

Fluorescence and antioxidant properties of Mn(II), Co(II), and Zn(II) complexes of 3-hydroxyflavone in methanolic solution

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ABSTRACT

The photophysical and antioxidant properties of 3-hydroxyflavone (3HF) and its complexes with Mn(II), Co(II), and Zn(II) ions were investigated. Fluorescence spectra of 3HF in methanol revealed a pronounced excitation-wavelength dependence characteristic of the excited-state intramolecular proton transfer (ESIPT) process. Complexation with d-electron metal ions significantly altered the emission properties. The Zn(II) complex exhibited higher fluorescence intensity than the free ligand, consistent with the chelation-enhanced fluorescence effect and partial suppression of the ESIPT process. In contrast, Mn(II) and Co(II) complexes showed strongly reduced intensities, indicating fluorescence quenching associated with the paramagnetic character of these ions and the promotion of intersystem crossing. Antioxidant activity assessed by the 2,2-diphenyl-1-picrylhydrazyl (DPPH) method showed moderate inhibition for 3-hydroxyflavone (24.0%). Among the complexes, Mn-3HF exhibited the highest activity (33.4%), while Co-3HF and Zn-3HF showed only minimal effects (7.1% and 5.9%). These results indicate that metal coordination modulates the antioxidant properties of 3HF, enhancing them in the case of Mn(II) and suppressing with Co(II) and Zn(II). The results demonstrate that coordination with d-electron metal ions exerts a strong influence on both the fluorescence properties and the antioxidant activity of 3HF.

Keywords: 3-hydroxyflavone, fluorescence, metal complexes, antioxidants

1. Introduction

Flavonoids are naturally occurring chemical compounds with a diverse structure, classified as phytochemicals and secondary metabolites. They cannot be synthesized by animal cells but are widely present in plants, where they perform many essential functions. They are responsible for the color and taste of flowers and fruits, act as antioxidants, and protect plants from bacterial, viral, and fungal infections, as well as from herbivores [1,2]. The basic skeleton of flavonoids consists of three rings (A-C-B) arranged in a C₆-C₃-C₆ structure, based on the molecule of 2-phenyl-1-benzopyran-4-one. Depending on the substituents such as hydroxyl, methyl, or sugar groups, flavonoids are classified into different classes, including flavones, flavonols, isoflavones, flavanones, flavanols, and anthocyanins. Each of these classes exhibits distinct chemical and biological properties [1,2]. Flavonols are the largest and most common subgroup of flavonoids. They are characterized by the presence of a hydroxyl group at position 3 and a carbonyl group at position 4. Their structure is nearly completely planar due to the presence of aromatic rings [3,4].

3-Hydroxyflavone (C₁₅H₁₀O₃, IUPAC: 3-hydroxy-2-phenylchromen-4-one, Fig. 1) is the simplest representative of flavonols, from which the name of this group is derived. 3HF is a synthetic compound that does not occur naturally. It can be obtained through both chemical and biotechnological methods. In chemical synthesis, 3HF is typically produced via a multi-step process involving the condensation of suitable aromatic substrates, such as 2-hydroxyacetophenone and benzaldehyde, followed by the cyclization of the resulting chalcone. This reaction

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can be carried out under acidic or basic conditions, and often involves the Claisen-Schmidt condensation followed by oxidative cyclization to form the flavone structure [5,6]. In contrast, microbial and enzymatic methods provide a greener alternative, enabling regio- and stereoselective modifications under mild conditions. Early studies demonstrated that filamentous fungi such as *Aspergillus niger* were capable of converting flavanone into several products, including 3HF, through sequential dehydrogenation at C-2/C-3 and hydroxylation at C-3 [7]. Inspired by these findings, attention has shifted towards bacterial systems as potential biocatalysts.

Bacteria from the genus *Streptomyces* possess oxygenases that can introduce hydroxyl groups into flavonoids. For example, *S. coeruleorubidus* hydroxylates 2'-hydroxyflavanone at the C-3 position, while the CYP105P2 enzyme from *S. peucetius*, expressed in *E. coli* with redox partners from *Pseudomonas putida*, catalyzed flavone hydroxylation mainly at the 3' position [8,9]. These studies highlight the potential of bacterial oxygenases, although direct 3HF biosynthesis remains challenging. To improve efficiency, metabolic engineering has been applied. Recombinant *E. coli* strains carrying plant genes encoding flavanone 3-hydroxylase and flavonol synthase converted flavanones (e.g., naringenin) into flavonols such as kaempferol and quercetin [10]. Similarly, *Streptomyces albus* equipped with a complete flavonoid pathway produced flavonols de novo, confirming the usefulness of actinobacteria as microbial hosts for flavone hydroxylation pathways [11].

Although the current titers in bacterial systems remain modest (on the order of micrograms to milligrams per liter), these findings provide a solid foundation for the development of scalable, sustainable biosynthetic routes to 3HF.

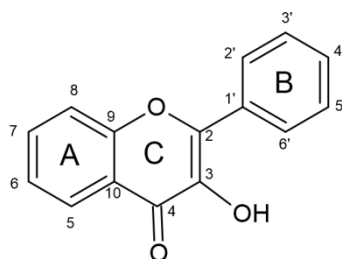


Fig.1. Structure of 3-hydroxyflavone.

3-Hydroxyflavone is one of the best-studied compounds exhibiting excited-state intramolecular proton transfer (ESIPT). Upon UV excitation, a proton from the hydroxyl group at position 3 (donor) is transferred extremely rapidly (<100 fs) to the carbonyl oxygen at position 4 (acceptor). This process is facilitated by a strong intramolecular hydrogen bond present in the ground state (Fig.2) [12]. Theoretical studies indicate that the ESIPT process may proceed via the second excited singlet state (S_2) and involve a multi-mode transfer pathway [13]. Energy calculations further show that the barrier for ESIPT in the excited state is very low (~2–4 kcal/mol), accounting for its ultrafast nature [14]. Importantly, the ESIPT process is highly sensitive to the surrounding environment. McMorro and McHale [15] demonstrated that even small fluctuations of solvent molecules can modulate the balance between the normal (N^*) and tautomeric (T^*) emission, underlining this environmental dependence. In general, although the absorption maxima of 3HF remain relatively stable across different solvents, the character and intensity of the emission vary significantly depending on the medium. Aprotic solvents such as acetonitrile and dimethylformamide favor efficient proton transfer and strong emission from the tautomer (T^*) [16]. In contrast, protic solvents such as water, methanol, and ethanol disrupt the essential intramolecular hydrogen bond by forming additional intermolecular hydrogen bonds with 3HF. This effect suppresses ESIPT and leads to the dominance of emission from the normal form (N^*) [16]. Theoretical calculations confirm that protic solvents stabilize the solvated enol form through hydrogen-bonding interactions, thereby reducing the efficiency of ESIPT [17]. Computational studies further indicate that the main factor limiting ESIPT in such environments is the interruption of the intramolecular hydrogen bond [18].

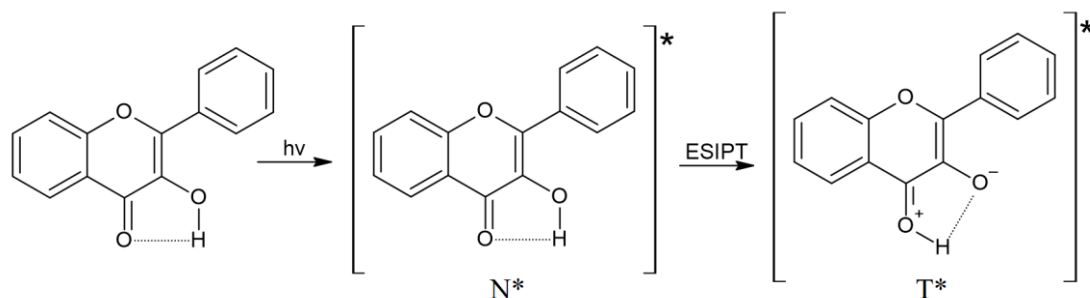


Fig. 2. Excited-state proton transfer (ESIPT) in 3HF: N – normal form, T – tautomeric form, * – excited state.

Fluorescence spectra of 3-hydroxyflavone typically display two distinct emission bands: the normal excited enol (N*), emitting in the blue region (~420 nm), and the tautomeric excited keto form (T*), emitting in the green region (~530 nm). The ratio between N* and T* bands reflects the efficiency of ESIPT. The presence of large Stokes shifts, reaching up to 200 nm, is characteristic of ESIPT and indicates substantial structural reorganization in the excited state [19,20]. These shifts also prevent reabsorption of the emitted radiation, which is advantageous in optoelectronic applications [21]. The timescale of the proton transfer in 3HF is in the femtosecond range (10^{-15} s), posing challenges for experimental observation [22]. However, by carefully selecting the solvent polarity, excitation wavelength, and temperature, the process can be slowed down to several nanoseconds, enabling detailed study [23].

The ESIPT mechanism in 3HF has numerous practical applications, including in the design of fluorescent probes and moisture sensors, as well as in laser dyes and photostabilizers [20,21]. Based on this, four types of fluorescent sensors based on flavonols can be distinguished: (1) sensors responsive to environmental changes affecting ESIPT, (2) inhibition of ESIPT through complexation with metal ions, (3) chemical attachment of a signal group to the hydroxyl group, and (4) structural modifications unrelated directly to the fluorescence mechanism [20]. Understanding the ESIPT mechanism and the factors influencing it is therefore essential for further development of flavonol-based applications in industry, particularly in the creation of chemical sensors.

In addition to their photophysical properties, flavonols such as 3HF are also recognized for their significant antioxidant activity. The hydroxyl group at the C-3 position facilitates electron donation and transfer, thereby enhancing the ability of 3HF to scavenge free radicals [24]. This process is further stabilized by resonance, which increases the overall antioxidant potential of the molecule compared to other flavones [25]. Importantly, 3HF can form complexes with transition metal ions such as Fe(II), Cu(II), or Zn(II). Such interactions not only modify the electronic properties of the molecule but may also suppress the pro-oxidant role of metal ions in Fenton-type reactions, which are responsible for the generation of highly reactive hydroxyl radicals [26,27]. Consequently, both free 3HF and its metal complexes are considered promising agents with potential biological and pharmacological relevance, particularly in the prevention of oxidative damage to biomolecules [28].

The aim of this study was to investigate the antioxidant and photophysical properties of methanolic solutions of Mn(II), Co(II), and Zn(II) complexes with 3-hydroxyflavone. Particular attention was focused on the influence of metal complexation on the fluorescence spectra of 3HF, as well as on its excited-state intramolecular proton transfer (ESIPT) process. Moreover, the ability of these complexes to scavenge free radicals was examined in order to assess their potential antioxidant activity.

2. Experimental

2.1. Materials

All reagents used in this study were of analytical grade and were employed without further purification. 3HF was sourced from Alfa Aesar (Waltham, MA, USA) while ZnCl_2 , $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Na}_2\text{H}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$, NaOH, chloric(VII) acid, and HPLC-grade methanol were obtained from POCh (Gliwice, Poland). The synthesis of the complexes was carried out according to a previously reported procedure [29]. The molecular formulas and molar masses of the complexes are as follows: Zn-3HF: $\text{C}_{30}\text{H}_{20}\text{ZnO}_7$, 557.85 [g mol^{-1}]; Mn-3HF: $\text{C}_{30}\text{H}_{22}\text{MnO}_8$, 565.43 [g mol^{-1}]; Co-3HF: $\text{C}_{30}\text{H}_{22}\text{CoO}_8$, 569.06 [g mol^{-1}].

2.2. Methods

UV-Vis absorption spectra in the range of 200–600 nm were recorded on a Jasco UV-Vis-NIR V-670 double-beam spectrophotometer (Hachioji, Tokyo, Japan). Fluorescence measurements were performed in the range of 220–800 nm using a Hitachi F-2710 spectrofluorometer (Tokyo, Japan) equipped with a 1 cm quartz

cuvette. For fluorescence experiments, solutions of 3HF and its metal complexes were prepared in methanol at a concentration of $40 \mu\text{mol}\cdot\text{dm}^{-3}$ by dissolving accurately weighed samples of each compound.

2.2.1 Antioxidant activity assay

The antioxidant properties of 3HF and its complexes were evaluated using the DPPH radical scavenging assay. A stock solution of 2,2-diphenyl-1-picrylhydrazyl (DPPH) was prepared by dissolving 3.5 mg of the radical in 50 cm^3 of methanol and subsequently diluted fivefold. For each measurement, 2.5 cm^3 of the DPPH solution was mixed with 0.5 cm^3 of previously filtered saturated solutions of the tested complexes or with a 1 mM solution of 3HF. The absorbance of the reaction mixtures was measured at 515 nm immediately after mixing ($t = 0$) and again after 60 minutes. Measurements were performed using a Jasco UV-Vis-NIR V-670 spectrophotometer.

The antioxidant capacity of 3-hydroxyflavone and its complexes was calculated according to the following equation (1):

$$\% \text{ inhibition} = \frac{A_0 - A_K}{A_0} \cdot 100\% \quad (1)$$

where: A_0 – initial absorbance of the DPPH solution, A_K – absorbance of the tested solution after 60 minutes.

3. Results and discussion

3.1. Fluorescence properties of 3-hydroxyflavone and its metal complexes

The fluorescence of 3-hydroxyflavone is closely associated with the excited-state intramolecular proton transfer (ESIPT) mechanism, which gives rise to its characteristic dual emission. Complexation with transition metal ions can significantly affect this process, altering both the intensity and the nature of the emission spectra. In this section, the fluorescence properties of 3HF and its complexes with Mn(II), Co(II), and Zn(II) ions are presented and discussed.

3.1.1. Excitation wavelength dependence of 3HF emission

Experiments on 3-hydroxyflavone in methanol confirm a pronounced excitation-wavelength dependence of its dual fluorescence, which arises from the ESIPT mechanism. According to Kasha's rule, fluorescence generally occurs only from the lowest excited singlet state (S_1), regardless of the excitation energy. The strong variation in the relative intensities of the 'normal' enol emission (N, blue $\sim 420 \text{ nm}$) and the tautomer emission (T, green $\sim 530 \text{ nm}$) with excitation wavelength therefore provides clear evidence of anti-Kasha behavior [30–32]. Under short-wavelength UV excitation (240–300 nm), which populates higher electronic states, the tautomeric T band dominates and its intensity exceeds that of the N band by several fold. In contrast, excitation near the onset of the first absorption band (400–420 nm, close to S_1) leads to a markedly higher N^*/T^* ratio. Thus, at high excitation energy tautomer emission is highly efficient, whereas near-resonant long-wavelength excitation (e.g., 418 nm) partially suppresses ESIPT and results in relatively stronger N^* emission (Fig. 3) [30,33,34]. Literature reports further support this anti-Kasha behavior, showing that excitation into higher electronic states (S_2 , S_3) accelerates proton transfer and enhances tautomer emission, whereas direct excitation into S_1 slows down or even suppresses ESIPT, leading to stronger normal-form fluorescence [32,34,36]. The strong reduction of the T^* band observed at 418 nm in our study is therefore consistent with the idea that lower-energy excitation decreases the efficiency of ESIPT.

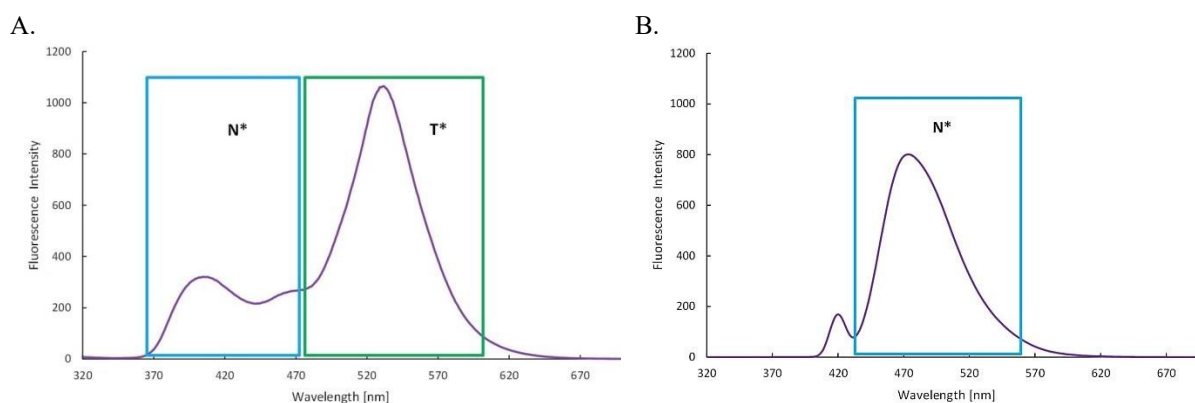


Fig. 3. Fluorescence spectra of 3HF in methanol upon excitation at (A) 240 nm and (B) 418 nm.

3.1.2. Effects of metal ion complexation

Complexation of 3HF with transition metal ions significantly alters both the relative intensities of the N* and T* bands and the total fluorescence yield. The Zn(II) complex exhibits much higher emission intensity than the free ligand, both under short-wavelength (240 nm) and near-resonant (418 nm) excitation (Fig.4). This enhancement is a characteristic example of chelation-enhanced fluorescence: coordination with Zn²⁺ rigidifies the flavonol skeleton, reduces nonradiative vibrational relaxation, and increases photostability [33, 34]. Moreover, Zn(II) has a closed-shell d¹⁰ configuration with no low-lying d–d states or paramagnetic effects, and therefore does not quench emission. Instead, it stabilizes the excited states and facilitates radiative decay [34]. Literature consistently reports that Zn(II)–flavonol complexes display stronger emission than the free ligands, often with a relative increase of N* emission due to partial suppression of ESIPt under rigid coordination [33].

In contrast, complexes with Mn(II) and Co(II) exhibit significantly lower fluorescence intensity than both the free 3HF and the Zn-3HF complex. Although the dual emission pattern remains discernible, the overall emission is strongly quenched and the relative balance shifts toward tautomeric fluorescence. This behavior can be attributed to the paramagnetic nature of Mn²⁺ (high-spin d⁵) and Co²⁺ (high-spin d⁷), which facilitates spin–orbit coupling and promotes intersystem crossing from singlet to triplet states [35–37]. These nonradiative processes compete effectively with fluorescence, thereby reducing the quantum yield. Additionally, low-lying metal-centered d–d or charge-transfer states can act as energy sinks, channeling excitation energy away from the ligand [35–37].

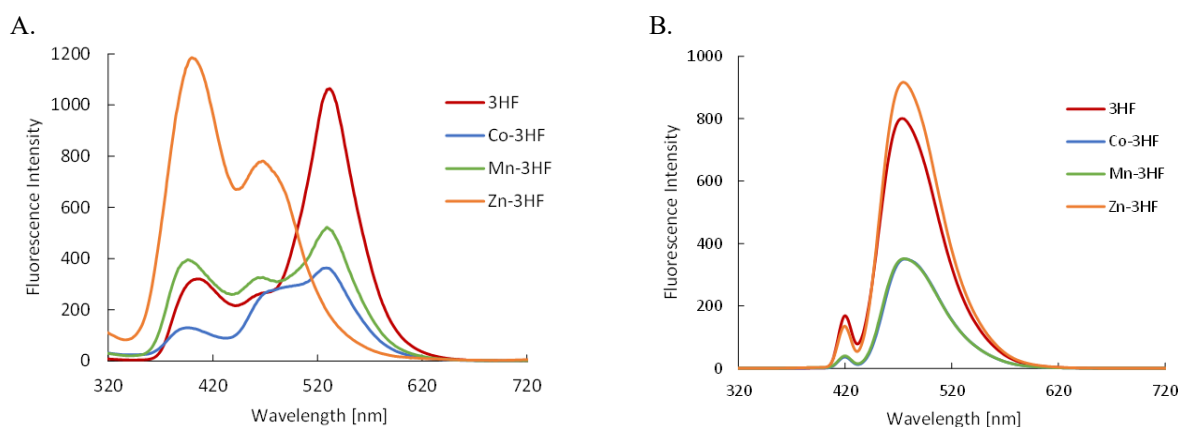


Fig.4. Emission spectra of 3HF and its Mn-, Co-, and Zn-complexes in methanol, recorded at excitation wavelengths of (A) 240 nm and (B) 418 nm.

The sharp contrast between the fluorescence enhancement by Zn(II) and quenching by Mn(II) and Co(II) underscores the decisive role of the metal ion in modulating the excited-state deactivation pathways. Diamagnetic d¹⁰ ions such as Zn²⁺ or Cd²⁺ are generally “fluorescence-friendly,” while paramagnetic ions with unpaired electrons are strong quenchers. This principle has been widely demonstrated for flavonols and related chromophores, and it highlights the utility of 3HF as an environment-sensitive probe whose emission character and intensity can be tuned by the choice of coordinating metal ion.

Taken together, the results demonstrate that 3HF in methanol exhibits a classical ESIPt mechanism, with tautomeric emission dominating under short-wavelength excitation and a higher contribution of the N* band at 418 nm excitation. Complexation with Zn(II) enhances fluorescence and shifts the equilibrium toward N* emission, whereas the presence of Mn(II) and Co(II) ions results in pronounced fluorescence quenching. These findings confirm that the nature of the metal ion strongly determines the excited-state deactivation pathways and can be exploited to modulate the photophysical properties of flavonoids. The results highlight the potential of 3HF as a ligand acting as an environmental probe, whose emission character and intensity can be controlled by appropriate choice of the metal center.

3.2. DPPH radical scavenging activity of 3-hydroxyflavone and its complexes with Mn(II), Co(II), and Zn(II)

3-Hydroxyflavone, in addition to its interesting photophysical properties, also exhibits biological activity. Despite the absence of a classical catechol moiety in the B-ring, this compound can display antioxidant activity due to the ESIPt mechanism [38]. In the present study, the antioxidant capacity of the free ligand and its complexes with Mn(II), Co(II), and Zn(II) ions was evaluated using the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH•) assay, which monitors the decrease in absorbance at $\lambda = 515$ nm. The results, expressed as percentage of inhibition relative

to the control, were obtained for a 1 mmol·dm⁻³ solution of 3HF and for saturated solutions of the metal complexes. The inhibition values are summarized in Table 1.

Table 1. Percentage inhibition of DPPH radicals by 3-hydroxyflavone and its metal complexes.

Compound	% Inhibition
3HF (1 mmol dm ⁻³)	24.0
Mn-3HF (saturated sol.)	33.4
Co-3HF (saturated sol.)	7.1
Zn-3HF (saturated sol.)	5.9

The results show that free 3HF exhibits moderate antioxidant activity (24.0%). Notably, complexation with Mn(II) enhanced radical scavenging capacity, with the Mn-3HF complex reaching 33.4% inhibition and thus surpassing the free ligand. This suggests that, in addition to the intrinsic activity of 3HF, the Mn(II) ion itself may contribute to redox processes, effectively reinforcing the radical neutralization mechanism. In contrast, complexation with Co(II) and Zn(II) resulted in only minimal activities (7.1% and 5.9%, respectively). This indicates that coordination with these metals blocks the reactive hydroxyl group of 3HF, essential for hydrogen atom or electron donation, without providing additional redox pathways as in the case of Mn(II).

Comparison with literature data reveals that the highest activity in the DPPH assay is reported for flavonols containing the 3',4'-dihydroxy catechol system in the B-ring, such as myricetin, quercetin, and fisetin [39–41]. Flavonols lacking these groups, such as kaempferol and morin, exhibit much lower antioxidant capacity [42,43]. The results obtained for 3HF are consistent with this trend, as its activity is moderate but still significant, most likely supported by stabilization of the radical form through the ESIPT process. The increase observed upon Mn(II) coordination highlights that metal complexation can, depending on the redox properties of the ion, either enhance or suppress the antioxidant capacity of flavonols.

In summary, 3-hydroxyflavone demonstrates moderate antioxidant activity despite the absence of a classical catechol system. Its coordination with Mn(II) improves radical scavenging efficiency, while Co(II) and Zn(II) markedly reduce it. These findings underline the importance of hydroxyl groups in the antioxidant mechanism of flavonols and demonstrate that metal coordination represents a powerful tool to modulate their biological properties.

3.3. Conclusions

In this study, the photophysical and antioxidant properties of 3-hydroxyflavone and its complexes with Mn(II), Co(II), and Zn(II) were examined. Fluorescence spectroscopy showed that 3HF has excitation-dependent dual emission governed by the ESIPT mechanism. Zn(II) complexation enhanced fluorescence and promoted enol emission, while Mn(II) and Co(II) led to strong quenching due to paramagnetism. Antioxidant activity evaluated by the DPPH assay showed very high radical scavenging efficiency for 3HF, whereas metal complexes displayed significantly reduced activity, with only Mn-3HF retaining partial capacity. These findings demonstrate that both the optical and biological properties of 3HF can be modulated by metal coordination, highlighting its potential as an environment-sensitive probe and as a scaffold for tunable antioxidant activity.

References

- [1] Panche, A.N., Diwan, A.D., Chandra, S.R., Flavonoids: an overview, *J. Nutr. Sci.*, 5, e47 (2016). <https://doi.org/10.1017/jns.2016.41>
- [2] Chen, S., Wang, X., Cheng, Y., Gao, H., Chen, X., A Review of Classification, Biosynthesis, Biological Activities, and Potential Applications of Flavonoids, *Molecules*, 28, 4982 (2023). <https://doi.org/10.3390/molecules28134982>
- [3] Todorova, T.Z., Traykov, M.G., Tadjer, A.V., Velkov, Zh.A., Structure of flavones and flavonols. Part I: Role of substituents on the planarity of the system, *Comput. Theor. Chem.*, 1017, 85–90 (2013). <https://doi.org/10.1016/j.comptc.2013.05.005>
- [4] Spiegel, M., Andruniów, T., Sroka, Z., Flavones' and Flavonols' Antiradical Structure–Activity Relationship – A Quantum Chemical Study, *Antioxidants*, 9, 461 (2020). <https://doi.org/10.3390/antiox9060461>
- [5] Gunduz, S., Goren, A.C., Ozturk, T., Facile Syntheses of 3-Hydroxyflavones, *Org. Lett.*, 14, 1572–1575 (2012). <https://doi.org/10.1021/ol300310e>
- [6] Pereira, A.M., Cidade, H., Tiritan, M.E., Stereoselective Synthesis of Flavonoids: A Brief Overview, *Molecules*, 28, 426 (2023). <https://doi.org/10.3390/molecules28010426>

- [7] Kostrzewa-Susłow, E., Dmochowska-Gładysz, J., Białońska, A., Ciunik, Z., Rymowicz, W., Microbial transformations of flavanone and 6-hydroxyflavanone by *Aspergillus niger* strains, *J. Mol. Catal. B: Enzym.*, **39**, 18–23 (2006). <https://doi.org/10.1016/j.molcatb.2006.01.020>
- [8] Ren, X., Zhang, J., Wang, X., Zhou, W., Sun, W., Biotransformation of 2'-hydroxyflavanone by *Streptomyces coeruleorubidus* leading to 3-hydroxylated and glucuronidated derivatives, *J. Biosci. Bioeng.*, **129**, 172–181 (2025). <https://doi.org/10.1016/j.jbiosc.2024.11.004>
- [9] Niraula, N.P., Kuroda, M., Doi, M., Komori, T., Ohashi, Y., Yamane, H., Noguchi, H., CYP105P2, a cytochrome P450 from *Streptomyces peuceitius* capable of flavone hydroxylation in *Escherichia coli*, *J. Microbiol. Biotechnol.*, **22**, 1059–1065 (2012). <https://doi.org/10.4014/jmb.1201.01037>
- [10] Leonard, E., Koffas, M.A.G., Engineering *E. coli* for flavonoid biosynthesis and hydroxylation, *Metab. Eng.*, **8**, 172–181 (2006). <https://doi.org/10.1016/j.ymben.2005.11.001>
- [11] Marín, L., Gutiérrez-Delgado, S., Lombó, F., De novo biosynthesis of flavonols by engineered *Streptomyces* strains, *PLoS ONE*, **13**(11), e0207278 (2018). <https://doi.org/10.1371/journal.pone.0207278>
- [12] Winkler, V.S.; Fournier, J.A.; Characterizing excited-state intramolecular proton transfer in 3-hydroxyflavone with ultrafast transient infrared spectroscopy, *Chem. Commun.*, **60**, 12417–12420 (2024). <https://doi.org/10.1039/D4CC03427A>
- [13] Anand, N.; Welke, K.; Irle, S.; Vennapusa, S.R.; Nonadiabatic excited-state intramolecular proton transfer in 3-hydroxyflavone: S₂ state involvement via multi-mode effect, *J. Chem. Phys.*, **151**, 214304 (2019). <https://doi.org/10.1063/1.5127271>
- [14] Ash, S.; De, S.P.; Pyne, S.; Misra, A.; Excited states potential energy calculations support the ES IPT process in 3HF, *J. Mol. Model.*, **16**, 1683–1691 (2010). <https://doi.org/10.1007/s00894-009-0578-y>
- [15] McMorro, D.; McHale, J.L.; Intramolecular excited-state proton transfer in 3-hydroxyflavone. Hydrogen-bonding solvent perturbations, *J. Phys. Chem.*, **88**, 11, 2235–2243 (1984). <https://doi.org/10.1021/j150655a012>
- [16] Zhao, X., Liang, S., Dong, X., Zhang, Z., 3-Hydroxyflavone derivatives: promising scaffolds for fluorescence imaging—emission mechanism and solvent effects, *RSC Adv.*, **11**, 28851–28862 (2021). <https://doi.org/10.1039/D1RA04767A>
- [17] Salaeh, R., Prommin, C., Chansen, W., Kerdpol, K., Daengngern, R., Kungwan, N., The effect of protic solvent on ESPT reaction of 3-hydroxyflavone: A TD-DFT static and molecular dynamics study, *J. Mol. Liq.*, **252**, 303–310(2018). <https://doi.org/10.1016/j.molliq.2017.12.148>
- [18] Klymchenko, A. S., Pivovarenko, V. G., Demchenko, A. P., Elimination of the Hydrogen Bonding Effect on the Solvatochromism of 3-Hydroxyflavones. *J. Phys. Chem. A*, **107**, 4211–4216 (2003). <https://doi.org/10.1021/jp027315g>
- [19] Strandjord, A.J.G., Barbara, P.F., Excited-state intramolecular proton transfer of 3-hydroxyflavone, *J. Phys. Chem.*, **89**, 2355–2361 (1985). <https://doi.org/10.1021/j100257a041>
- [20] Lazzaroni, S., Dondi, D., Mezzetti, A., Protti, S., Excited state intramolecular proton transfer: state of the art and new insights on 3-hydroxyflavone derivatives, *Photochem. Photobiol. Sci.*, **17**, 923–933 (2018). <https://doi.org/10.1039/C8PP00053K>
- [21] Durko-Maciąg, M., Ulrich, G., Jacquemin, D., Mysliwiec, J., Massue, J., Large Stokes shift emission via ES IPT in 3-hydroxyflavone analogues for optoelectronic applications, *Phys. Chem. Chem. Phys.*, **25**, 15085–15098 (2023). <https://doi.org/10.1039/D3CP00938F>
- [22] Liang, R., Li, Y., Yan, Z., Bai, X., Lai, W., Du, L., Phillips, D.L., Mechanistic details of excited-state intramolecular proton transfer in 3-hydroxyflavone revealed by femtosecond stimulated Raman spectroscopy, *ACS Phys. Chem. Au*, **3**, 181–189 (2023). <https://doi.org/10.1021/acspchemau.2c00036>
- [23] Kerdpol, K., Daengngern, R., Sattayanon, C., Namuangruk, S., Rungrotmongkol, T., Wolschann, P., Kungwan, N., Hannongbua, S. Effect of Water Microsolvation on the Excited-State Proton Transfer of 3-Hydroxyflavone Enclosed in γ -Cyclodextrin., *Molecules*, **26**, 843. (2021). [doi:10.3390/molecules26040843](https://doi.org/10.3390/molecules26040843)
- [24] Cao, H., Chen, X., Jassbi, A.R., Xiao, J., Microbial biotransformation of bioactive flavonoids, *Biotechnol. Adv.*, **33**, 214–223 (2015). <https://doi.org/10.1016/j.biotechadv.2014.10.012>
- [25] Heim, K.E., Tagliaferro, A.R., Bobilya, D.J., Flavonoid antioxidants: chemistry, metabolism and structure-activity relationships, *J. Nutr. Biochem.*, **13**, 572–584 (2002). <https://doi.org/10.1016/S0955-2863%2802%2900208-5>
- [26] Leopoldini, M., Russo, N., Toscano, M., The molecular basis of working mechanism of natural polyphenolic antioxidants, *Food Chem.*, **125**, 288–306 (2011). <https://doi.org/10.1016/j.foodchem.2010.08.012>

- [27] Litwinienko, G., Ingold, K.U., Abnormal solvent effects on the reaction of phenols with 2,2-diphenyl-1-picrylhydrazyl (DPPH•) in alcohols, *J. Org. Chem.*, **68**, 3433–3438 (2003). <https://doi.org/10.1021/jo026917t>
- [28] Leopoldini, M., Marino, T., Russo, N., Toscano, M., Antioxidant properties of phenolic compounds: H-atom versus electron transfer mechanism, *J. Phys. Chem. A*, **108**, 4916–4922 (2004). <https://doi.org/10.1021/jp037247d>
- [29] Dyba, B., Miłoś, A., Woźnicka, E., Rudolphi-Szydło, E., Ciszkowicz, E., The effects of 3-hydroxyflavone complexes with transition metal ions on the physicochemical and microbial properties of bacterial cell membranes, *Sci. Rep.*, **15**, 20743 (2025). <https://doi.org/10.1038/s41598-025-07358-y>
- [30] Fan, K.W.; Luk, H.L.; Phillips, D.L. Anti-Kasha Behavior of 3-Hydroxyflavone and Its Derivatives. *Int. J. Mol. Sci.*, **22**, 11103 (2021). <https://doi.org/10.3390/ijms222011103>
- [31] Tomin, V.I., Javorski, R. Dependence of the properties of the dual luminescence of 3-hydroxyflavone on the excitation wavelength. *Opt. Spectrosc.* **102**, 242–247 (2007). <https://doi.org/10.1134/S0030400X07020129>
- [32] Sengupta, P. K., & Kasha, M., Excited state proton-transfer spectroscopy of 3-hydroxyflavone and quercetin. *Chem. Phys. Lett.*, **68**, 382–385 (1979). [https://doi.org/10.1016/0009-2614\(79\)87221-8](https://doi.org/10.1016/0009-2614(79)87221-8)
- [33] Shekhovtsov, N. A., Nikolaenkova, E. B., Vorobyova, S. N., Plyusnin, V. F., Vinogradova, K. A., Sukhikh, T. S., Tikhonov, A. Y., Bushuev, M. B. Luminescence of ESIPT-capable zinc(II) complexes with a 1-hydroxy-1H-imidazole-based ligand: Exploring the impact of substitution in the proton-donating moiety. *Dalton Trans.*, **50**, 2124–2134 (2021). <https://doi.org/10.1039/D3DT01190A>
- [34] Diana, R., Panunzi, B., The Role of Zinc(II) Ion in Fluorescence Tuning of Tridentate Pincers: A Review. *Molecules*, **25**, 4984 (2020). <https://doi.org/10.3390/molecules25214984>
- [35] Lustig, W. P., Mukherjee, S., Rudd, N. D., Desai, A. V., Li, J., & Ghosh, S. K. Metal–organic frameworks: Functional luminescent and photonic materials for sensing applications. *Chem Soc Rev.*, **46**, 3242–3285 (2017). <https://doi.org/10.1039/C6CS00930A>
- [36] Lakowicz, J.R. Principles of Fluorescence Spectroscopy, 3rd ed.; Springer: New York, 2006.
- [37] Yersin, H., Tsuboi, T., Hoshina T., Intersystem crossing, phosphorescence, and spin–orbit coupling: Two different theoretical descriptions and their comparison, *Proc Jpn Acad Ser B Phys Biol Sci.*, **99**, 482–97. (2023). <https://doi.org/10.2183/pjab.99.031>.
- [38] Tang, X., Wang, L., Zhang, Y., Sun, C., Relationship between antioxidant activity and ESIPT process based on flavonoid derivatives: A comprehensive analysis. *Spectrochim Acta A Mol Biomol Spectrosc.*, **15**, 327–125370 (2025). <https://doi.org/10.1016/j.saa.2024.125370>
- [39] Rice-Evans, C.A., Miller, N.J., Paganga, G., Structure–antioxidant activity relationships of flavonoids and phenolic acids, *Free Radic. Biol. Med.*, **20**, 933–956 (1996). [https://doi.org/10.1016/0891-5849\(95\)02227-9](https://doi.org/10.1016/0891-5849(95)02227-9)
- [40] Heim, K.E., Tagliaferro, A.R., Bobilya, D.J., Flavonoid antioxidants: chemistry, metabolism and structure–activity relationships, *J. Nutr. Biochem.*, **13**, 572–584 (2002). [https://doi.org/10.1016/S0955-2863\(02\)00208-5](https://doi.org/10.1016/S0955-2863(02)00208-5)
- [41] Pietta, P.G., Flavonoids as antioxidants, *J. Nat. Prod.*, **63**, 1035–1042 (2000). <https://doi.org/10.1021/np9904509>
- [42] Seyoum, A., Asres, K., El-Fiky F.K., Structure–radical scavenging activity relationships of flavonoids. *Phytochem.*, **67**, 2058–70 (2006). <https://doi.org/10.1016/j.phytochem.2006.07.002>
- [43] Katalinić, V., Možina, S.S., Skroza, D., Generalić, I., Abramović, H., Miloš, M., Ljubenković, I., Piskernik, S., Pezo, I., Terpinc, P., Boban, M., Polyphenolic profile, antioxidant properties and antimicrobial activity of grape skin extracts of 14 *Vitis vinifera* varieties grown in Dalmatia (Croatia), *Food Chem.*, **119**, 715–723 (2010). <https://doi.org/10.1016/j.foodchem.2009.07.019>