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A salicylal-derived Schiff base as Co (II) selective fluorescent probe

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ABSTRACT

A salicylal-derived Schiff base L was synthesized and exploited as a fluorescence probe for its selective detection of Co^{2+}. L exhibited enhanced fluorescence response at 350 nm for Co^{2+} in ethanol medium, distinguishing Co^{2+} from other cations with high selectivity. The formation of a 4:1 complex between L and Co^{2+} was suggested by Job's Plot. Additionally, the fluorescence intensity was directly proportional to the concentration of Co^{2+} ($R^2 = 0.9910$) from 8.0×10^{-7} to 2.0×10^{-6} mol L^{-1} with a detection limit of 7.82×10^{-7} mol L^{-1} (3σ) under optimized conditions. The small molecular compound could be used as a promising fluorescent probe for monitoring levels of Co^{2+} in environmental and physiological systems.

1. Introduction

Cobalt is an indispensable transitional metal and trace element in our bodies [1,2]. As an ingredient of Vitamin B12 and enzymes, it plays an important role in the metabolism of iron and synthesis of hemoglobin [3]. However, when cobalt reaches a certain concentration in the human body it causes and catalysts vasodilatation, flushing and cardiomyopathy [4], adverse effects on blood and kidneys as well as other disorders of the respiratory and central nervous systems. Simultaneously, animals deprived of cobalt suffer from retarded growth, anemia, loss of appetite, decreased lactation [8]. Sensors that are easily prepared and possess selective and sensitive signaling mechanisms have become increasingly important in environmental and clinical chemistry.

Various methods have been used for the determinations of metal ions, including cyclic voltammetry, stripping voltammetry, electrothermal atomic absorption spectrometry [4], flame atomic absorption spectrometry, inductively coupled plasma-atomic emission spectrometry and spectrophotometry [2,4]. Among these methods, fluorescence analysis techniques are favored without limitations of long extraction time, expensive cost of maintenance, complicated operation and strong interferences from other ions [4–7]. Numerous fluorescent probes that display fluorescence responses for transition metal ions such as Cu^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, Hg^{2+}, Pb^{2+} have been reported [6–16]. These ions bind to different functional groups according to their metal preferences [17]. The probes are always designed containing specific coordination geometry, binding with metal ions at the active sites and exhibiting particular functions [16]. However, merely a few, surprisingly, reports on developing selective probes for Co^{2+} with fluorescent response has been put forward, largely due to the paramagnetic nature of cobalt ions [4]. Also, cobalt probes synthesized are of complex structures and require many steps to obtain. What's more, these probes can only distinguish cobalt form several metal ions with no anion tests mentioned [11–13]. Developing readily available fluorescent probes displaying an enhanced fluorescence signal by means of coordination with Co^{2+}, therefore, is fresh and in demand.

It is the two novel emission mechanisms, aggregation-induced emission (AIE) [18] and excited-state intramolecular proton transfer(ESIPT) [19] via restriction of intramolecular rotation around the bonds, that has been applied to Salicylal-derived fluorophores. Aggregation-induced emission (AIE) materials, to name a few, Hexaphenylsilole (HPS), Tetraphenylethene (TPE) [20], 1-methyl-pentaphenyl silole (MPPS) [21] salicylaldehyde azine derivatives [22], have been discovered somewhere from Tang et al. in 2012 onward [23]. Fluorescent sensors based on AIE mechanism for metal ions, temperature, pH, and biomolecules catch our eyes in that they emit efficiently in their aggregate or solid states [24] and are preferred in contrast with aggregation caused quenching (ACQ)

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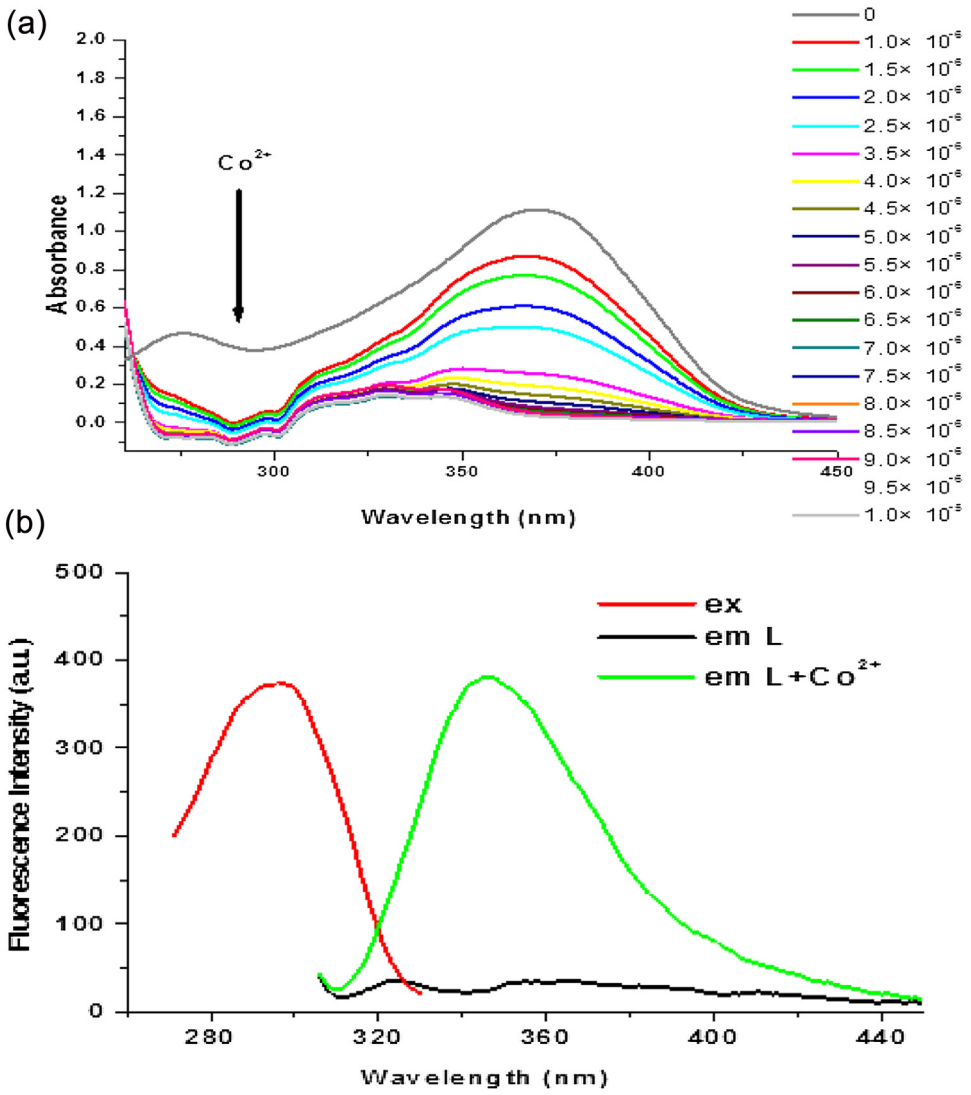
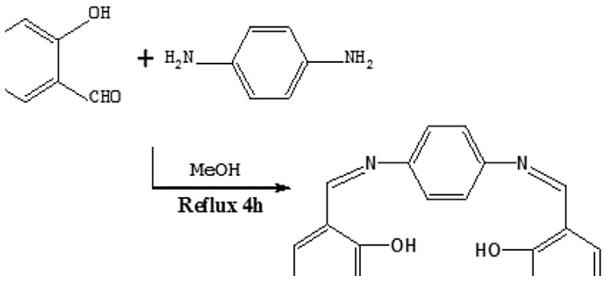


Fig. 1. (a) UV–vis absorption spectra of L with gradual addition of Co^{2+} (5×10^{-7} to 1.0×10^{-5} respectively) in ethanol solution (b) Excitation and emission spectra of L, L + Co^{2+} in ethanol solution. [L] = 5.0×10^{-6} M, [Co^{2+}] = 1.0×10^{-6} M.



Scheme 1. Synthetic routes of compound L.

[25] which quenches fluorescence intensity at high sensor concentration or in their solid state and becomes more severe especially when imaging low-abundant molecular species in biological systems.

Schiff bases based chem-probes have excellent selectivity and sensitivity [26]. Herein, we report a Schiff-base as a fluorescent "OFF–ON" probe for distinct detection of Co^{2+} in ethanol. The fluorescent probe, 2-((4-(2-hydroxybenzylideneamino) phenylimino)methyl)phenol (named L hereinafter), has been synthesized before [27] but has not yet been exploited in the fields of fluorescence detection of Co^{2+}. Schiff bases based chem-probes have excellent selectivity and sensitivity. The function of the hydroxyl groups and double-bonded carbonic acids is to provide functional characteristics so that it could form assemblies with particular ions [28–30] and Oxygen donor atoms for metal chelation bind with these ions. The small non-cyclic imine-linked probe for cation sensing, possessing multiple hydroxyl groups, is easy to synthesize with only one step. L shows eminent fluorescence enhancement after coordinating with Co^{2+} than other metal ions. To the best of our knowledge, the 1:4 combination ratio of Co^{2+} to L suggests a special combination mode of the probe provided other 1:1 style cobalt complexes [31–33]. Furthermore, the selectivity and sensitivity of L towards Co^{2+} announces its promising application in the detection of trace amounts of cobalt ions.