

1 **The investigation of fluorescence and metal interaction properties of racemic**

2 **7,8,9,10-tetrahydro-3-hydroxy-4-(1-hydroxyethyl)benzo[c]chromen-6-one**

3 Hayrettin Ozan GÜLCAN<sup>1,\*</sup>, Karar Tawfeeq SHUKUR<sup>1</sup>, Açelya MAVİDENİZ<sup>1</sup>, Okan

4 SİRKECİOĞLU<sup>2</sup>, Mustafa GAZİ<sup>3</sup>

5 <sup>1</sup> Eastern Mediterranean University, Faculty of Pharmacy, Gazimağusa, TR. North

6 Cyprus, via Mersin 10, Turkey

7 <sup>2</sup> Istanbul Technical University, Faculty of Arts and Science, Department of Chemistry,

8 Istanbul, Turkey

9 <sup>3</sup> Eastern Mediterranean University, Faculty of Arts and Science, Department of

10 Chemistry, Gazimağusa, TR. North Cyprus, via Mersin 10, Turkey

11 \*Correspondence: ozan.gulcan@emu.edu.tr

12 ORCIDs:

13 Hayrettin Ozan GÜLCAN: <https://orcid.org/0000-0002-9503-5841>

14 Karar Tawfeeq SHUKUR: <https://orcid.org/0000-0002-0012-1748>

15 Açelya MAVİDENİZ: <https://orcid.org/0000-0002-1923-9340>

16 Okan SİRKECİOĞLU: <https://orcid.org/0000-0001-8720-7394>

17 Mustafa GAZİ: <https://orcid.org/0000-0001-7736-752X>

18  
19 **Abstract:** The design or investigation of fluorescence probes continues to receive  
20 attention with respect to the diverse applications of spectrofluorometry. Depending on the  
21 highly sensitive character, fluorescence spectroscopy **based methodologies** have been  
22 used widely in recent years in different sciences, including analytical, environmental, and  
23 medicinal chemistry areas. In our previous works, we have shown the Iron (III) selective  
24 On-Off sensor properties of benzo[c]chromen-6-one derivatives. In this study, we have

1 extrapolated this research to 4-substituted analogues and investigated both fluorescent  
2 and metal interaction properties. Following the synthesis and structure identification  
3 studies, (±)-7,8,9,10-tetrahydro-3-hydroxy-4-(1-hydroxyethyl)benzo[c]chromen-6-one  
4 was found a fluorescent molecule displaying fluorescence enhancement in the presence  
5 of metals. This feature has been found quite different in comparison to the previous  
6 urolithins investigated. This finding suggested the substituent dependent effects and  
7 variations on the fluorescent properties of benzo[c]chromen-6-one system.

8 **Key words:** Urolithin, synthesis, fluorescence, metal interaction.

## 9 **1. Introduction**

10 The employment of fluorescence techniques and their applications have been increased  
11 worldwide in the last couple of decades with respect to the high sensitivity of this  
12 methodology [1-2]. In particular, the design of fluorescent molecules depending on the  
13 scientific requirements has led to the generation of diverse molecules with different  
14 scaffolds [3]. Diagnostic molecules, biomarkers, environmental pollutant sensitive agents  
15 are typical examples for the outcomes in the related scientific field [4-6]. Among them,  
16 the investigation of fluorescent changes depending on metals is another significant  
17 research area. At one hand, metal use increases globally with the development of  
18 technologies. On the other hand, it becomes critical to generate molecular sensing systems  
19 for both detection and quantification purposes [7-9].

20 The interaction of fluorescent molecules against metal ions can vary depending on the  
21 structural organization. Some fluorescent probes display Off-On characteristics. Mainly,  
22 a non-fluorescent molecule gains fluorescent character with respect to its interaction with  
23 a specific metal or a group of metals [10-11]. There have been many Off-On fluorescent  
24 probes designed and synthesized so far with diverse heterocyclic structures [11]. On the

1 other hand, there are some fluorescent compounds lose their fluorescence property when  
2 it comes to interaction with another compound. This type of molecules has been referred  
3 to as On-Off probes [12-13]. There have also been many compounds introduced  
4 possessing this feature, particularly in the presence of metals. Overall, On-Off, or Off-On  
5 type fluorescence sensor applications are valuable tools for the diagnosis and  
6 quantification of metals.

7 Beside these, the metal interaction of specific fluorescence compounds can also trigger  
8 increase of the initial fluorescence intensity of a fluorescent probe. This process is  
9 referred to as fluorescence enhancement [14-15]. This type of application is not only  
10 utilized for the detection of metals but also for the development of more available systems  
11 in which the original fluorescent intensity is lower and needed to be upgraded for better  
12 fluorometric measurements [15-17].

13 In our previous studies, we have synthesized 3-hydroxy-6H-benzo[c]chromen-6-one (i.e.,  
14 also referred to as Urolithin B) and discovered its On-Off fluorescence probe property in  
15 the presence of Iron (III) [18]. In the continuation of this work, the alternative hydroxyl  
16 substituted, methyl ether derivatives, and 7,8,9,10-tetrahydro-3-  
17 hydroxybenzo[c]chromen-6-one, the partial saturated form of Urolithin A, were  
18 synthesized and it was observed that all these compounds, similar to Urolithin A, possess  
19 On-Off fluorescent sensor character selective towards Iron (III) [19-20]. All these  
20 alternative substitution patterns and the constant Iron (III) sensor On-Off character of the  
21 derivatives considered pointed out the significance of the lactone group in the interaction.  
22 In order to question the effect of an electron withdrawing group on the fluorescence and  
23 metal interacting properties of these types of compounds, in this study, we have first  
24 aimed to synthesize 4-acetyl-7,8,9,10-tetrahydro-3-hydroxybenzo[c]chromen-6-one (i.e.,

1 THU-4-Ac), an acetylated derivative of partially saturated Urolithin B. At one hand, the  
2 presence of an **electron-withdrawing** group on the general fluorescence features has been  
3 aimed to be analyzed. On the other hand, the ketone function has been aimed to be reduced  
4 to obtain racemic 7,8,9,10-tetrahydro-3-hydroxy-4-(1-hydroxyethyl)benzo[c]chromen-6-  
5 one (i.e., THU-4-ALC), the alcohol derivative, to further see the changes in fluorescence  
6 properties, particularly in relation to metal interaction.

## 7 **2. Experimental analysis**

### 8 **2.1. Materials and equipment**

9 The chemicals, and solutions employed in this study were reagent grade and they were  
10 used upon obtaining without further purification. 2,6-Dihydroxyacetophenone, ethyl 2-  
11 oxocyclohexanecarboxylate,  $ZrCl_4$ ,  $NaBH_4$ , ethanol, acetonitrile,  $MgCl_2$ ,  $PbCl_2$ ,  $KCl$ ,  
12  $NaCl$ ,  $AgCl$ ,  $BaSO_4$ ,  $ZnSO_4 \cdot 7H_2O$ ,  $Co(NO_3)_2 \cdot 6H_2O$ ,  $Ni(NO_3)_2 \cdot 6H_2O$ ,  $HgCl_2$ ,  $CuSO_4$ ,  
13  $Fe(NO_3)_3 \cdot 9H_2O$ , and  $Al_2(SO_4)_3$  were all purchased from Sigma Aldrich through the aid  
14 of local distributors in Turkish Republic of Northern Cyprus. The solutions of metal ions  
15 were prepared in ultra-pure distilled water.

16 A Thermoscientific spectrofluorometer (Varioskan Flash model multi-plate reader) was  
17 employed for the fluorescence measurements. Thin-layer chromatography studies were  
18 conducted on Merck aluminum-packed silica gel plates employing ethyl acetate / n-  
19 hexane as mobile phase at 1:1 and 1:3 ratios. An Electrothermal IA 9200 Model melting  
20 point apparatus was used to measure the melting points and the data presented was  
21 uncorrected. Elemental analysis was performed using a Flash Smart model ThermoFisher  
22 elemental analyzer. In order to obtain the **infrared** spectrums of the title molecules, FTIR  
23 Prestige 21 model Shimadzu instrument was employed. An Agilent VNMSR-500 NMR  
24 spectrometer was used to get the NMR spectrums of the title molecules.  $CDCl_3$  was used

1 as solvent with the presence of tetramethylsilane as internal standard and the chemical  
2 shifts were presented in ppm ( $\delta$ ).

### 3 **2.2. Synthesis of 3-hydroxy-7,8,9,10-tetrahydro-6H-benzo[c]chromen-6-one** 4 **(THU-OH)**

5 THU-OH was synthesized according to the previously published methodology [20-21].  
6 Briefly, 0.22 g resorcinol, 0.37 g ethyl 2-oxo-cyclohexancarboxylate, and 0.4 g  $ZrCl_4$  was  
7 mixed in a 20 mL reaction flask and heated at 85°C for one hour. The precipitate formed  
8 was filtered off and washed with ice-cold water. The spectral analysis of the compound  
9 was found identical with our previous findings [20-21].

### 10 **2.3. Synthesis of ( $\pm$ )-4-acetyl-7,8,9,10-tetrahydro-3-hydroxybenzo[c]chromen-6-** 11 **one (THU-4-Ac)**

12 6.5 mmol acetophenone, 6.8 mmol of ethyl 2-oxocyclohexancarboxylate, and 2.5 mmol  
13 of  $ZrCl_4$  was heated at 95°C for 1 hour under neat conditions. At the end of the period, 10  
14 mL of ice-cold water was added and the precipitate formed was filtered off. Light yellow  
15 powder. Melting point 143°C (uncorrected data). IR: 1669  $cm^{-1}$ .  $^1H$  NMR (500 MHz,  
16 Chloroform-d)  $\delta$  13.43 (s, 1H), 7.63 (d, J = 9.0 Hz, 1H), 6.87 (d, J = 8.9 Hz, 1H), 2.95 (s,  
17 3H), 2.73 (q, J = 5.8 Hz, 2H), 2.55 (t, J = 6.3 Hz, 2H), 1.95 – 1.70 (m, 4H).  $^{13}C$  NMR  
18 (125 MHz, Chloroform-d)  $\delta$  (ppm): 204.1, 163.8, 161.5, 150.2, 149.1, 133.7, 122.2,  
19 118.5, 113.4, 111.9, 30.8, 28.7, 24.8, 24.3, 23.7. Yield obtained 88%. Anal. calc. for  
20  $C_{15}H_{14}O_4$ : C 69.76, H 5.46; found C 69.82, H 5.44.

### 21 **2.4. Synthesis of ( $\pm$ )-7,8,9,10-tetrahydro-3-hydroxy-4-(1-** 22 **hydroxyethyl)benzo[c]chromen-6-one (THU-4-ALC)**

23 13.2 mmol of sodium borohydride is dissolved in 10 mL ethanol and added dropwise to  
24 the solution of 5.5 mmol of THU-4-Ac in 10 mL ethanol. Following stirring at room

1 temperature for 20 minutes, the mixture was acidified with 20 mL of 1N HCl and  
2 extracted with ethyl acetate (3 × 50 mL). The organic layer collected was added dry  
3 magnesium sulfate and it was filtered off. The product was obtained upon the evaporation  
4 of the organic phase under reduced pressure. White-yellow powder. Melting point 121°C  
5 (uncorrected data). IR: 1628 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ 9.75 (s, 1H),  
6 7.31 (d, J = 8.8 Hz, 1H), 6.81 (d, J = 8.7 Hz, 1H), 5.88 (q, J = 6.6 Hz, 1H), 4.62 (bs, 1H),  
7 2.69 (q, J = 5.8 Hz, 2H), 2.47 (t, J = 6.3 Hz, 2H), 2.08 – 1.70 (m, 7H). <sup>13</sup>C NMR (125  
8 MHz, Chloroform-d) δ 162.5, 151.8, 150.7, 147.5, 127.4, 122.1, 118.6, 112.5, 111.4, 58.7,  
9 31.1, 24.8, 23.6, 23.0, 22.9. Yield obtained 81%. Anal. calc. for C<sub>15</sub>H<sub>16</sub>O<sub>4</sub>: C 69.22, H  
10 6.20; found C 68.87, H 6.49.

### 11 2.5. Fluorescence studies

12 Employing a Varioskan Flash model multi-plate reader spectrofluorometer, the  
13 fluorometric measurements were performed. 1 mM solutions of the title molecules (i.e.,  
14 THU-OH, THU-4-Ac, and THU-4-ALC) were prepared in Acetonitrile – Water (9:1) and  
15 they were screened to measure the excitation λ<sub>max</sub>. The emission spectrums were  
16 obtained accordingly for the compounds display fluorometric properties. The aqueous  
17 solutions of selected metal ions were prepared in appropriate stock solutions and the effect  
18 of metal solutions on fluorescence intensity of fluorescence title molecules were  
19 investigated in 1:1 probe-metal ratio.

20

## 21 3. Results and Discussion

22 The synthetic scheme is provided in Figure 1 for the title compounds. THU-OH was  
23 obtained according to the protocol previously published [20]. The 4-acetyl and 4-(1-  
24 hydroxyethyl) derivatives of THU-OH were obtained in good yields. The spectral and the

1 elemental analysis of the compounds were employed for the structure identification  
2 studies.

3 -----Please insert Figure 1-----

4 The fluorescence scanning of THU-4-OH was found identical with our previous  
5 measurements [20]. The UV spectrum of THU-4-Ac has revealed out 320 nm as the  
6 wavelength for the maximum absorption. The emission spectrum based on this  $\lambda_{\text{max}}$   
7 generated no emission. In other words, THU-4-Ac did not display any fluorescent  
8 property. This observation was critical, since we have shown that benzo[c]chromen-6-  
9 one derivatives with hydroxyl-, or methoxy-substituents possess fluorescent  
10 characteristics and an electron-withdrawing group, such as in the case of 4-acetyl  
11 substituted derivative in THU-4-Ac have blocked this feature.

12 Employing a reduction reaction on THU-4-Ac yielded out its corresponding secondary  
13 alcohol racemic molecule, THU-4-ALC. The UV spectrum generated a  $\lambda_{\text{max}}$  at 310 nm.  
14 Therefore, the presence of the 1-hydroxyethyl substituent on the 4<sup>th</sup> position generated a  
15 hypsochromic shift, in comparison to its 4-deacetylated analogue, THU-OH. The further  
16 scanning for the emission spectrum revealed out the fluorescent characteristics of THU-  
17 4-ALC. Therefore, the fluorescence property lost was gained back with the reduction of  
18 ketone function. In other words, the removal of the electron withdrawing character of the  
19 substituent on the 4<sup>th</sup> position has made the benzo[c]chomen-6-one scaffold retain its  
20 fluorescent properties. The excitation and emission spectrum characteristics of the title  
21 molecules are shown in Figure 2.

22 -----Please insert Figure 2-----

23 In our previous studies, we have pointed out the specific interaction of urolithins and a  
24 partially saturated analogue, THU-OH, with Iron (III). The presence of Iron (III) resulted

1 in the quenching of fluorescent properties of these compounds. Mainly, urolithins were  
2 shown to act as On-Off probes in the presence of Iron (III). Since the title molecule, THU-  
3 4-Ac was found a non-fluorescent molecule, we first examined whether the compound  
4 can act as Off-On probe in the presence of different metals. It was observed that the 4-  
5 acetyl derivative of THU-OH did not display any fluorescent feature in the presence or  
6 absence of any metals.

7 The reduced form of THU-4-Ac, the THU-4-ALC compound, was shown to have  
8 fluorescent properties. As seen in Figure 2, the fluorescence intensity of the molecule  
9 appeared to be lower in comparison to the fluorescence intensity of THU-OH at the same  
10 concentration. The interaction of THU-4-ALC with metals was also investigated with  
11 fluorescence titrations. The initial experiments with the selected metals have shown that  
12 almost all of the metals employed resulted in the enhancement of fluorescence intensity  
13 at varying degrees. Particularly,  $Zn^+$ , followed by  $Ba^{+2}$ ,  $Mg^{+2}$ , and  $Al^{+3}$ , generated  
14 apparent increase in the fluorescence intensity of THU-4-ALC. This observation was  
15 totally different with the fluorescent characteristics of THU-4-OH. The results obtained  
16 are shown in Figure 3.

17 -----Please insert Figure 3-----

18 In the continuation of this study, another set of experiments were planned to measure the  
19 concentration dependent effect on the metal-induced enhancement of fluorescence  
20 intensity. With respect to the highest effect obtained with Zinc, its different  
21 concentrations were prepared and titrated with the constant concentration of the  
22 fluorescence probe (i.e., THU-4-ACL). As seen Figure 4, the effect was observed  
23 concentration dependent.

24 -----Please insert Figure 4-----



1 The overall results have pointed out that the fluorescence properties of benzo[c]chromen-  
2 6-one bearing systems are substituent dependent. Particularly electron-withdrawing  
3 groups can terminate the fluorescence property, whereas the On-Off character might be  
4 also replaced with fluorescence enhancement properties in the presence of alternative  
5 substituents.

## 6 **Conclusion**

7 Within the concept of this research, two alternative derivatives of a previously shown  
8 fluorescent molecule, THU-OH, were prepared and screened both for their fluorescence  
9 properties, and the change in fluorescence in the presence of different metals. Different  
10 than THU-OH, an Iron (III) selective On-Off probe, the title molecule THU-4-Ac was  
11 found non-fluorescent. Therefore, it was shown apparent that electron-withdrawing  
12 groups can totally convert the system a non-fluorescent molecule. Moreover, this  
13 compound did not display any Off-On character in the presence of selected metals. The  
14 reduction of THU-4-Ac yielded out the THU-4-ALC molecule and the fluorescence  
15 measurements on this molecule have shown its fluorescence characteristics. Although  
16 fluorescence intensity was lower in comparison to the fluorescence of THU-OH, the  
17 compound displayed quite distinct features in terms of interaction with metals. Unlike to  
18 the Iron (III) selective On-Off probe character of THU-OH, the fluorescent feature of  
19 THU-4-ALC was not affected too much with Iron (III). More important than that THU-  
20 4-ALC displayed fluorescence enhancement in the presence of majority of the metals  
21 employed. The highest effect was observed with Zinc. Besides, the effect of Zinc was  
22 found concentration dependent.

23 The difference observed between THU-OH and THU-4-ALC might be related to the  
24 different interaction characteristics of these compounds with different metals. At first

1 hand, it might be postulated that the lactone group in THU-OH is not sterically hindered  
2 in comparison to THU-4-ALC. On the other hand, the additional alcohol functional group  
3 within the vicinity of the phenolic hydroxyl on THU-4-ALC can generate energetically  
4 and sterically optimum pocket for the interaction of diverse metals. The net fluorescence  
5 enhancement character obtained might be mechanistically explained via this approach  
6 (Figure 5). However, these results warrant not only the design of different  
7 benzo[c]chromen-6-one derivatives with alternative substitutions to see the fluorescence  
8 properties and its change in the presence of different metals but also additional complex-  
9 crystallization studies to ensure the mode of interaction between these probes and metal  
10 ions.

11 -----Please insert Figure 5-----

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Figure Captions

Figure 1: The synthetic scheme of the title molecules

Figure 2: The excitation and emission spectra of THU-OH and THU-ALC

Figure 3: Fluorescence enhancement of THU-ALC through interaction with selected metals

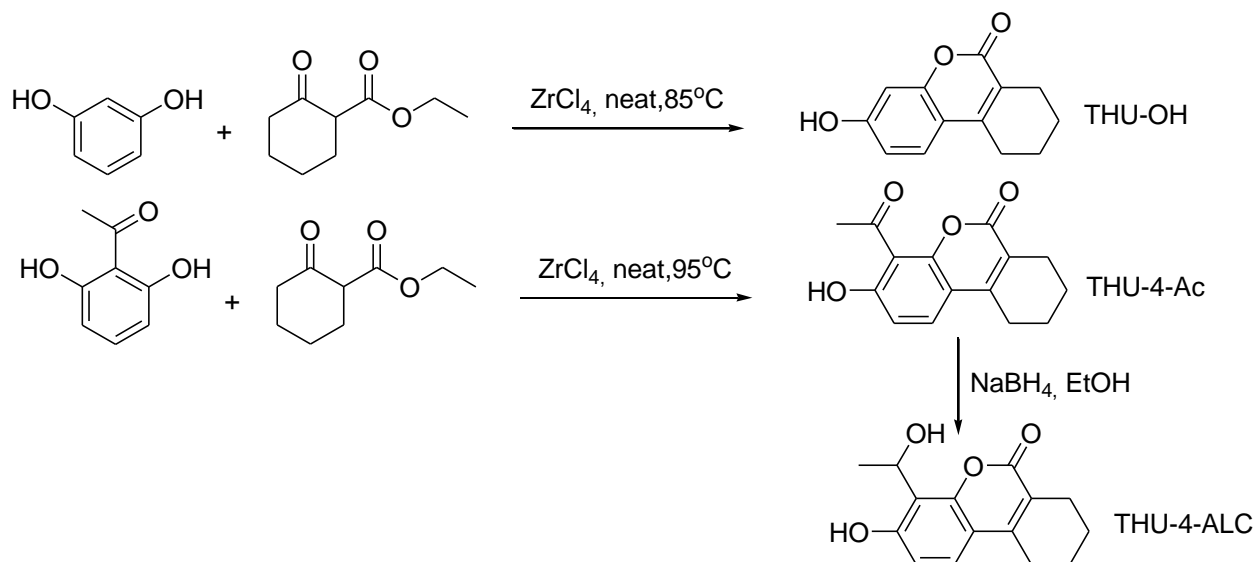
Figure 4: Fluorescence enhancement with increasing concentration of Zinc

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4 Figure 1: The synthetic scheme of the title molecules



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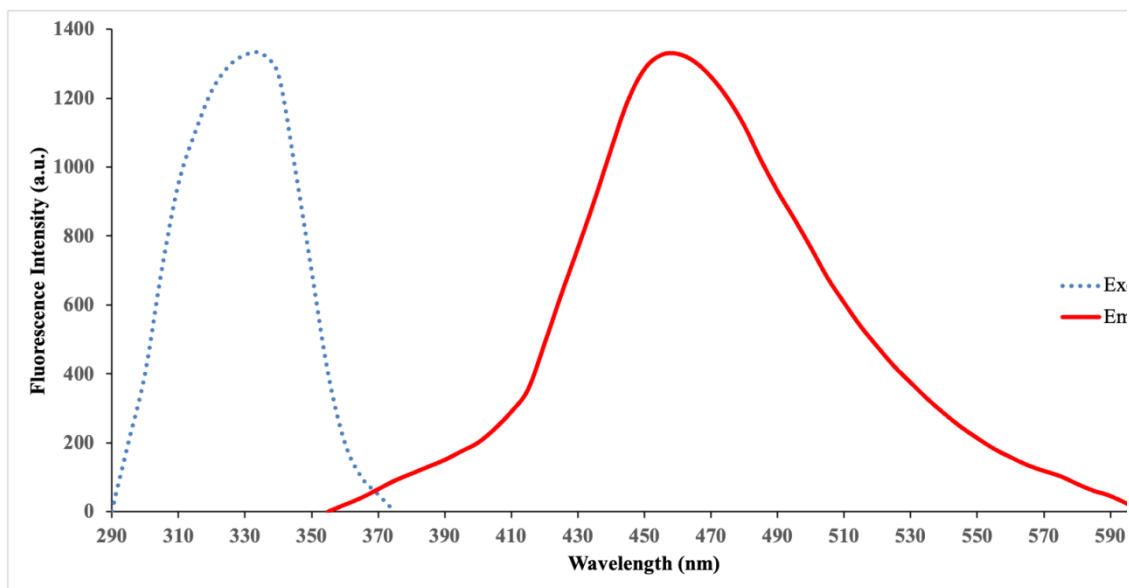
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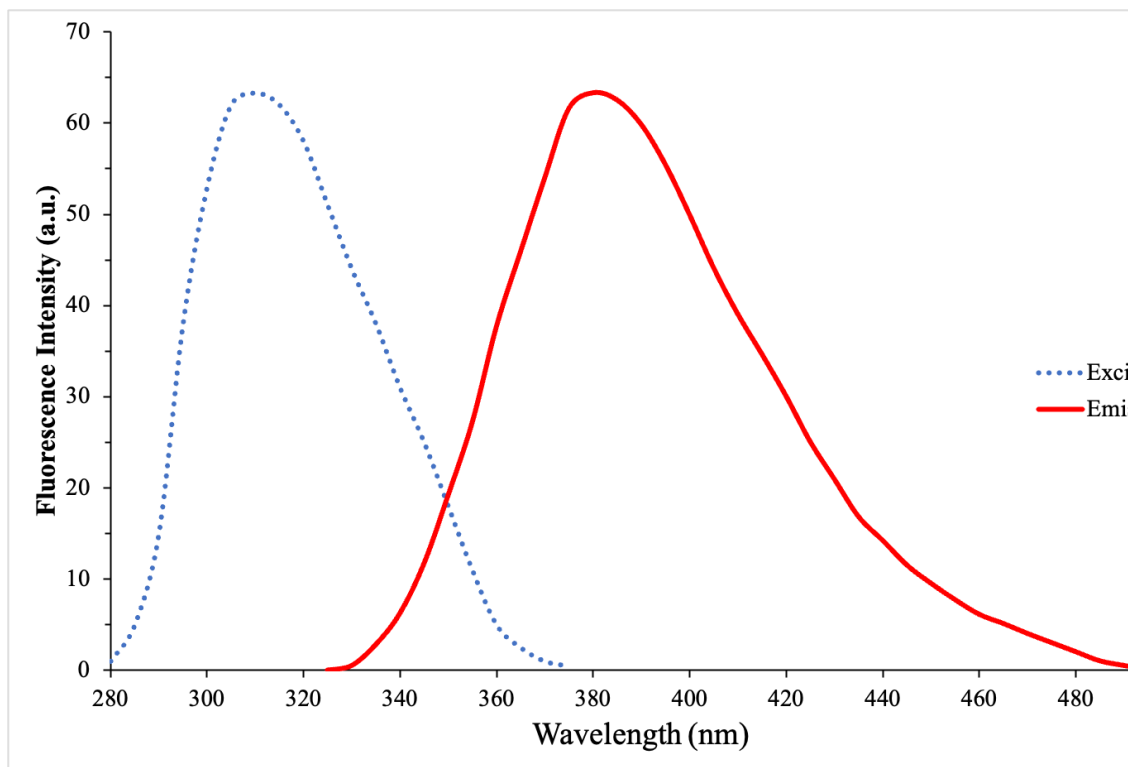
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4 Figure 2: The excitation and emission spectra of THU-OH and THU-ALC

### THU-OH



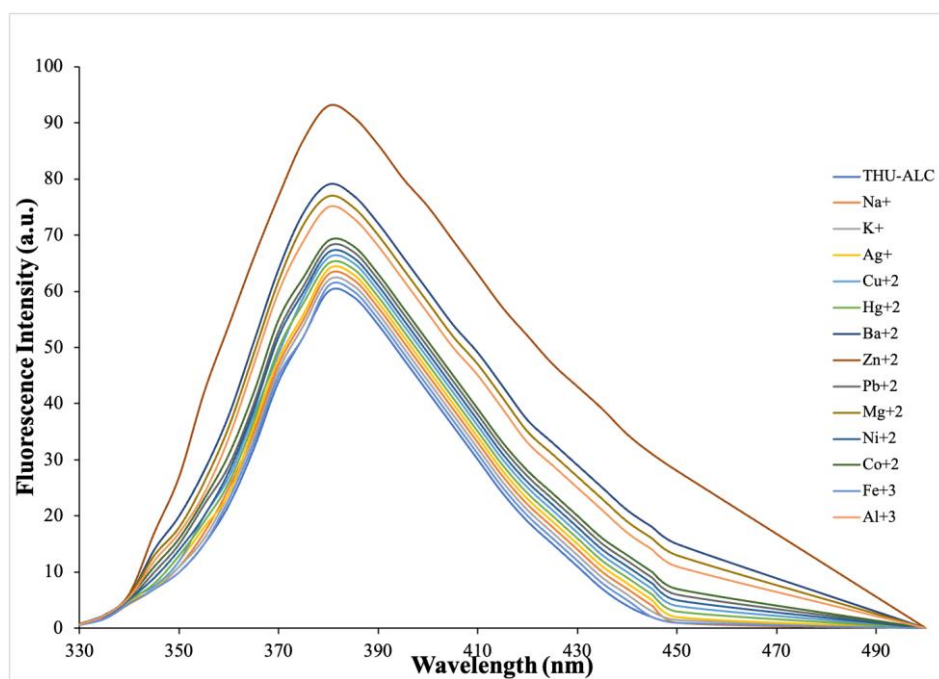
### THU-ALC



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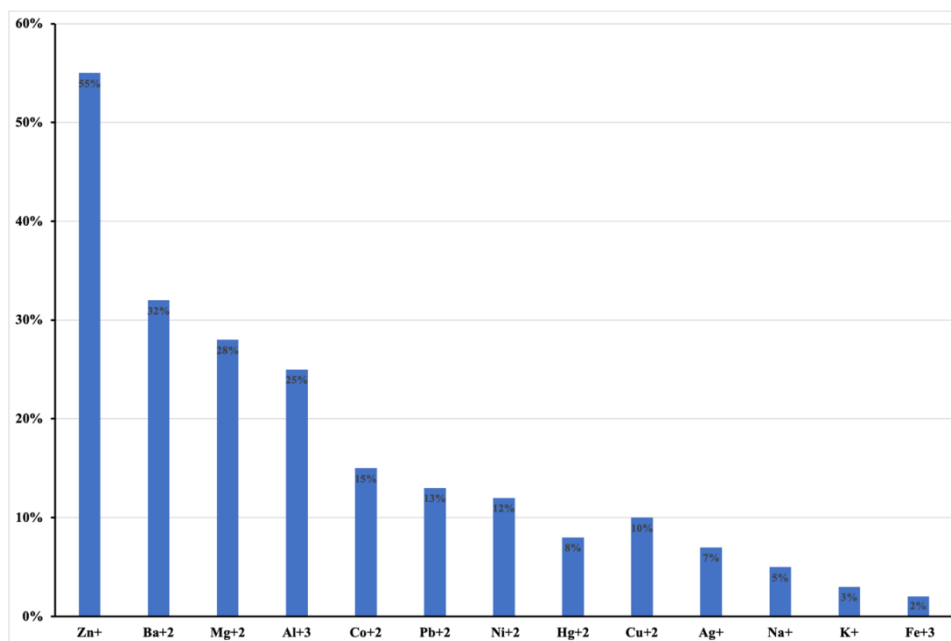
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3 Figure 3: Fluorescence enhancement of THU-ALC through interaction with selected  
4 metals





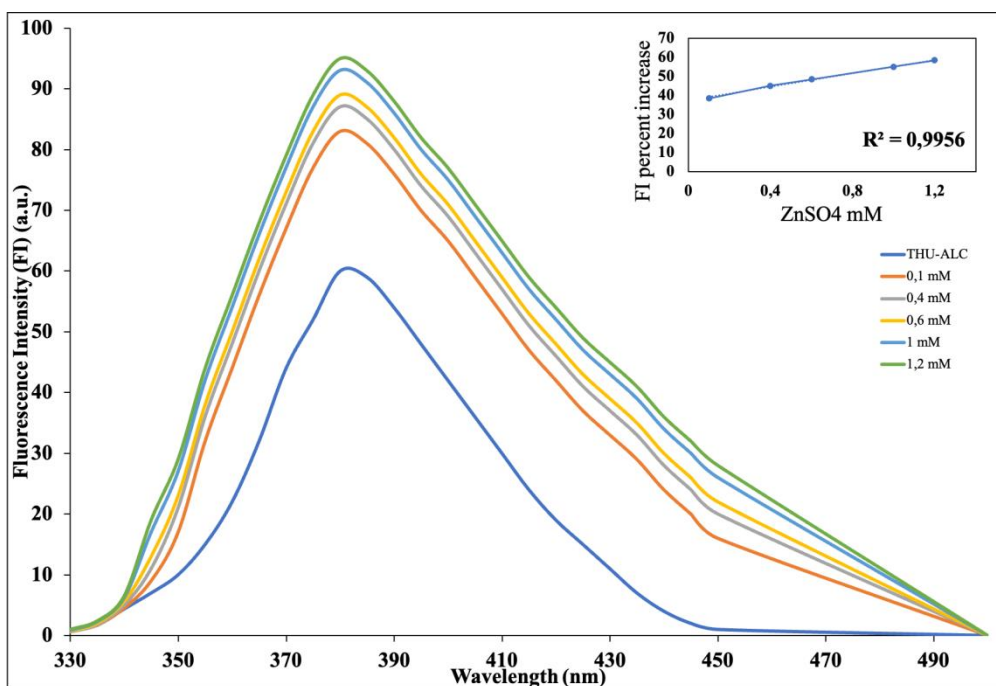
Percent increase in the presence of metals



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3 Figure 4: Fluorescence enhancement with increasing concentration of Zinc



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