



Detection of Fe²⁺ in acetonitrile/water mixture by new 8-hydroxyquinolin based sensor through metal displacement mechanism

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ABSTRACT

A 8-hydroxyquinoline-based (8-HQ) fluorescent ligand (**2**) was designed and synthesized by condensation of pyridine-2-carboxaldehyde with 2-(quinolin-8-yloxy)acetohydrazide (**1**). Fluorometric titrations with various metal ions in 1:1 M ratio showed that Cu²⁺ and Ni²⁺ ions were fully quenched the fluorescence intensity of **2**. But, a significant enhancement in the fluorescent intensity was observed when the bound Ni²⁺ and Cu²⁺ ions in the **2**-Ni and **2**-Cu complexes were displaced by Cr³⁺ and Fe²⁺ ions, respectively. While **2**-Ni exhibited low sensitivity toward Cr³⁺ ion, the fluorescent titration measurements showed that **2**-Cu could be a good “on-off-on” selective and sensitive sensor (**S**) candidate for determination of Fe²⁺ in aqueous medium.

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1. Introduction

Iron is an essential trace element for human nutrition. The World Health Organization (WHO) has been reported that daily iron need of a human body is about 10–50 mg/day depending on sex, age and physiological condition [1]. Iron deficiency causes to low oxygen delivery to cells, resulting in low blood pressure, anemia and decreased immunity. But excess amount of iron ions in metabolism can trigger the formation of reactive oxygen species (ROS) causing cellular damage [2]. Advanced analytical instruments, such as ICP (OES/MS) and AAS, have been developed to analyze metal ion concentrations in water samples [3]. Although this type of instruments has high sensitivity and selectivity, they have high operation cost and low mobility to work in on-site. Thus the development of fluorescent chemosensors with high selectivity, sensitivity and low detection limit has received considerable attention in recent years [4–6]. These chemosensors, especially fluorescent-based ones, have been extensively investigated and widely used in medical, environmental and biological applications thanks to their powerful ability to improve analytical sensitivity

[7–11].

Herein, we designed and characterized an 8-hydroxyquinoline-based fluorescent chemosensor (**2**) by displacement strategy on **2**-Cu (**S**). Molecular structure of the sensor was characterized by IR, UV–vis, elemental analysis, LC-MSMS, ¹H NMR, ¹³C NMR analysis and DFT calculations. Limit of detection (LOD), limit of quantification (LOQ), bonding stoichiometry and stability constants of the sensor have been investigated.

2. Experimental

2.1. General procedures

The chloride salts of Na⁺, K⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Cr³⁺, Mn²⁺, Fe²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Al³⁺, Cd²⁺, Hg²⁺ and Pb²⁺, were purchased from Merck (Darmstadt). 8-Hydroxyquinoline was obtained ADR chemicals. 2-(Quinolin-8-yloxy)acetohydrazide (**1**) was synthesized by previously reported literature procedure [12].

2.2. Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer equipped with an ATR

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apparatus. Elemental analyses were performed using a LECO truspect analyzer at the Central Research Laboratory of Recep Tayyip Erdogan (RTE) University. Mass spectra were recorded using Thermo Sci. TSQ Quantum Access MAX Triple Stage Quadrupole mass spectrometer equipped with heated electrospray ionization (H-ESI) probe at the Central Research Laboratory of RTE University. ^1H and ^{13}C NMR spectra were recorded on an Agilent Technologies 400/54 spectrometer at the Central Research Laboratory of RTE University. UV–vis spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer.

2.3. Fluorometric assays

Fluorometric measurements of the sensors were performed on Agilent Cary Eclipse in a 1-cm quartz fluorescence cuvette. Fluorometric measurements were recorded after 10 min of incubation at room temperature. Excitation and emission slits were recorded at 680 V PTV voltage (excitation/emission slits were 5 nm). Because of the low solubility of the ligand in water, the fluorometric experiments were performed in MeCN/tris-HCl buffer solution (pH 7.2, 50 mM) in 2:1 ratio. Fluorometric response of the Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} , Cd^{2+} , Hg^{2+} and Pb^{2+} ions for the sensor, firstly, was monitored by adding their salts into the 5.5×10^{-5} M solution of the **2** in 1:1 M ratio. Secondly, Fluorometric spectral changes were monitored by adding these metal ions to each other for the metal displacement testing. Finally, the fluorometric titration is performed by adding increasing amounts of 9.0×10^{-5} M solution of the Fe^{2+} to a series of tubes containing 0.1 mL solution of **2**–Cu (**S**) (5.5×10^{-5} M), and final volume was adjusted to 3 mL with tris-HCl buffer.

2.4. Theoretical calculations

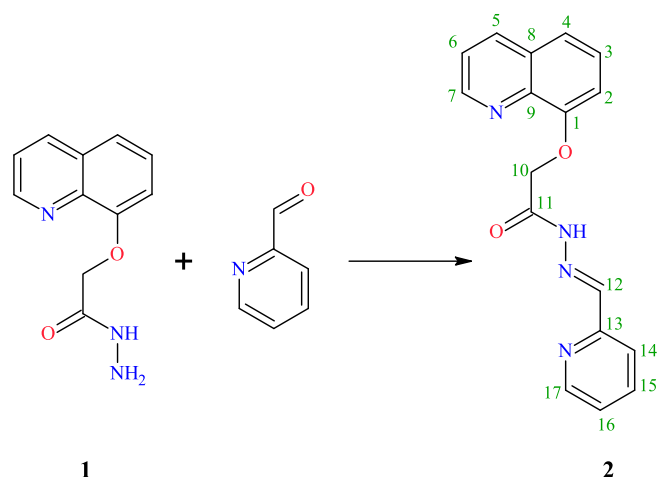
All calculations were carried out with the GAMESS 2013 (R1) program [13]. The molecular structure, vibrational frequencies and the electronic excitations on gas phase of sensor were calculated by using Becke-3-Lee Yang Parr (B3LYP) [14,15] density functional theory method with 6-31G(d, p) basis set for the H, C, N and O atoms in ground state [16]. A typical calculation has been executed by using M06 functional with 6-31G(d, p) basis set for the H, C, N and O atoms and LanL2Dz for metal ions [17]. The positive values of all calculated vibrational wavenumbers show that the optimized molecular structure is stable at a minimum on the potential energy surface. Gabedit program was used to visualize the geometric and electronic results of the computations [18].

Electronic excitations and emissions were calculated using the time dependent density functional theory (TD-DFT) formalism. We computed the lowest 15 singlet-singlet transitions of the sensor. Gabedit were also used to calculate the fractional contributions of various groups to each molecular orbital and to describe the excitation energies of UV–vis bands.

2.5. Synthesis of *N*–[(*E*)-pyridin-2-ylmethylidene]-2-(quinolin-8-yloxy)acetohydrazide (**2**)

An ethanolic solution of **1** (0.108 g, 0.5 mmol) was added dropwise from a dropping funnel to solution of the pyridine-2-carboxaldehyde (0.105 g, 1.0 mmol) in ethanol with vigorous stirring. The white solution was filtered and, the supernatant liquid was kept in air for slow evaporation. The microcrystalline product was obtained and, recrystallized from ethanol (Scheme 1). **2** is highly soluble in common organic solvents such as chloroform, dichloromethane, acetone, methanol, ethanol and acetonitrile.

Yield: 0.119 g (78%). Mp: 143 °C. Color: White. Anal. Calc. for



Scheme 1. Synthetic route of the compound **2**.

$\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2$ ($M = 306.18$ g/mol): C, 66.66; H, 4.61; N, 18.29; Found: C, 66.41; H, 4.59; N, 17.62%. ESI-MS, m/z (%): 307.01 (44%) $[\text{M}+\text{H}]^+$, 328.99 (100%) $[\text{M}+\text{Na}]^+$. FT-IR (cm^{-1}): 3524 $\nu(\text{N-H})$, 1667 $\nu(\text{C=O})$, 1650 $\nu(\text{C=N-})$, 1590–1560 $\nu(\text{Ar-H})$, 1251 $\nu(\text{C-O})$. ^1H NMR δ (ppm): 12.13 (s, 1H, –OH); 11.83 (s, 1H, –NH); 8.92 and 8.86 (s, 1H, H^{12}); 8.59 (s, 1H, H^7); 8.32 (s, 1H, H^{17}); 8.06 (s, 1H, H^5); 7.91 (m, 2H, $\text{H}^{4,15}$); 7.52 (m, 2H, $\text{H}^{3,14,6}$); 7.40 (s, 1H, H^2); 7.15 (s, 1H, H^{16}); 5.42 and 4.94 (s, 2H, CH_2). ^{13}C NMR δ (ppm): 167.29, 156.33, 145.730, 142.10, 136.22, 134.41, 133.71, 131.96, 129.66, 129.24, 127.74, 124.38, 120.11, 112.78, 79.17, 70.53, 69.45, 67.93. UV–vis/nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$): 274 (11 219), 294 (16 345), 443 (430).

3. Results and discussion

3.1. Structural characterization

The sensor (**2**) was characterized by IR, UV–vis, ^1H and ^{13}C NMR, mass and elemental analysis. Disappearance of $\nu(\text{N-H})$ stretching mode of the primer amine group on the **1** strongly supports the condensation reaction of **1** with pyridine-2-carboxaldehyde to form **2**. The characteristic N–H, C=O and C=N stretching bands in the IR spectrum were observed at 3524, 1667 and 1650 cm^{-1} for **2**, respectively (Fig. S1). The ^1H and ^{13}C NMR spectra of the sensor have been recorded in d_6 -dimethylsulfoxide (Figs. S2–S4). Because of the keto-amine tautomeric equilibrium, the O–H/N–H, HC=N and $-\text{CH}_2$ proton signals were observed as separated two singlets at 12.13–11.83 ppm, 8.92–8.86 ppm, and 5.42–4.94 ppm, respectively, in the ^1H NMR spectrum of the sensor (for the detailed assignments of aromatic protons see Section 2.5). Amine form in equilibrium has been calculated by using ^1H NMR integrations and found as 62%. The positive charged molecular ion, $[\text{M}+\text{H}]^+$, and sodium adduct, $[\text{M}+\text{Na}]^+$, have been detected at m/z 307.01 and m/z 328.99 in the mass analysis (for detailed spectral information, see Supplementary Figs. S5–S6).

3.2. Selectivity of **2**

Because of the low solubility of the **2** in water, fluorometric experiments were performed in MeCN/water (2:1) at pH 7.2. **2** exhibits relatively strong fluorescence emission at 400 nm upon excitation at 318 nm. The fluorescence emission spectra of **2** upon addition of various metal ions (Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} , Cd^{2+} , Hg^{2+} and Pb^{2+}) in MeCN/water (2:1) at pH 7.2 were given in Fig. S7. Upon

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