Multicomponent synthesis and investigations fluorescence activity of chromenone –pyrazole compounds

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Research Article

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Abstract

A synthetic method is described to produce some chromenone-pyrazole derivatives through a one-pot multicomponent reaction using $SrFe_{12}O_{19}$ as a magnetic catalyst. This method provides quite a few merits, including the use of an effective and easy separable nanocatalyst, high yields of products, short reaction time, and easy work-up. Two of the products showed fluorescence properties, which have detected mercury ions without any interference with other ions. They can detect a tiny amount of mercury ions, which were comparable with other chemosensors. The detection limit is 4×10^{-7} and 3×10^{-8} M, respectively, for the compound I and II, respectively, which were considered very low amounts. The effect of mercury on health and environmental pollution is essential in medical science.

Introduction

Coumarin is a familiar scaffold found in many natural products isolated from a wide range of species, especially plants. Dicoumarol is an anticoagulant agent that was discovered by Professor Link in 1933. This compound is a metabolized product of coumarin in the infected sweet clover (*Melilotus*) by some molds such as *Penicillium nigricans*. Warfarin is another important and famous coumarin derivative, which is used as an oral anticoagulant agent.[1] In addition to the pharmaceutical application of coumarin derivatives, some of them are beneficial sensors, such as 3-acetoacetylcoumarin (Fig. 1), which was used as a probe to find intracellular hydrazine in glioma cell lines because of the formation of a fluorescent coumarin-pyrazole product [2].

In recent years, a combination structure of coumarin and pyrazole has become an attractive scaffold in medicinal chemistry. Saeed *et al.* designed coumarinyl pyrazolinyl thioamide derivatives and determined their potential antioxidant activity against the urease enzyme.[3]

Among the various pyrazoles prepared by Wardakhan and Louca, coumarin-pyrazole compounds showed the highest activity against *Candida albicans*.[4] Moreover, the antibacterial activity of quinolinepyrazoline-based coumarinyl thiazole derivatives has been assigned.[5] Al-Ayed developed the synthesis of antioxidant coumarin containing a 4-arylbut-3-en-2-one moiety through the condensation of 3-acetylcoumarin with aryl aldehydes. [6]

Mercury pollution is one of the most challenging problems since its accumulation in the human body can lead to various neurological damages.[7–8] Some industrial activities, including fossil-fuel combustion,[9] gold mining,[10] solid-waste burning,[11] and natural sources, such as forest fires and volcanic emissions [12] lead to rapid enhancement of Hg^{2+} levels in the environment. Additionally, ionic mercury can be converted to methylmercury naturally, which is more toxic than the mercury element and its salts.[13] When methylmercury enters the environment, it results in bioaccumulation and high concentrations among populations of some species through the food chain.[14] The Food and Drug Administration (FDA) and the United States Environmental Protection Agency (US EPA) advise the maximum allowable concentration

for methylmercury and mercury salts as 1 ppm (1 mg/L)[15] and 2 ppb (0.002 mg/L),[16] respectively. Hence, an appropriate and fast technique is essential to detect Hg^{2+}. In recent years, extensive studies have been performed to develop sensitive and straightforward methods, such as resonating microcantilevers,[17] voltammetry,[18] colorimetric, and fluorescence spectroscopy[19] for quick recognition of mercury ions.

In continuation of our research,[20–23] herein a synthetic method for the synthesis of chromenone-pyrazole derivatives through a one-pot multicomponent reaction using $SrFe_{12}O_{19}$[24–25] as a magnetic catalyst is described, and then the fluorescence properties of chromenone-pyrazole compounds against metal cations were investigated.

Experimental Section

General procedure for the preparation of the $SrFe_{12}O_{19}$ catalyst

$SrFe_{12}O_{19}$ magnetic nanoparticles (MNPs) were prepared by employing a simple sol-gel auto-combustion method, as reported before in literature.[26–27]

General procedure for the synthesis of coumarin-pyrazole derivatives (4a-g)

A combination of salicylaldehyde derivative **1** (1 mmol) and 4-hydroxy-6-methyl-2*H*-pyran-2-one **2** (1 mmol, 0.13 g), and $SrFe_{12}O_{16}$ (0.02 g) was heated at the temperature of 120°C about approximately 15 min. Then, hydrazine (1 mmol) was added to the reaction mixture, which was stirred under the same conditions within (3–7 min) until reaction completion (traced by TLC method). Then, the raw product was dissolved in EtOAc, and the magnetic catalyst was separated using an external magnet. By evaporating the solvent, the product was precipitated out, and then crystals were filtered off, washed well with *n*-hexane, and then with water, respectively.

3-(3-Methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (**4d**): Yield: 96%, yellow powder, mp: 182–184°C, FT-IR (KBr) ν_{max}: 3427 (NH), 3037, 3091 (CH stretch), 1720 (-O-C = O), 1605 (C = N), 1576, 1474 (C = C), 1382 (CH_3) cm^{-1},^{1}H NMR (500 MHz, DMSO-d_6), 2.3 (s, 1H, CH_3), 6.7 (s, 1H, Pyrazole ring C-H), 7.3 (dd, 1H, Ar-H), 7.4 (d, 1H, Ar-H), 7.6 (t, 1H, Ar-H), 7.8 (s, 1H, Ar-H), 8.5 (s, 1H, Ar-H), 12.8 (s, 1H, NH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): 10.9, 105, 115.83, 119.2, 124.5, 128.5, 131.3, 136.59, 152.63, 158.8 ppm

3-(3-Methyl-1-(4-nitrophenyl)-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (**4e**):

Yield: 97%, yellow powder, mp: 270–272°C, FT-IR (KBr) ν_{max}: 3079 (CH stretch), 1741 (-O-C = O), 1599 (C = N), 1548, 1513, 1465 (C = C), 1384 (CH_3) cm^{-1}. ^{1}H NMR (500 MHz, DMSO-d_6): 2.3 (s, 3H, CH_3), 6.6 (s, 1H, Pyrazole ring C-H), 7.4 (t, 1H, Ar-H), 7.4 (d, 1H, Ar-H),7.668 (t, 1H, Ar-H),7.7 (d, 2H, Ar-H),7.783 (d, 1H, Ar-H), 8.23 (d, 2H, Ar-H), 8.3 (s,1H, Ar-CH) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): 13.2 (CH_3), 111.9, 116.2, 117.8, 118.7, 122.8, 124.8, 129.1, 132.7, 137.5, 144.2, 145.1, 145.2, 150.1, 153.5, 157.9 ppm.

5-Hydroxy-3-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (**4f**):

Yield: 96%, white powder, mp: 280–281°C, FT-IR (KBr) ν_{max}: 3415 (OH), 33070, 2923 (CH), 1684 (CO_2), 1605, 1585,, 1534 (C = C), 1374 (CH_3) cm^{-1} ^{1}H NMR (500 MHz, DMSO-d_6): 2.3 (s, 3H, CH_3), 6.5 (s, 1H, Pyrazole ring C-H), 7.1 (d, 1H, Ar-H), 7.1 (d, 1H, Ar-H), 7.2 (t, 1H, Ar-H), 7.3 (m, 1H, Ar-H), 7.4 (m, 4H, Ar-H), 10.2 (s, 1H, Ar-H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): 13.2 (CH_3), 109.9, 118.2, 118.8, 118.8, 119.5, 123.3, 124.8, 127.0, 129.1, 136.8, 140.3, 141.9, 144.0, 144.4, 148.3, 157.9 ppm.

6-Bromo-3-(3-methyl-1*H*-pyrazol-5-yl)-2*H*-chromen-2-one (**4g**):

Yield: 89%, yellow powder, mp: 241 – 239°C, FT-IR (KBr) ν_{max}: 3442 (NH), 3106, 2957 (CH), 1721 (CO_2), 1598 (C = N), 1566,1474, 1436 (C = C) cm^{-1}. ^{1}H NMR (125 MHz, DMSO-d_6): 2.3 (s, 3H, CH_3), 6.7 (s, 1H, Pyrazole ring C-H), 7.4 (d, 1H, Ar-H), 7.7 (d, 1H, Ar-H), 8.1 (s, 1H, Ar-CH), 8.5 (s, 1H, Ar-H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): 9.9, 104.7, 115.8, 117.7, 120.9, 121.2, 133.1, 134.7, 138.8, 143.8, 151.3, 158.1 ppm.

Results And Discussion

Chromenone-pyrazole can be synthesized *via* a three-component reaction of salicylaldehydes **1**, 4-hydroxy-6-methyl-2H-pyron-2-one **2**, and phenylhydrazine **3**. Initially, the reaction conditions were optimized, and the results were shown in Table 1. Among the employed catalysts of SiO_2-Pr-SO_3H and $SrFe_{12}O_{19}$, in the case of the last one, the reaction time significantly reduced and gave the highest yield of product. This reaction was then investigated in the presence of $SrFe_{12}O_{19}$ magnetic catalyst in different solvents, including EtOH, H_2O, and a mixture of H_2O and EtOH, besides under solvent-free conditions. By comparing the obtained results, it was found that solvent-free condition at 120°C is the best condition in terms of reaction efficiency and time.

Afterward, this reaction was generalized with several salicylaldehydes and hydrazine compounds under the optimized conditions (Scheme 1), and the derivatives have been classified in Table 2. After completing the reaction (monitored by TLC), the raw product was dissolved in boiling EtOAc; furthermore, the catalyst was simply separated from the solution using a magnet, and the product was obtained via gradual solvent evaporation. The new products were characterized by melting point, FT-IR, GC–MS, and NMR spectral data. Melting points of synthesized derivatives were compared with data reported in the literature, as illustrated in Table 2.

The proposed mechanism for this reaction was presented in Scheme 2. At first, enol carbon of 4-hydroxy-6-methyl-2*H*-pyron-2-one **2** was added to the activated carbonyl group of salicylaldehyde **1** through the Knoevenagel condensation, and then the dehydration process gave the adduct product **6**, which is then cyclized intramolecularly to gain intermediate **7**. The dehydration process of compound 7 leads to the ring-opening of the pyran moiety to give chromenone **8**, which was reacted hydrazine compound **3**, followed by dehydration, cyclization, and another dehydration process to yield the final product **4**.

In comparison with the published methods in literature as shown in Table 3, the present methodology has several advantages such as the use of inexpensive magnetic catalyst, simple procedure, the short

reaction time, and the high purity of products. The nanomagnetic catalyst can be easily separated from the reaction mixture using an external magnet.

Investigation of fluorescence properties and sensitivity of chromenone-pyrazole compounds against metal cations

The fluorescence responses of chromenone-pyrazole derivatives were examined toward metal cations using fluorescence spectroscopy. As shown in Fig. 1, the fluorescence spectra of ethanolic solution of all derivatives (1×10^{-5} M) were recorded, and only **4d** and **4g** showed the fluorescence emission with λ_{ex} = 348 nm and λ_{em} = 300 nm, respectively. The presence of the aryl group on the nitrogen atom of the pyrazole group leads to the lack of fluorescence emission because the non-bonding electrons of the nitrogen atom participate in the resonance of the phenyl ring. Thus, the resonance energy of the pyrazole ring is decreased. Therefore, participating in the non-bonding electrons of the nitrogen atom in the pyrazole ring's resonance is essential for the product's fluorescence properties.

To investigate the interaction of various cations with compound $\mathbf{L_1}$, Fe^{2+}, Fe^{3+}, Mn^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Cr^{3+}, Pb^{2+}, Co^{2+}, Hg^{2+}, K^{+}, Ca^{2+}, Cu^{2+}, Cd^{2+} and Ag^{+} cations (100 µL, 0.01 M) were separately added to the ethanolic solution of $\mathbf{L_2}$ (3 mL, 10^{-5} M) and the changes were indicated at the emission wavelength of 418 nm. The intensity of emission peak was decreased significantly only in the presence of $Hg^{2,}$ as shown in Fig. 2.

To explore the selectivity of the $\mathbf{L_1}$ against mercury ions, competitive experiments were performed against other metal cations (Fe^{2+}, Fe^{3+}, Ca^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Ag^{+}, Mg^{2+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, Na^{+}, $Al^{3+}$and K^{+}). As shown in Fig. 3, no significant interference is observed, and therefore, it can be claimed that compound $\mathbf{L_1}$ is a selective fluorescence chemosensor for the discernment of mercury ions even in the presence of other metal cations.

Titration experiment was accomplished in absolute EtOH solution of $\mathbf{L_1}$ with different amounts of Hg^{2+}. As shown in Fig. 4, the emission of chemosensor $\mathbf{L_1}$ regularly decreases by increasing Hg^{2+} concentration. The Fig. 4 inset shows good linear relations between the emission at 418 nm and the concentration of Hg^{2+} with the linear equation of emission = -218.96 $[Hg^{2+}]$+609.12 in the equivalent range and R^2 = 0.987. The detection limit for chemosensor $\mathbf{L_1}$ to detect mercury has been found from the following equation: DL= $(kS_d)/m$, where k is a constant factor equal to 3, S_d is the standard deviation obtained from the determination of the sample emission intensity at 412 nm for 6 replicates, and *m* is the slope of emission intensity against Hg^{2+} concentration. So the detection limit of $\mathbf{L_1}$ for Hg^{2+} was calculated as 4×10^{-7} M.

Another derivative of 6-boromo-chromenone-pyrazole ($\mathbf{L_2}$), also represents fluorescence properties. Thus, the effect of cation on the fluorescence properties of $\mathbf{L_2}$ was also investigated. The ligand's interaction was selective toward mercury ions because a sharp decrease is observed after adding a certain aliquot of

Hg^{2+} solution (Fig. 5). Therefore, the effect of interfering ions was then studied to explore the selectivity of **L_2** for the detection of mercury ions. Fortunately, any of the cations did not interfere with L2-Hg^{2+} (Fig. 6).

The titration experiment for **L_2** was accomplished as the same **L_1** (**Fig. 7**). The emission of chemosensor **L_2** again decreases by the gradually increasing amount of Hg^{2+}. The inset in (**Fig. 7)** shows a well linear relation between the emission at 426 nm and the concentration of Hg^{2+} with the linear equation of emission=-275.01[Hg^{2+}] + 346.23 and R^2 = 0.9899. The detection limit was also calculated like the method mentioned above and was **L_2** 3×10^{-8} M.**Fig. 7**: Fluorescence emission of chemosensor **L_2** upon addition of Hg^{2+} ions in absolute EtOH solution; Inset: plot of fluorescence emission as a function of Hg^{2+} concentration.

The presented compounds have shown very distinct advantages over the previously reported compounds in the detection and measurement of mercury ions. The analytical performance of mercury ions' current chemosensor and some of the significant reported methods are summarized in Table 3. One of the essential factors in the synthesis of new compounds 1, 2, and 3 is using a green solvent. In this regard, EtOH is an undoubtedly better solvent than CH_3CN. Compound 3 showed an excellent detection limit, but the synthesis method was complicated. In the case of compound **5**, while the applied solvent DMF is poisonous, the obtained detection limit is remarkably lower than the reported one. For compounds **6** and **7** as novel fluorescence sensors with excellent detection limit, a simple, green, and short time synthesis method was reported.

Conclusions

In summary, the chromenone-pyrazoles derivatives were synthesized by the multicomponent reaction approach in solvent-free conditions using a nanomagnetic catalyst. Among the seven derivatives, only two compounds have had fluorescence properties and responded to the Hg^{2+} ion with the low detection limit. The two fluorescent compounds in the pyrazole group have not aromatic groups. Then, *N* group is the main factor in generating the fluorescence property of these compounds.

Declarations

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Authors' Contributions

Ghodsi Mohammadi Ziarani: Corresponding author, concept design, Review writing and editing.

Shirin Mohammadsaeed: concept design, editing, Performed the experiments and modification.

Alireza Badiei: Contributed reagents, materials, Review modification, editing, and analysis data.

Jahan B. Ghasemi: Review modification, editing, and Analyzed and interpreted the data.

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Tables

Due to technical limitations the Tables are available as a download in the Supplementary Files.

Figures

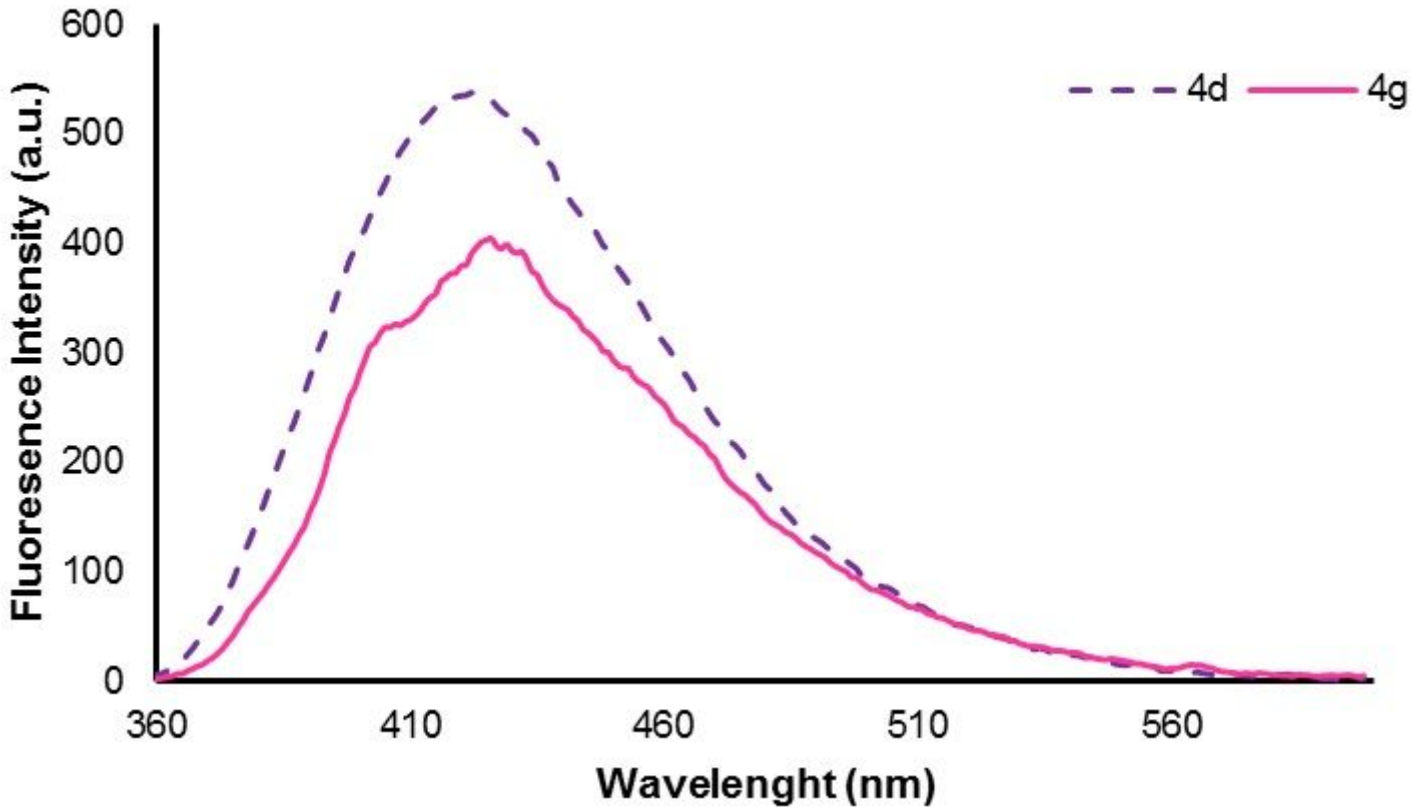

Figure 1

Fluorescence emission of chromenone-pyrazole 4d (L1) and 4g (L2)

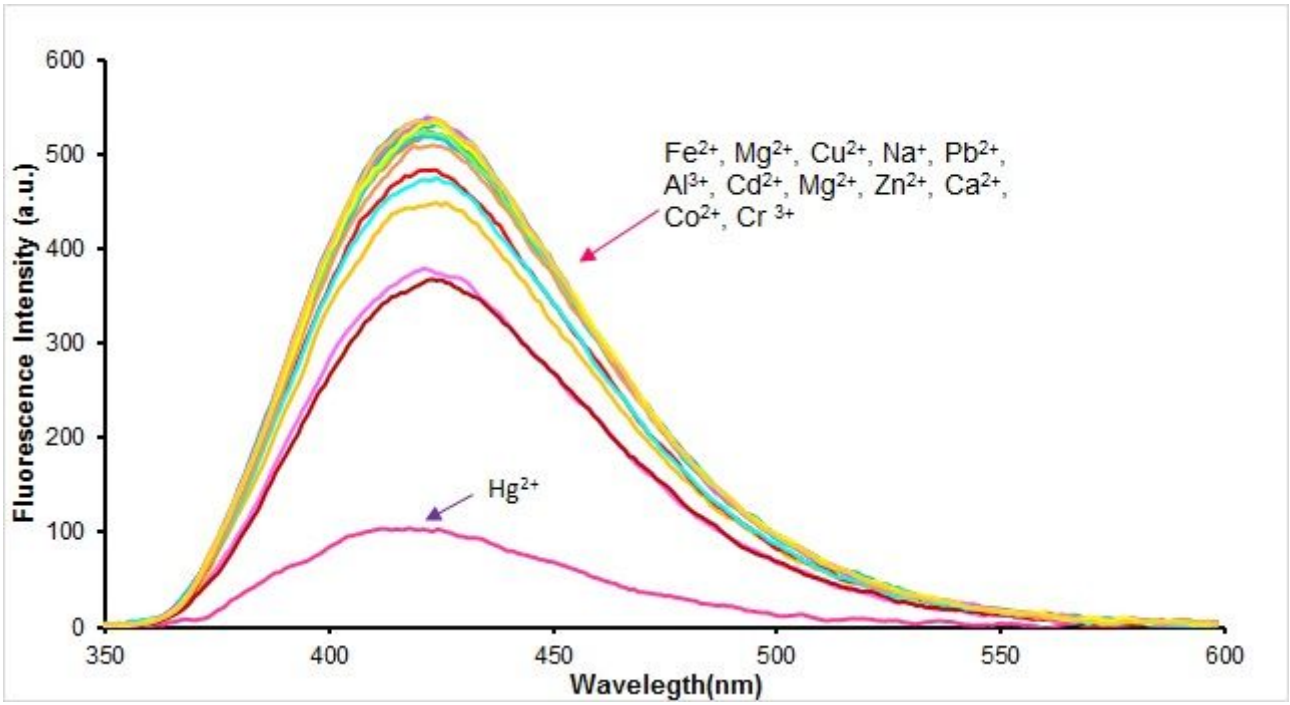

Figure 2

Fluorescence emission for a new compound of L1 in the presence of 100 µL (0.01 M) of metal cations (Ca2+, Cd2+, Co2+, Pb2+, Cu2+, Ag+, Mg2+, Ni2+, Hg2+, Zn2+, Al3+, K+, Hg2+) in absolute ethanol (λex= 300 nm and λ em= 334 nm).

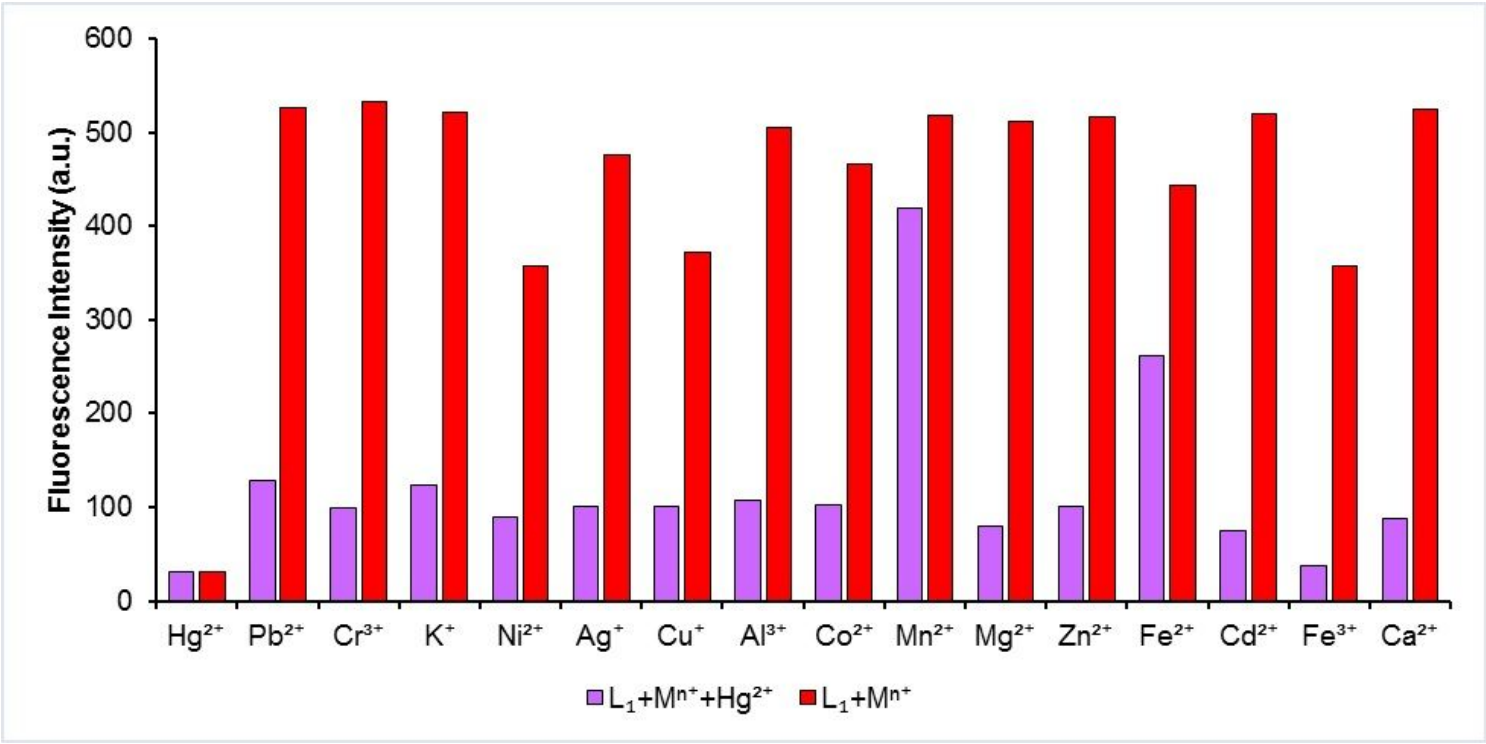

Figure 3

Selectivity of chemosensor L1 for Hg2+ against other metal cations in an ethanolic solution (λex= 300 nm and λ em= 334 nm).

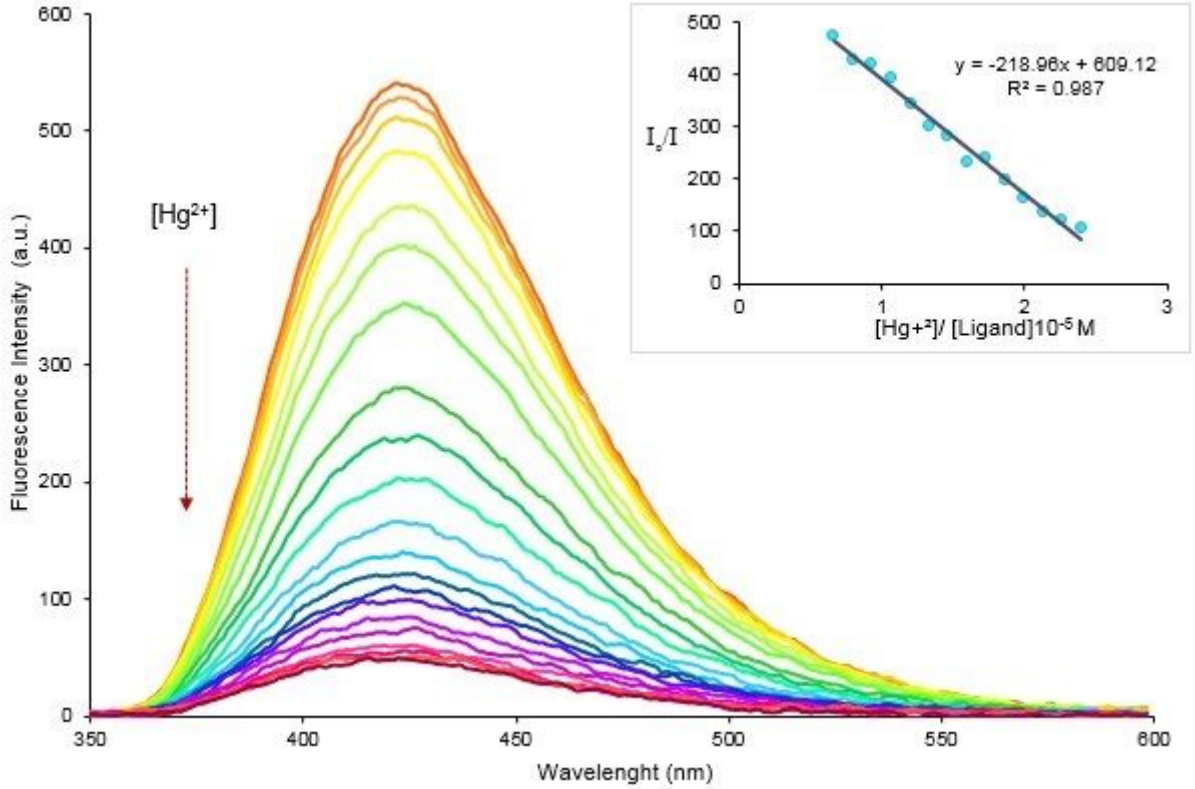

Figure 4

Fluorescence emission of chemosensor L1 over addition of Hg2+ in EtOH absolute solution; inset: plot of fluorescence emission as a function of Hg2+ concentration (λex= 300 nm and λ em= 334 nm).

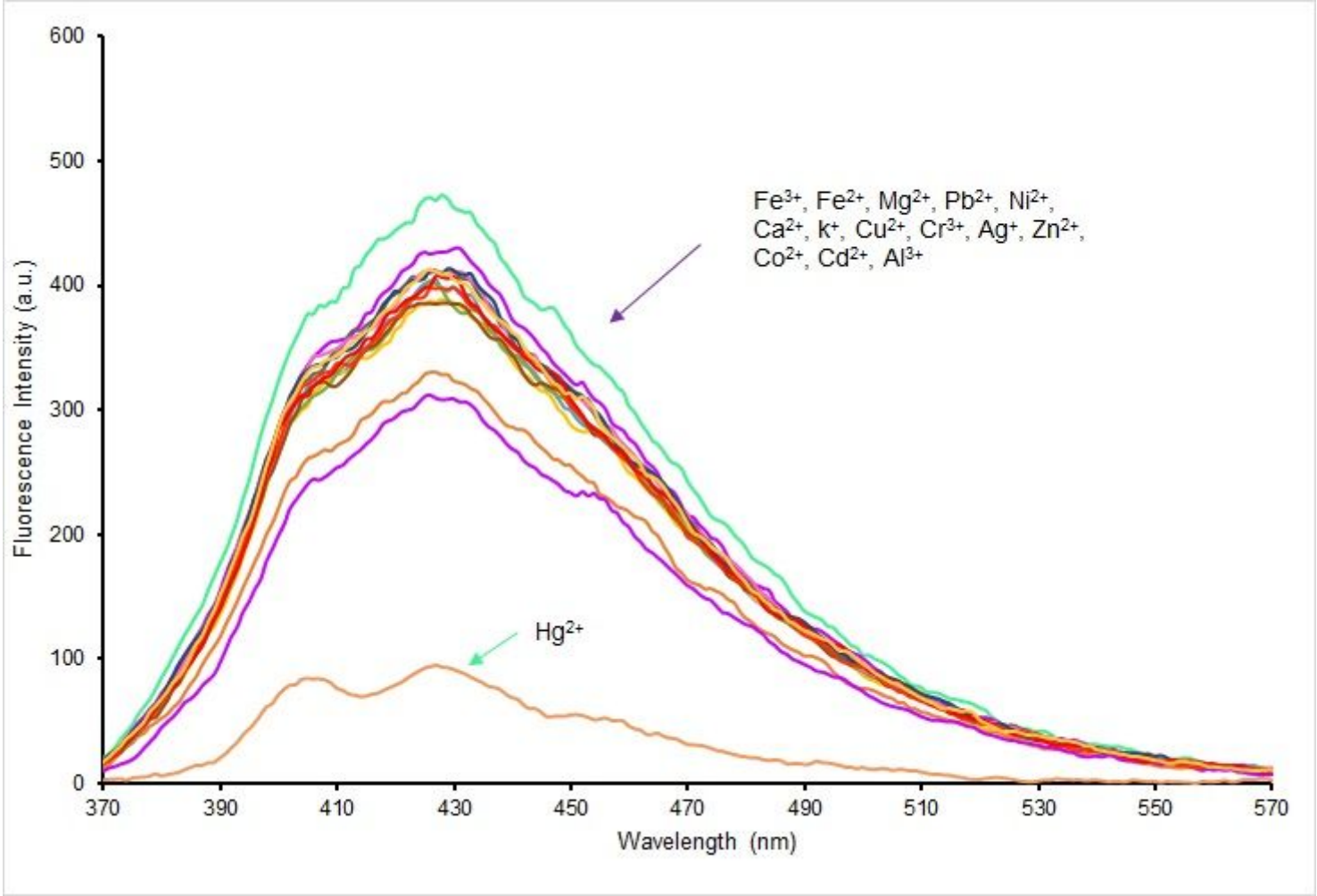

Figure 5

Fluorescence emission of chemosensor L2 in the presenment of several metal cations (Fe3+, Fe2+, Cd2+, Co2+, Cr3+, Cu2+, Ag+, K+, Al3+, Zn2+, Pb2+, Mg2+, Hg2+, Ca2+, Ni2+) in absolute EtOH, λ ex=300 and λ em=348

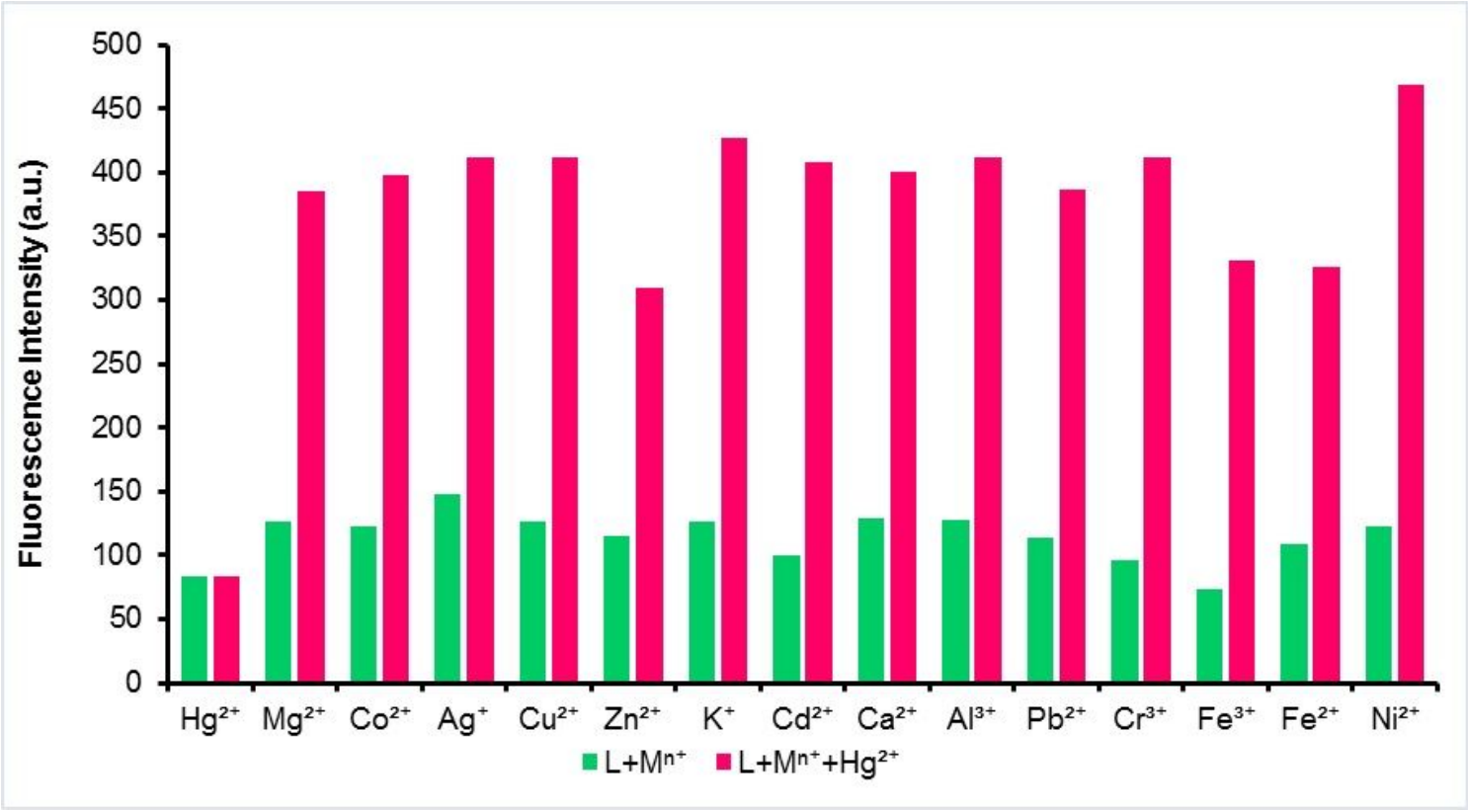

Figure 6

Selectivity of chemosensor 4g (3mL) for Hg2+ (100µL, 1×10-3 M) in the presence of metal cations in an absolute ethanol solution, (λ ex=300, λ em=348)

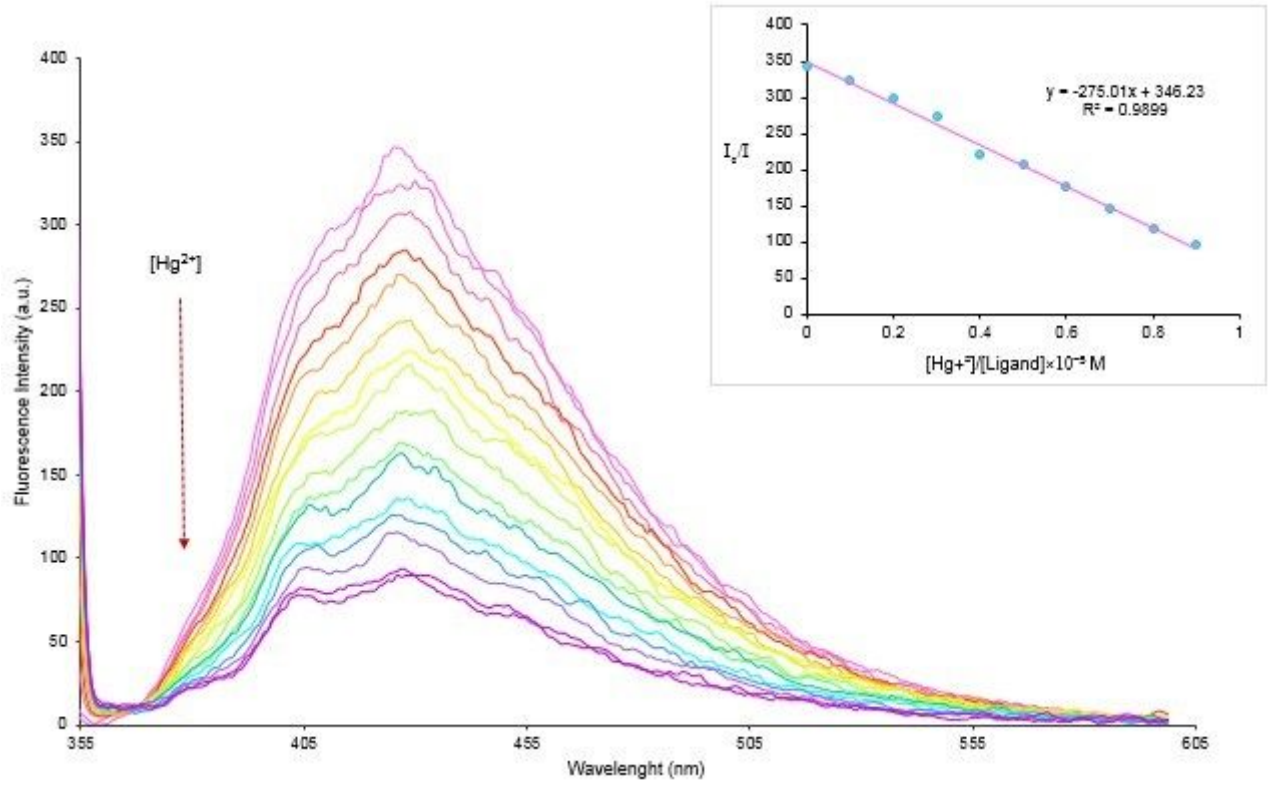

Figure 7

Fluorescence emission of chemosensor L2 upon addition of Hg2+ ions in absolute EtOH solution; Inset: plot of fluorescence emission as a function of Hg2+ concentration.

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