

# Synthesis and crystal structure of imidazole containing amide as a turn on fluorescent probe for nickel ion in aqueous media. An experimental and theoretical investigation



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## ABSTRACT

Imidazole containing amide fluorescence probe (PAIC) for Ni<sup>2+</sup> was designed and successfully synthesized in good yield by reaction between 1-methyl-1H-imidazole-2-carboxylic acid and L-phenylalanine methyl ester. The probe was characterized by FTIR, <sup>1</sup>H NMR, ESI-MS, UV–vis and fluorescence spectroscopy. Single crystal XRD analysis reveals that PAIC crystallizes in a monoclinic crystal lattice system with the space group of P<sub>2</sub><sub>1</sub>/n. Chemosensor property of PAIC was tested against different metal ions by UV–vis and fluorescent techniques in aqueous medium. Test results show that PAIC has high selectivity for Ni<sup>2+</sup> compared to other metal ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Hg<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup> and Pb<sup>2+</sup>). Time-dependent density functional theory (TD-DFT) and configuration interaction singles (CIS) calculations were carried out to understand the sensing mechanism. The practical applicability of PAIC was tested in real water samples.

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## 1. Introduction

The detection of metal ions in environmental and biological systems is an area of importance because heavy metals play crucial roles in ecological, biological, and clinical applications [1–5]. Nickel plays dual nature as an essential and toxic element in nature. Nickel deficiency causes reduced iron resorption and leads to anemia. Also, the deficiency lowers the activities of different enzymes and affects carbohydrate metabolism [6–8]. Nickel is a moderately toxic element that can lead to respiratory system cancer [9–11]. Nickel can cause a disorder known as nickel-eczema [12,13]. Nickel is widely used in electroplating and manufacturing of nickel-cadmium batteries. Nickel alloys are mainly used as a raw-material for the production of tools, machinery, ornaments etc [14–16]. As this metal ion is an environmental pollutant and yet also an essential trace element in biological systems, the determination of nickel ion is thus important. Fluorescence sensing is the most efficient approach to detect the low concentration of analytes. There are many efforts devoted to the development of

small fluorescent chemical sensors for the detection metal ions [17]. Very few investigations were reported for the detection of nickel ions when compared to other heavy metal ions [18,19]. Also, most of the reported probes were utilized only in pure organic solvents. Chemosensors should have high sensitivity and selectivity, and ideally should be able to operate in an aqueous medium. Chelation-enhanced fluorescence (CHEF) is an attractive designing principle for developing new fluorescent chemosensors [20]. Fluorescent chemosensors based on biomolecules, such as amino acids, peptides and DNA have been reported as chemosensor for transition metal ions in an aqueous solution. The biomolecules have hydrophilic and potent binding affinities to target metal ions [21].

In continuation of our earlier work on chemosensor [22], herein we report a novel imidazole containing amide based chemosensor, 2-(1-methyl-1H-imidazole-2-carboxamido)-3-phenyl propanoic acid (PAIC) prepared by the condensation of amino acid, phenylalanine and imidazole carboxylic acid. Among the various metal ions tested, the chemosensor (PAIC) exhibits fluorescence enhancement selectively towards Ni<sup>2+</sup> ions in aqueous media. Various spectral studies (UV–visible, emission, ESI-MS and <sup>1</sup>H NMR) and theoretical calculations (Time-dependent density functional theory (TD-DFT) and configuration interaction singles (CIS)) have been used to understand the mechanism through which PAIC

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recognizes Ni<sup>2+</sup> ion. The practical applicability of PAIC was tested in real water samples.

## 2. Experimental section

The chemicals used in this study were purchased from Sigma Aldrich and used as received. The solvents were procured from the commercial suppliers. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in DMSO-d<sub>6</sub> solvent on Bruker-AMX 400 MHz instrument. Electrospray ionization mass spectra (ESI-MS) were obtained from Thermo Finnigan LCQ 6000 advantage max ion trap mass spectrometer. FT IR spectra on KBr pellets were recorded on a Shimadzu FT IR-8400 spectrometer in the range of 4000–400 cm<sup>-1</sup>. The absorption spectra were recorded at room temperature using Shimadzu-2450 UV–visible spectrophotometer. The emission spectra were recorded using Perkin–Elmer LS45 luminescence spectrometer. Single crystal XRD data were collected from Bruker Kappa Apex II single crystal diffractometer and X Shell software was used for solving the structure.

### 2.1. Synthesis of 2-(1-methyl-1H-imidazole-2-carboxamido)-3-phenyl propanoic acid (PAIC)

A mixture of 1-methyl-1H-imidazole-2-carboxylic acid (0.130 g, 1 mmol), EDC.HCl (0.29 g, 1.5 mM), HOBT (0.20 g, 1.5 mmol) and Et<sub>3</sub>N (0.15 g, 1.5 mM) in dichloromethane (10 mL) was stirred for 1 h at 0 °C. Then, L-phenylalanine methyl ester.HCl (1.05 mM) was added into the solution. The reaction mixture was stirred for 12 h at 25 °C and then evaporated to dryness. The ester obtained was washed with water and extracted with dichloromethane (Scheme 1). To a solution of the ester (1 equiv) in a dichloromethane/methanol (9:1 v/v) mixture, was added a methanolic solution of NaOH (3 equiv) with final concentration of the alkali being about 0.1–0.2 N. The reaction was monitored by TLC for the disappearance of starting ester. After the completion of the reaction, the solvents were removed under vacuum and the residue was diluted with water. Then, the aqueous phase was acidified to pH 2–3 with dilute HCl and extracted with ethyl acetate. The combined organic layers were dried with anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed to afford the acid (PAIC). Single crystal of PAIC was isolated by slow evaporation of the solvent. Yield: 143 mg (74%), M.P 129 °C; Anal. Calc. for C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>: C, 61.53; H, 5.53; N, 15.38. Found C, 61.13; H, 5.45; N, 15.18; <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz): δ/ppm 3.16 (d, J = 4 Hz, 2H, CH<sub>2</sub>), 3.8 (s, 3H, N–CH<sub>3</sub>), 4.6 (m, H, chiral H), 6.9–7.2 (m, 7H, Aromatic H), 8.2 (d, J = 8.4 Hz, 1H, amide-NH); <sup>13</sup>C NMR: 34.9 (CH<sub>3</sub>), 36.2 (–CH<sub>2</sub>), 52.9 (C–NH), 158.5 (CO–N), 172(–COO); FT-IR (KBr,

cm<sup>-1</sup>) 1555 (N–H), 1602 (–C=N), 3292 (HO–CO), 1673 (C=O amide), 2931 (C–H); ESI mass: m/z 272.9.

### 2.2. X-ray diffraction studies

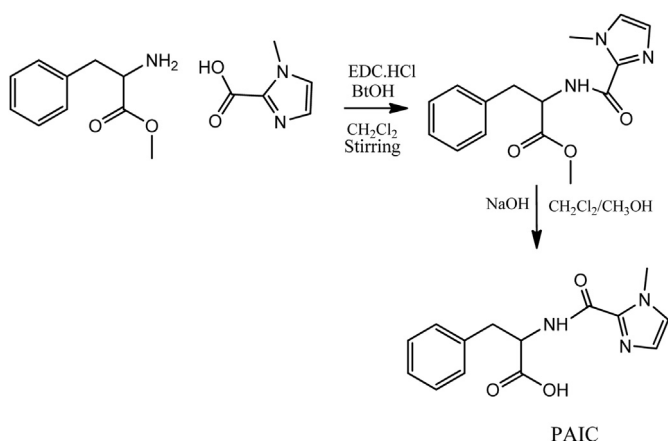
Single crystal X-ray diffraction experiments were performed on a Bruker Kappa Apex II single crystal diffractometer operating at 50 kV and 0.6 mA using MoKα radiation (λ = 0.71073 Å). Yellow colored crystal of PAIC with dimensions of 0.40 mm × 0.35 mm × 0.30 mm was fixed on the top of a glass fiber and transferred to the diffractometer. The data collected at 293 (2) K is shown in Table 1. The structure was solved by direct methods procedure using SHELXS-97 program and refined by full-matrix least-square method SHELXL-97 program [23]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. Hydrogen atoms bonded to oxygen were located from difference map and allowed to refine with temperature factors riding on those of the carrier atoms. The geometrical parameters were obtained using PARST [24] and SHELXL-97.

### 2.3. Procedure for chemosensor analysis

The PAIC (1.032 mg, 1 mM) was dissolved in water (5 mL). From the stock, 20, 40, 60, 80, 100, 120, 140, 160, 180 μL of the solution was transferred to a vial. To make a total volume of 200 μL in vial, the remaining volume (180, 160, 140, 120, 100, 80, 60, 40, 20 μL of the Ni<sup>2+</sup> solution) was taken from stock solution of Ni<sup>2+</sup> (0.48 g, 1 mmol). Then, the solutions were diluted to 4 mL with water. The solutions were shaken well before recording the fluorescence spectra at room temperature. The Job's plot was constructed by using change in fluorescence intensity for free PAIC and metal bound PAIC (F–F') vs. mole fraction of metal ion. The binding constant (K<sub>b</sub>) was estimated using Benesi–Hildebrand plot involving inverse of metal ion concentration against the inverse of changes in its absorbance (1/(I–I<sub>0</sub>) vs. 1/[Ni<sup>2+</sup>]).

**Table 1**  
Crystallographic data of PAIC.

Parameters	PAIC
CCDC	891115
Identification code	SHELXL
Empirical formula	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub>
Formula weight	273.29
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P21/n
Unit cell dimensions	a = 12.2173(5) Å alpha = 90 deg. b = 7.9742(3) Å beta = 91.993(2) deg. c = 14.1979(6) Å gamma = 90 deg.
Volume	1382.37(10) Å <sup>3</sup>
Z, Calculated density	4, 1.313 Mg/m <sup>3</sup>
Absorption coefficient	0.095 mm <sup>-1</sup>
F(000)	576
Crystal size	0.25 × 0.20 × 0.20 mm
Theta range for data collection	2.16–28.28 deg.
Limiting indices	–16 ≤ h ≤ 16, –10 ≤ k ≤ 9, –18 ≤ l ≤ 18
Reflections collected/unique	12631/3388 [R(int) = 0.0253]
Completeness to theta = 28.28	98.50%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9813 and 0.9768
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	3388/0/186
Goodness-of-fit on F <sup>2</sup>	1.064
Final R indices [I > 2σ(I)]	R1 = 0.0553, wR2 = 0.1601
R indices (all data)	R1 = 0.0832, wR2 = 0.1854
Largest diff. peak and hole	0.460 and –0.289 e.Å <sup>-3</sup>



**Scheme 1.** Synthetic scheme of PAIC.

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