БЕНЗАНТРОНОВОГО БАРВНИКА

У. Маловиця[a], О. Житняківська[a], К. Єльцов[a], К. Вус[a], В. Трусова[a], Е. Кірілова[b], Г. Горбенко[a]

[a]*Кафедра медичної фізики та біомедичних нанотехнологій, Харківський національний університет імені В.Н. Каразіна м. Свободи 4, Харків, 61022, Україна*

[b]*Кафедра прикладної хімії, Інститут наук про життя та технологій, Даугавпільський університет, LV-5401 Даугавпілс, Латвія*

Розробка чутливих, недорогих та біосумісних сенсорів для виявлення токсичних важких металів залишається актуальним завданням у сфері екологічного моніторингу. Наноструктури на основі білків надають унікальні можливості для створення таких сенсорів. Поєднання амілоїдних фібрил з амілоїд-чутливими флуоресцентними барвниками, які демонструють характерні спектральні зміни при взаємодії з амілоїдними структурами та іонами металів, може створити перспективну сенсорну платформу. В даній роботі досліджено чутливість бензантронового зонда АВМ до іонів важких металів у водних розчинах та у присутності амілоїдних фібрил β-лактоглобуліну (β-lgF). У воді зонд характеризується спектром випромінювання з домінуючим піком при 690 нм. Зв'язування з β-lgF спричиняє значне збільшення інтенсивності флуоресценції та ~ 65 нм гіпсохромний зсув положення максимуму, що вказує на перехід барвника у гідрофобне середовище фібрил. У водних розчинах АВМ реагує на важкі метали характерними спектральними змінами: Pb^{2+} та Ni^{2+} зменшують смугу випромінювання при 690 нм та формують смугу при 560 нм, тоді як Cu^{2+} та Zn^{2+} повністю гасять флуоресценцію при 690 нм, що супроводжується утворенням максимум на 560 нм, що, найбільш імовірно, є наслідком утворенням комплексів переносу заряду метал–ліганд. У присутності амілоїдних фібрил АВМ має широкий спектр флуоресценції з максимумом на 560 нм. Додавання важких металів модулює інтенсивність і форму цієї смуги в іон-специфічний спосіб. Деконволюція спектрів випромінювання показала наявність двох спектральних компонентів, амплітуди та характеристики яких змінювались під дією Ni^{2+} та Cu^{2+}, тоді як Zn^{2+} та Pb^{2+} мали менший вплив. Ці результати демонструють, що флуоресценція АВМ чутливо відображає специфічність взаємодії важких металів з амілоїдними фібрилями, підтверджуючи його потенціал як оптичного сенсора для вивчення систем «білок–метал».

Ключові слова: *бензантронові барвники; детекція металів; важкі метали*