

Dedicated to Academician Cristian Silvestru
on the occasion of his 70th anniversary

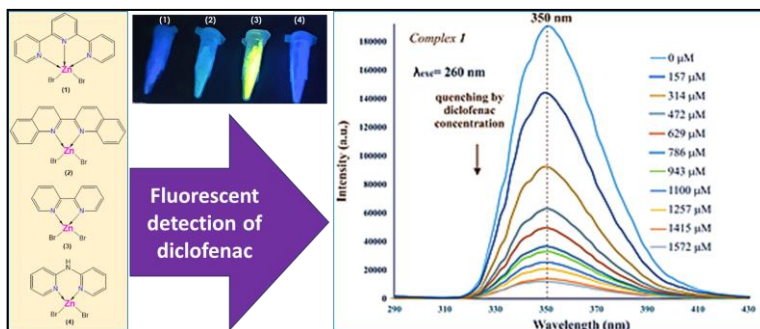
FLUORESCENT DETECTION OF SODIUM DICLOFENAC BY ZINC(II) COMPLEXES CONTAINING PYRIDYL-TYPE LIGANDS

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A series of previously reported mononuclear zinc(II) complexes, [Zn(tpy)Br₂] (**1**), [Zn(bq)Br₂] (**2**), [Zn(bpy)Br₂] (**3**) and [Zn(dpa)Br₂] (**4**) (tpy = 2,2':6',2''-terpyridine, bq = 2,2'-biquinoline, bpy = 2,2'-bipyridyl, dpa = 2,2'-dipyridylamine), was synthesized via a simplified one-step ethanol-based procedure and investigated for their photoluminescent properties and sensing performance toward sodium diclofenac. Fluorescence spectroscopy revealed that complexes **1**, **3** and **4** display prominent emission bands in the UV region upon excitation at 260 nm, attributed to ligand-centered $\pi-\pi^*$ transitions. These complexes demonstrated significant and selective fluorescence quenching in the presence of sodium diclofenac, with low limits of detection (LOD as low as $4.98 \times 10^{-3} \mu\text{M}$) and quantification (LOQ down to $1.66 \times 10^{-2} \mu\text{M}$). Binding studies confirmed a 1:1 stoichiometry and yielded association constants in the range of $0.0117-0.0146 \mu\text{M}^{-1}$. Stern-Volmer analyses indicated a predominantly static quenching mechanism via supramolecular complex formation. These findings highlight the potential of structurally simple Zn(II) complexes, synthesized through a facile protocol, as efficient fluorescent sensors for pharmaceutical contaminants such as diclofenac, with relevance to environmental and analytical applications.



INTRODUCTION

Zinc(II) complexes are considered suitable candidates for fluorescence detection of various compounds, such as pharmaceutical substances (antibiotics, analgesics or anti-inflammatories),¹⁻⁶ pollutants⁷⁻¹² or biological samples¹³⁻¹⁵ due to their reach photophysical properties and low cost. Zinc(II) complexes can exhibit tunable fluorescence in both

intensity and emission maximum, depending on the type of ligands and the coordination mode imposed by the ligands. In addition, these metal complexes can add versatility to the luminescent levels, both in solution and in the solid state.¹⁶

In order to expand the structural diversity of Zn(II)-based complexes with tunable photoluminescent properties, as well as biologically active properties, many researchers have combined different bipyridyl

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derivatives at the Zn(II) metal center, using both classical and green synthesis methods.^{17–19} Among the most widely used chelating bidentate N-donor ligands in obtaining Zn(II) complexes with tunable fluorescent properties are 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen).²⁰ Unlike phen, bpy was used as a chelating ligand due to its high redox stability and possibility of being functionalized.²¹ Also, tridentate ligands containing pyridine rings, such as terpyridine (tpy), are well-known chelating ligands in transition metal complexes. Various tpy-type ligands have been shown to be emissive in the solid state, with photoluminescence yields depending on their molecular structure and substituents, with relevant tuning of emission upon metal ion coordination.²²

Photoluminescent zinc(II) complexes with aromatic N-donor dipyridine and terpyridine chelating ligands could have the potential to serve as efficient fluorescent sensors for pharmaceuticals, combining sensitivity with chemical specificity. In the present study, four photoluminescent complexes based on zinc bromide and the N-donor organic ligands 2,2':6',2''-terpyridine (tpy), 2,2'-biquinoline (bq), 2,2'-bipyridyl (bpy) and 2,2'-dipyridylamine (dpa) were synthesized and used for the first time in the fluorescent detection of a pharmaceutical substance from the anti-inflammatory class, such as sodium diclofenac. The novelty of this approach lies in the ability of zinc(II) complexes to selectively and sensitively interact with target compounds, providing an innovative and precise method for monitoring pharmaceuticals in solution. This technique has significant potential for applications in healthcare and environmental protection, where accurate detection of trace amounts of pharmaceuticals is essential.

In contrast to our previous study, which investigated a photoluminescent Cu(I) thiocyanate complex with the ligands triphenylphosphine and dipyridylamine,²³ the present work explores entirely different Zn(II) complexes with pyridyl ligands, exhibiting distinct interaction properties with diclofenac. Each analyte interacts specifically with a given complex, and our current approach places emphasis on a more detailed characterization of the fluorescence quenching mechanisms and on the quantification of the binding constants associated with these complexes. This difference in complexes and ligands, as well as the distinct methodology applied, underpins the originality and novelty of the present study. Compared to the previous work, this article

therefore provides an expanded perspective and additional experimental data, complementing and advancing current knowledge in the field, even though the analyte of interest remains the same.

RESULTS AND DISCUSSION

Synthesis and spectroscopic characterization of the obtained Zn(II) complexes

The preparation of the four mononuclear Zn(II) complexes followed a simpler and more straightforward synthetic route with respect to the already reported methods.^{24–27} The new synthetic approach adopted in the present work consisted in the reaction between zinc bromide dihydrate and tridentate (tpy) and bidentate (bq, bpy, dpa) pyridyl-type ligands in ethanol for just two hours, using a 1:1 metal:ligand molar ratio (Fig. 1), thus highlighting that changing the solvents and reaction times had no influence on obtaining the same complexes. Moreover, this new synthesis route represents an advancement over previously reported methods that required longer reaction time and different solvents, thus offering a more efficient and practical approach.

The corroboration of elemental analyses with FTIR and ¹H NMR spectroscopies have allowed to confirm the presence of the organic ligands in the obtained complexes, as well as its proposed stoichiometric formulation based upon the molar ratio (metal:ligand = 1:1) used in the synthesis. All complexes were obtained as powders of different colors (white for complexes **1**, **3** and **4**, and pale yellow for complex **2**), depending on the nature of the ligands used in the syntheses. Also, all obtained complexes are air-stable and showed good solubility in chloroform, acetonitrile and dimethylsulfoxide, while they are slightly soluble in alcohols and insoluble in water. In the FTIR spectra of all complexes the weak bands in the range 3100–3000 cm⁻¹ and medium/strong bands in the range 1600–1400 cm⁻¹ are indicative for the stretching vibrations of C–H bonds from the aromatic rings, and C=N and C=C double bonds from the aromatic rings of the ligands, respectively. In all ¹H NMR spectra the presence of the aromatic protons from the organic ligands is shown by the doublet, triplet or multiplet signals located in the range 7.4–9.0 ppm.

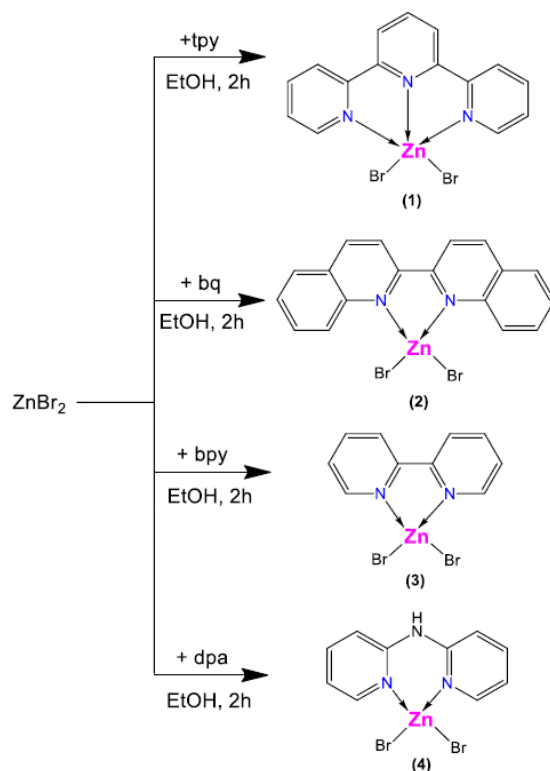


Fig. 1 – Synthesis route of Zn(II) complexes with pyridyl-type ligands.

Under the action of ultraviolet (UV) radiation at 365 nm, it was observed that all Zn(II) complexes possess the property of solid-state fluorescence, of a certain color in the UV and visible spectrum (Fig. 2). Complexes **1** and **4** give white fluorescence, complex **2** gives a pale

green fluorescence, and complex **3** gives a yellow fluorescence. To analyze the type of light emission given by the obtained complexes in solution, fluorescence spectra were recorded in ethanolic solutions (0.5 mg/mL), using an excitation wavelength of 260 nm (Fig. 3).

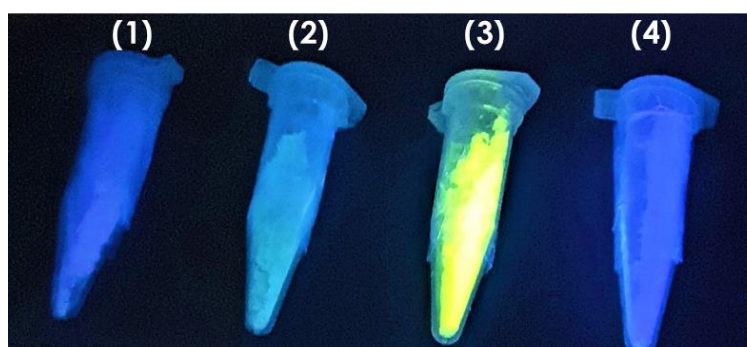


Fig. 2 – Visualization of the solid-state fluorescence effect of complexes **1-4** under UV lamp, following excitation at 365 nm.

From Fig. 3 it can be seen that only complexes **1**, **3** and **4** display prominent broad emission bands of different intensities, with maxima centered at 350 nm in the case of complexes **1** and **4**, and at 328 nm in the case of complex **3**. These emission bands in the UV range are due to the $\pi-\pi^*$ electronic transitions that occur at the level of the organic ligands,²⁸ without the contribution of the metal ion. For

complex **2**, on the other hand, the emissive effect is almost completely absent, probably due to its much poorer solubility in ethanol. It is also noteworthy that the yellow emissive effect observed for complex **3** in the solid state shifted to the UV region at 328 nm in ethanol solution, as a consequence of the influence of the solvent on the emissive effect by shifting the emission maximum.

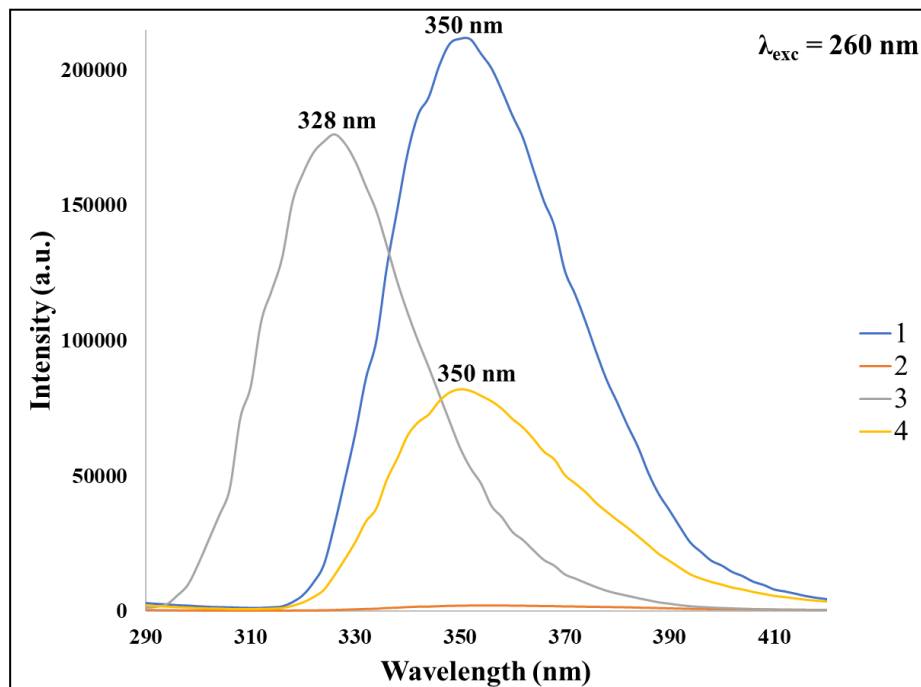


Fig. 3 – Fluorescence spectra of Zn(II) complexes in ethanol solutions (0.5 mg/mL).

Fluorescent detection of sodium diclofenac

The fluorescence properties observed in the ethanolic solutions of complexes **1**, **3**, and **4** were considered to investigate their fluorescent detection capability towards an anti-inflammatory drug, namely diclofenac in its sodium salt form. The selection of diclofenac is justified by its high relevance, both as a widely used nonsteroidal anti-inflammatory drug (AINSD) and as a frequent environmental contaminant. In comparison with other pharmaceutical compounds containing similar functional groups (*e.g.*, AINSDs such as ibuprofen or naproxen), diclofenac exhibits a distinct chemical structure characterized by the presence of two chlorine atoms on the phenyl aromatic ring, which confers unique interaction properties. Moreover, its aromatic nature and the presence of the carboxyl group facilitate the formation of stable coordination bonds with Zn(II) in the studied complexes.²⁹ This interaction results in a higher specific affinity toward zinc ions and pyridyl-type ligands, thereby enhancing the selectivity and sensitivity of detection. Previous reports in the literature have indicated that zinc–diclofenac systems form stable chemical interactions, further supporting the choice of diclofenac as a model compound due to the formation of robust complexes that can be selectively detected through fluorescence. This strategy also reduces interferences from other

pharmaceutical compounds that may be present in real matrices.^{29,30}

All three complexes under study demonstrated good detection capabilities for sodium diclofenac in ethanolic solution. The concentration of the complexes was kept constant (0.5 mg/mL), while the concentration of sodium diclofenac varied over the range of 0–1572 μM . The excitation wavelength (λ_{exc}) was identical for the three Zn complexes (260 nm), indicating similar absorption of excitation energy. In contrast, the emission wavelength (λ_{em}) showed slight shifts between the complexes: 350 nm for complexes **1** and **4**, and 328 nm for complex **3**, reflecting differences in the local electronic structure and chemical environment of each complex.¹

For all three complexes a significant decrease in the maximum emission intensity was observed with increasing diclofenac concentration, indicating a direct interaction that can lead to the formation of complex–diclofenac adducts and fluorescence quenching effects. The reduction in fluorescence intensity was visible even at the lowest concentrations tested, indicating a high sensitivity of the complexes towards diclofenac. At higher concentrations, the emission of the complexes progressively decreased, leading to the complete quenching of the signal, as can be seen in Fig. 4, suggesting a strong interaction between the functional groups of diclofenac and the metal ions in the complexes' structure.

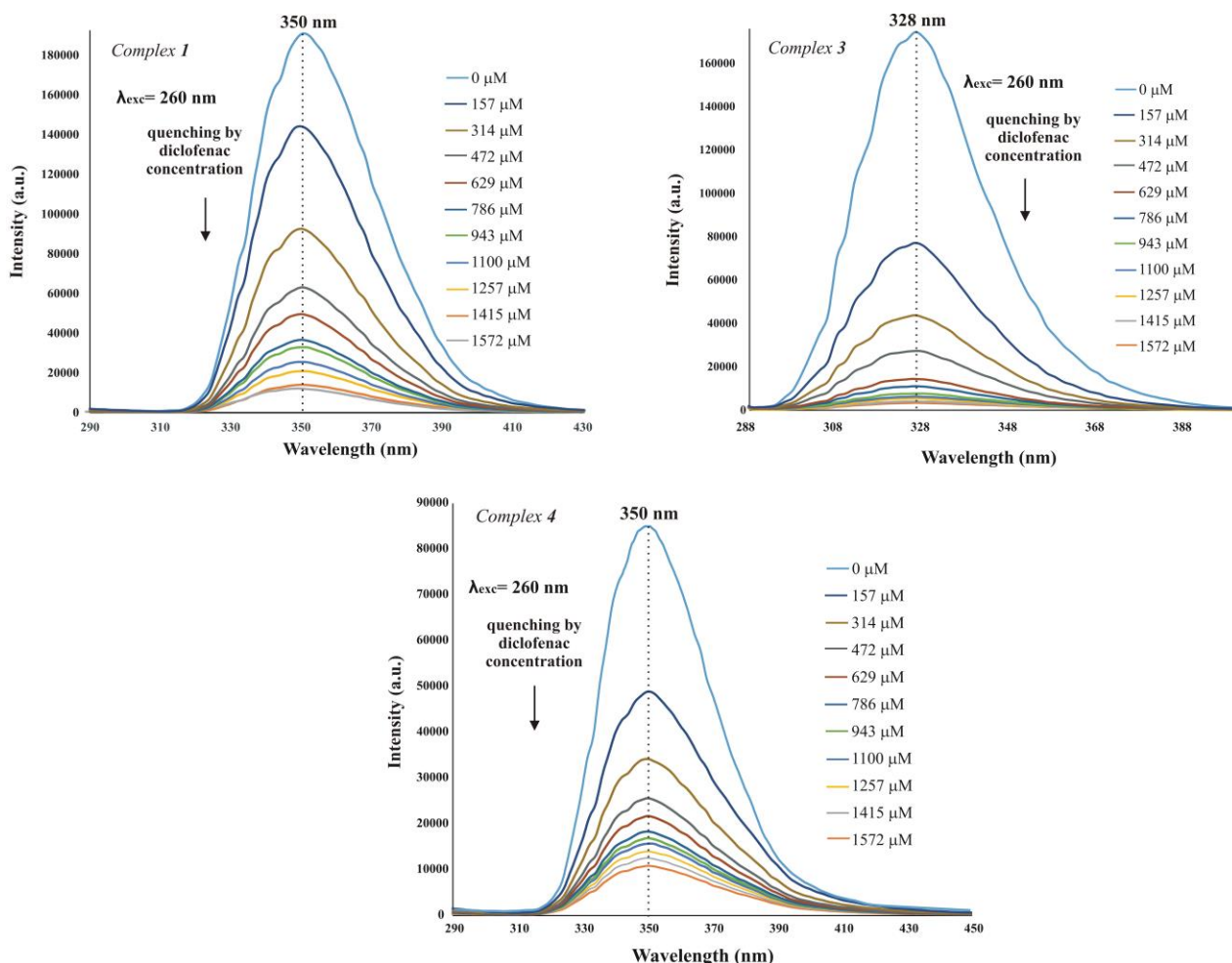


Fig. 4 – Fluorescence spectra of complexes **1**, **3** and **4** in ethanolic solutions treated with different diclofenac concentrations.

This fluorescence quenching effect of complexes **1**, **3**, and **4** was utilized for the detection of diclofenac. The graphical representation of fluorescence intensity for each complex as a function of varying diclofenac concentrations (0–1572 μM) led to the determination and calculation of characteristic

calibration parameters (Table 1). Worthy of note, the LOD values determined for such Zn(II) complexes are much lower compared to the LOD value determined for the Cu(I) complex used in the fluorescent detection of sodium diclofenac (3.14 μM), which was reported by us in a recent work.²³

Table 1

Sensitivity and regression parameters for the calibration data

Parameter	Values		
	1	3	4
Linear range	472–1572 μM	629–1572 μM	629–1572 μM
Slope	45.463	8.731	10.961
Intercept	78373	16654	27591
R ²	0.9807	0.989	0.9851
LOD	4.98×10^{-3} μM	1.83×10^{-2} μM	1.94×10^{-2} μM
LOQ	1.66×10^{-2} μM	6.12×10^{-2} μM	6.48×10^{-2} μM

To evaluate the precision and reproducibility of the method, repeated fluorescence intensity measurements were performed at fixed diclofenac concentrations for each complex under identical experimental conditions. The obtained intensity values were used to calculate the mean, standard deviation, and relative standard deviation (RSD), according to the following equation:

$$\text{RSD}\% = (\text{standard deviation}/\text{mean}) \times 100$$

The RSD values were below 0.25% for all complexes and concentrations evaluated, indicating excellent reproducibility and stability of

the analytical response. These findings confirm the reliable precision of the developed fluorescent detection method within the studied concentration range.

Fluorimetric titration curves are essential for determining the binding stoichiometry in molecular interactions.³¹ Figure 5 illustrates these curves for the interaction of diclofenac with the three complexes (**1**, **3** and **4**), where the fluorescence quenching ratio (I_0/I) is represented as a function of the molar ratio [diclofenac]/[complex].

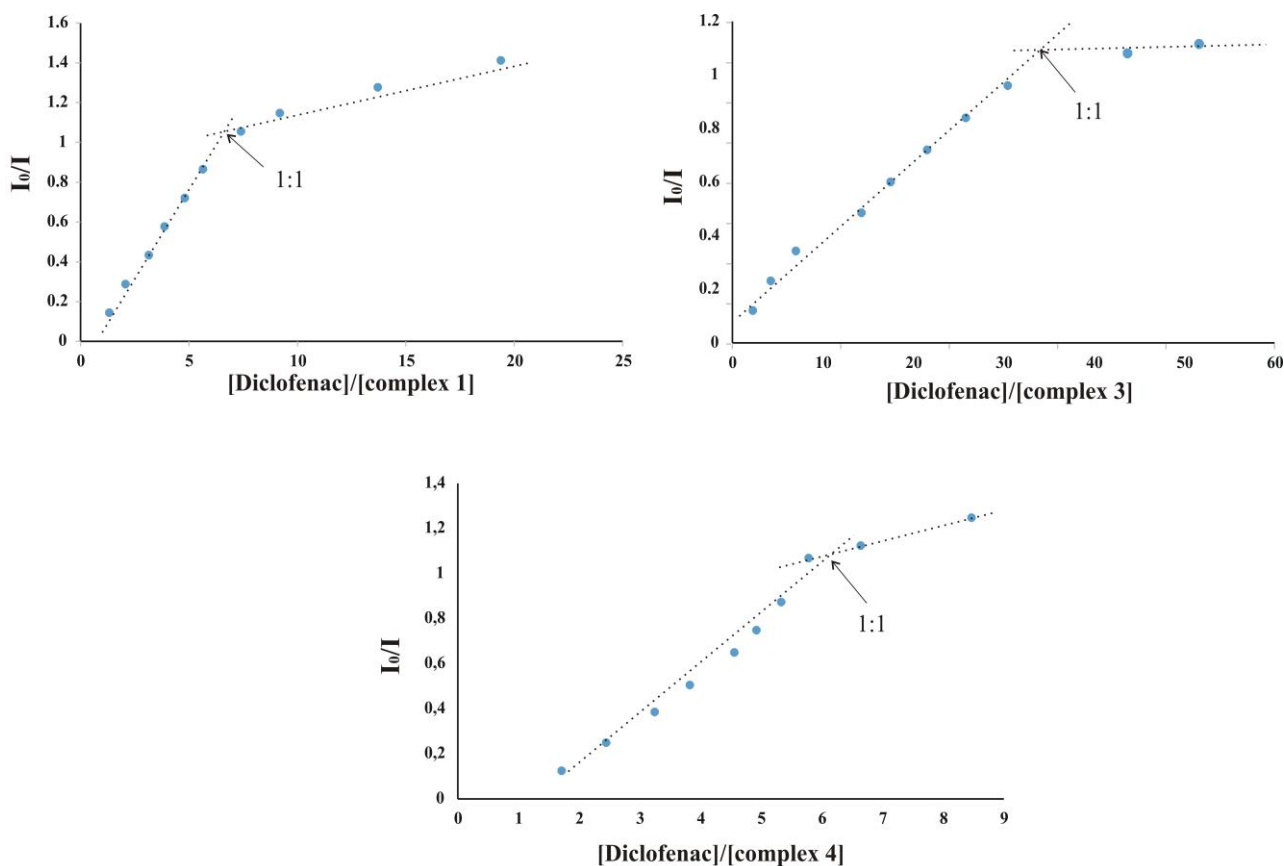


Fig. 5 – Dependence of the relative fluorescence intensity (I_0/I) of the complexes on the molar ratio of reactants ([diclofenac]/[complex]).

All three complexes indicate a 1:1 stoichiometry, evidenced by a clear inflection at this ratio, a fact that suggests the formation of supramolecular complexes with a stoichiometric [complex-diclofenac] composition in solution.³ This stoichiometry is also confirmed by other studies of Zn complexes.^{14,32}

The graphical representation of the ratio $(I_{\max} - I_0)/(I_x - I_0)$ as a function of $1/[\text{diclofenac}]$ provided binding constant values of $0.0123 \mu\text{M}^{-1}$, $0.0146 \mu\text{M}^{-1}$ and $0.0117 \mu\text{M}^{-1}$ for complexes **1**, **3**

and **4**, respectively (Fig. 6). These results indicate that the stability of the complexes increases in the order: complex **4** < complex **1** < complex **3**.

It is well-known that fluorescence quenching can occur through two main mechanisms. In the case of dynamic quenching, quencher molecules diffuse to the fluorophore during its excited state. In contrast, static quenching occurs when the fluorophore and the quencher form a non-fluorescent complex. The identification of the quenching mechanism is performed by analyzing the Stern-Volmer plot (Fig.

7).^{3,31} In this case, the nature of the Stern–Volmer curves indicates a predominantly static mechanism of fluorescence quenching in the presence of diclofenac, as the linearity is not perfect. A similar behavior has also been observed in other studies.^{33,34} Nonetheless, the slight deviations from ideal linearity point to secondary contributions, potentially of dynamic origin or arising from additional supramolecular interactions, a phenomenon frequently reported in comparable studies.^{16,35} This complexity is a well-

documented characteristic of supramolecular photophysical systems and was deliberately highlighted in our work to provide a realistic, rather than idealized, perspective on the quenching process. The Stern-Volmer constant values indicate the strength of the interaction between diclofenac and the three complexes, and implicitly, the fluorescence quenching efficiency, presenting in the following order: complex 4 ($K_{SV}=0.0035 \mu\text{M}^{-1}$) < complex 1 ($K_{SV}=0.01 \mu\text{M}^{-1}$) < complex 3 ($K_{SV}=0.0315 \mu\text{M}^{-1}$).

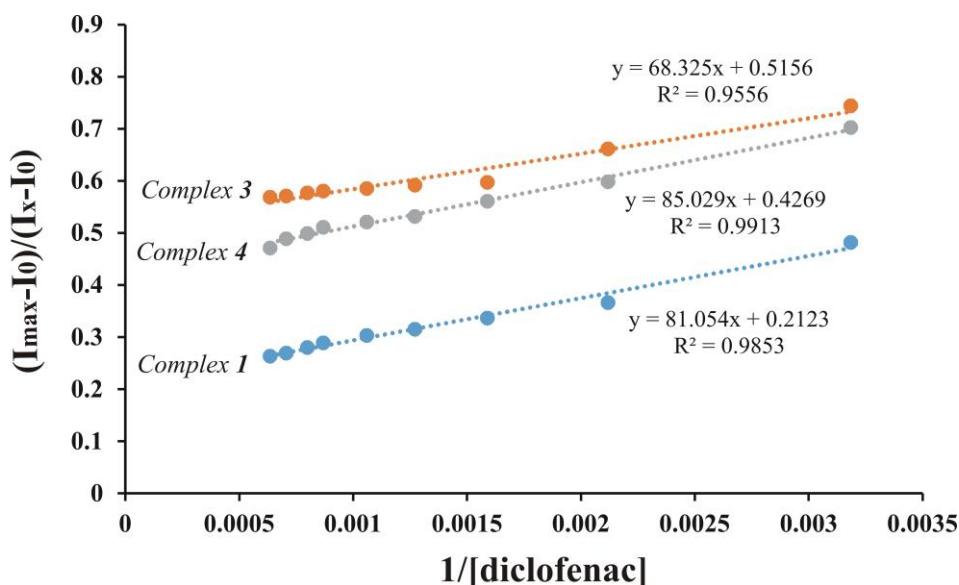


Fig. 6 – The Benesi-Hildebrand plots used for determining the binding constants of complexes 1, 3 and 4.

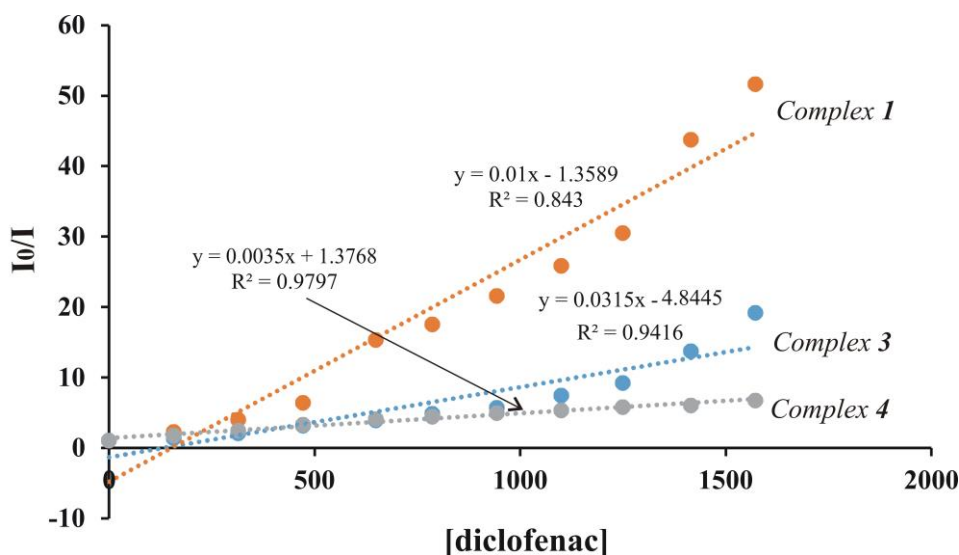


Fig. 7 – Stern-Volmer dependencies for complexes 1, 3, and 4 in the presence of diclofenac.

The values of the binding constants (K_b) and the Stern-Volmer constants (K_{SV}) show a clear correlation, indicating that the stability of the supramolecular complexes directly influences the

efficiency of fluorescence quenching. This correlation supports the fact that fluorescence quenching occurs predominantly via a static mechanism, being determined by the formation of

non-fluorescent complexes between the fluorophore and diclofenac.

EXPERIMENTAL

Materials and instrumentation

The reagents used for the synthesis of Zn(II) complexes were ZnBr₂·2H₂O, 2,2':6',2''-terpyridine (tpy), 2,2'-biquinoline (bq), 2,2'-bipyridyl (bpy), 2,2'-dipyridylamine (dpa) and ethanol (96%). They were purchased from Sigma-Aldrich and used as received.

Elemental analyses (N, C, H) were performed with a FISON'S INSTRUMENTS EA 1108 CHNS – O instrument. Melting points were taken on an SMP3 Stuart instrument with a capillary apparatus. Fourier transform infrared spectra (FTIR) of dry powder samples were recorded from 4000 to 400 cm⁻¹, at 4 cm⁻¹ resolution, by total reflectance on a CdSe crystal using a Perkin–Elmer system Spectrum 100 FTIR spectrometer. Solution ¹H NMR spectra were recorded in deuterated dimethylsulfoxide on a 400 Mercury Plus Varian spectrometer operating at room temperature (400 MHz). For the visualization of the photoluminescence of the synthesized Zn(II) complexes, the SPECTROLINE – MODEL CM – 10 instrument was used (short wave UV – 254 nm; long wave UV – 365 nm). Fluorescent spectra of ethanolic solutions containing Zn(II) complexes (0.5 mg/mL) were recorded at room temperature in the range of 200–400 nm with a Microplate reader with Infinite 200 PRO NanoQuant fluorescence spectrometer (Tecan, Switzerland). The samples were excited at a wavelength of 260 nm.

Synthesis of the Zn(II) complexes: general procedure

0.117 g (0.5 mmol) of tpy, 0.128 g (0.5 mmol) of bq, 0.078 g (0.5 mmol) of bpy and 0.085 g (0.5 mmol) of dpa were weighed and placed each in a 50-mL round-bottom flask containing 10 mL of ethanol, under stirring at room temperature. After complete dissolution of each ligand, 0.131 g (0.5 mmol) of ZnBr₂·2H₂O were added. The entire reaction mixture was left under continuous stirring at room temperature for 2 h. After this time, the complexes that were obtained in the form of white

or pale yellow precipitates were filtered off, washed with two portions (5 mL) of ethanol and dried in air.

[Zn(tpy)Br₂] (1): yield 88%; m.p. 289–292°C; Elem. Anal. calculated values for C₁₅H₁₁Br₂N₃Zn: N, 9.02; C, 39.11; H, 2.23%; found: N, 9.17; C, 39.30; H, 2.42%; IR (cm⁻¹): 3100-3000w ν(C–H_{aromatic}), 1594-1440m ν(C=N_{tpy} + C=C_{tpy}); ¹H NMR (DMSO-*d*₆, 293 K): δ (ppm) = 8.18 (t, 2H), 8.33–8.37 (m, 4H), 8.80–8.92 (m, 5H); PL: λ_{max} = 350 nm (λ_{exc} = 260 nm, ethanol solution).

[Zn(bq)Br₂] (2): yield 63%; m.p. 234–236°C; Elem. Anal. calculated values for C₁₈H₁₂Br₂N₂Zn: N, 5.59; C, 44.67; H, 2.38%; found: N, 5.82; C, 44.90; H, 2.51%; IR (cm⁻¹): 3100-3000w ν(C–H_{aromatic}), 1617-1434m ν(C=N_{bq} + C=C_{bq}); ¹H NMR (DMSO-*d*₆, 293 K): δ (ppm) = 8.10 (t, 2H), 8.23 (t, 2H), 8.37–8.42 (m, 4H), 8.61 (d, 2H), 9.18 (d, 2H).

[Zn(bpy)Br₂] (3): yield 83%; m.p. 302–305°C; Elem. Anal. calculated values for C₁₀H₈Br₂N₂Zn: N, 7.14; C, 31.27; H, 2.03%; found: N, 7.35; C, 31.49; H, 2.11%; IR (cm⁻¹): 3100-3000w ν(C–H_{aromatic}), 1607-1442m ν(C=N_{bpy} + C=C_{bpy}); ¹H NMR (DMSO-*d*₆, 293 K): δ (ppm) = 8.18 (t, 2H), 8.37 (d, 2H), 8.80 (t, 2H), 8.92 (d, 2H); PL: λ_{max} = 328 nm (λ_{exc} = 260 nm, ethanol solution).

[Zn(dpa)Br₂] (4): yield 73%; m.p. 257–259°C; Elem. Anal. calculated values for C₁₀H₉Br₂N₃Zn: N, 10.35; C, 30.07; H, 2.11%; found: N, 10.60; C, 30.30; H, 2.29%. IR (cm⁻¹): 3326w ν(N–H_{dpa}), 3148-3000w ν(C–H_{aromatic}), 1633-1413s ν(C=N_{dpa} + C=C_{dpa}). ¹H NMR (DMSO-*d*₆, 293 K): δ (ppm) = 7.44–7.47 (m, 4H), 8.38-8.43 (m, 4H); PL: λ_{max} = 350 nm (λ_{exc} = 260 nm, ethanol solution).

Fluorescent detection of sodium diclofenac

Fluorimetric detection studies of sodium diclofenac were conducted using a fluorescence spectrometer microplate reader (Infinite 200 PRO NanoQuant, Tecan, Männedorf, Switzerland). Sample excitation was set at a wavelength of 260 nm. Prior to measurements, 0.5 mg/mL stock solutions were prepared for each of the three Zn(II) complexes [Zn(tpy)Br₂] (1), [Zn(bpy)Br₂] (3) and [Zn(dpa)Br₂] (4) dissolved in ethanol. Additionally, a 1 mg/mL stock solution of sodium diclofenac in ethanol was prepared. Fluorescence measurements were performed in a 96-well microplate. The protocol involved adding 200 μL

of complex solution to the first well. Subsequently, 100 μL of complex solution and variable microvolumes of diclofenac solution (in 10 μL increments) were added to ten successive wells, maintaining a constant total volume.

To compare the stability of the obtained complexes, the binding constants were calculated. The binding constants of the complexes with diclofenac were estimated using the modified Benesi-Hildebrand equation:³⁶

$$(I_{\max} - I_0) / (I_x - I_0) = 1 + (1/K_b) \times (1/[diclofenac])^n$$

where: I_0 , I_x and I_{\max} are the emission intensities of the complexes in the absence of diclofenac, at an intermediate concentration, and at the maximum interaction concentration, respectively; K_b is the binding constant; $[diclofenac]$ is the diclofenac concentration; n is the number of diclofenac molecules bound per complex (here, $n = 1$).

The fluorescence quenching dependencies of the complexes as a function of diclofenac concentration were characterized within the Stern-Volmer theory using equation:³⁷

$$I_0/I = 1 + K_{SV} \times [diclofenac]$$

where: I_0 and I are the fluorescence intensities of the complex in the absence and presence of diclofenac, respectively; K_{SV} is the Stern-Volmer constant.

For calculating the limit of detection (LOD), the following formula was used:^{38,39}

$$LOD = 3 \sigma / S$$

The limit of quantification (LOQ) was determined using the formula:

$$LOQ = 10 \sigma / S$$

where: σ is the residual standard deviation derived from data regression; S is the slope of the regression line, indicating the method's sensitivity.

CONCLUSIONS

In this study, four novel photoluminescent Zn(II) complexes with aromatic N-donor ligands were synthesized and thoroughly characterized. These complexes exhibit distinctive optical properties in both solid state and solution. Complexes **1**, **3**, and **4** displayed broad emission bands in the ultraviolet region, attributable to characteristic $\pi-\pi^*$ electronic transitions within the ligands, which confers upon them potential for use as fluorescent sensors.

The novelty of this study lies in the application of these complexes for the selective and sensitive

detection of diclofenac, a widely used anti-inflammatory drug, via the fluorescence quenching phenomenon generated by the supramolecular interaction between the complex and diclofenac. A 1:1 stoichiometry for these interactions was confirmed, and the determined binding constants indicate variable stability among the complexes, directly impacting the efficiency of fluorescence quenching.

The results underscore the functionality and potential of these Zn(II) complexes as fluorescent sensors for monitoring pharmaceuticals in solutions, offering a precise and innovative method with broad applicability in bioanalytical and environmental protection fields.

For future studies, it is recommended to deepen the understanding of the molecular mechanisms governing the specific interactions between the complexes and various active substances, emphasizing the innovative nature of this selective and sensitive fluorescent detection method. Furthermore, the development of new sensors based on these photoluminescent complexes, with applications in real and biological environments, as well as the evaluation of their stability under different conditions, will be crucial for the practical implementation of these systems in portable technologies and real-time monitoring. This approach represents an original and promising contribution to the field of precise drug detection. For practical applications and full validation of the method, additional studies will be conducted on accuracy (*e.g.*, recovery in real samples) and the evaluation of potential interferences.

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