Journal of Luminescence 146 (2014) 234–238

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

A selective fluorescent receptor for the determination of nickel (II) in semi-aqueous media

Umesh Fegade [a,b], Jaromir Marek [c], Rahul Patil [a], Sanjay Attarde [b], Anil Kuwar [a,*]

[a] School of Chemical Sciences, North Maharashtra University, Jalgaon 425001, MS, India
[b] School of Environmental and Earth Sciences, North Maharashtra University, Jalgaon 425001, MS, India
[c] Central European Institute of Technology, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic

ARTICLE INFO

Article history:
Received 31 July 2013
Received in revised form
26 September 2013
Accepted 27 September 2013
Available online 7 October 2013

Keywords:
(7*E*,8*E*)-N1′N3′-bis(1-(2-hydroxyphenyl) ethylidene) malonohydrazide
Fluorescence probe
Stability constant

ABSTRACT

The malonohydrazide based fluorescent probe (7*E*,8*E*)–N1′,N3′-bis(1-(2-hydroxyphenyl)ethylidene) malonohydrazide (receptor **5**) was designed and synthesized. It was confirmed by spectroscopic methods and the single crystal X-ray method. The receptors **5** show strong intramolecular hydrogen bonding which is useful in host–guest complexation. The fluorescence spectra of receptor **5** have shown distinct enhancement with the addition of Ni^{2+} ion over other surveyed cations. The stability constant was obtained by Benesi–Hildebrand, Scatchard and Connor's fitting methodologies. The 1:1 stoichiometry of the host–guest complexation was confirmed by Job's continuous variation method.

1. Introduction

Design and synthesis of a selective fluorescent probes for the sensing of ionic species important from the environmental and material science point of view, mainly heavy metal ions, is a topic of growing interest in supramolecular chemistry [1–3]. A significant effort has been dedicated to the improvement of Ni^{2+} selective fluorescent receptors in the last few decades. However, in most cases fluorescence changes can only be observed in non-aqueous solvent and as well as gets affected by the common interference of other metal ions [4–9], which bound the limits for their analytical application in real samples analysis. Therefore, the development of highly sensitive and selective fluorescent receptor for Ni^{2+} in aqueous solution is very important and challenging area for the researchers [10–13].

Nickel can be found in the plasma of the blood. The absence of nickel from the plasma or red cells of a few subjects may be regarded as evidence against the existence of a physiologic function for this element [14]. In vitro nickel activates arginase, carboxylase and trypsin, and it may inhibit acid phosphatase. There is evidence that it affects the clotting mechanism by stabilizing the labile factor [15,16]. Nickel deliberation is a potential health hazard to fauna and flora if it exceeds the normal level than the cellular needs. Nickel toxicity can cause acute pneumonitis, dermatitis, asthma, eczema, cancer of lungs, sinus, stomachaches, unfavorable effects on blood (increases red blood cells) and kidneys (increases protein in urine) other disorders of respiratory system and central nervous system [17].

In current article, we report the synthesis of (7*E*,8*E*)–N1′,N3′-bis(1-(2-hydroxyphenyl)ethylidene) malonohydrazide (receptor **5)** and studied its binding properties towards Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+} and Bi^{3+} in DMSO/H_2O (1:1, v/v). Receptor **5** has interestingly shown significant enhancement in fluorescence emission maxima in the semi-aqueous phase with Ni^{2+} metal ion. This ability to grant fluorescent enhancement in semi-aqueous phase makes its application possible in the area of biology, environmental and material sciences.

2. Experimental

2.1. Chemical and apparatus

All commercial grade chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Varian NMR mercury System 300 spectrometer operating at 300 and 75 MHz in DMSO-d_6 solvent. The fluorescence spectra were recorded in DMSO/H_2O (1:1, v/v) namely on Fluoromax-4 spectrofluorometer and Shimadzu UV-24500 at room temperature using 1 cm pathlength cell.

2.2. Synthesis of (7E,8E)–N1′,N3′-bis(1-(2-hydroxyphenyl) ethylidene)malonohydrazide (receptor **5**)

Malonohydrazide (**3**) was synthesized from condensation of one mole diethyl malonate (0.32 g, 2 mM) with two moles of

* Corresponding author. Tel.: +91 257 2257 432; fax: +91 257 2257 403.
E-mail address: kuwaras@gmail.com (A. Kuwar).

0022-2313/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jlumin.2013.09.075

hydrazine hydrate (0.20 g, 4 mM) by stirring for 30 min in absence of solvent. Malonohydrazide (**3**) was obtained in good yield and having appearance of white powder. Receptor **5** was obtained from one mole of Malonohydrazide (**3**) (0.26 g, 2 mM) with two moles of o-hydroxy acetophenone (0.54 g, 4 mM) in ethanol with stirring and refluxing for 90 min (Scheme 1). Receptor **5** was obtained in good yield and having white appearance, solubility in DMSO; Yield 82%; Melting Point 198–200 °C. Crystals suitable for X-ray analysis for compound **5** were obtained by slow evaporation of a solution of the compound from a methanol solution in 8 days.

^{1}H-NMR (300 MHz, DMSO-d_6, ppm,)δ=2.42 (s, 6H, 2CH_3), 4.31 (s, 2H, CH_2), 6.91–7.13 (4H, m, Ar–H), 7.21–7.52 (t, J=7.5 Hz, 2H, Ar–H), 7.54–7.85 (d, 2H, J=7.5 Hz, Ar–H), 11.3 (s, 2H, NH), 13.2 (s, 2H, Ar–OH). ^{13}C-NMR (75 MHz, DMSO-d_6) δ=13.8, 40.5, 116.5, 118.6, 120.0, 131.3, 133.7, 159.0, and 163.25. IR (KBr, cm^{-1}): υ=623, 663, 684, 752, 781,798, 825, 893, 1033, 1099, 2937, 3057, and 3207. MS (EI): M+H$^+$ calcd. for ($C_{19}H_{20}N_4O_4 \cdot 2Na$)=413.40; found 413.74.

2.3. Cation recognition studies

The recognition studies were performed at room temperature, and the solution was shaken for enough time before recording fluorescence and absorption spectra to ensure uniformity. The cation binding ability of receptor **5** in a DMSO/H_2O (1:1, v/v) by keeping the solvent ratio constant throughout the experiment, was determined by preparing standard solutions of receptor **5** (c=1 × 10^{-5} M) along with fixed amounts (0.5 equiv.) of a metal nitrates (c=1 × 10^{-4} M) in DMSO/H_2O (1:1, v/v). The cation recognition performance of receptor **5** (c=1 × 10^{-5} M) was evaluated from changes in the fluorescence spectra of the sensor upon addition of the salts (c=1 × 10^{-4} M).

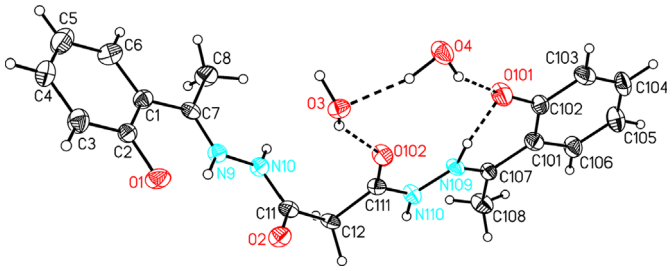

Fig. 1. ORPET diagram of receptor **5**.

Table 1
Crystal data and structural refinement for receptor **5**.

Parameter	Receptor **5**
Molecular formula	$C_{19}H_{20}N_4O_4 \cdot 2(H_2O)$
Formula weight	404.42
Temperature	123 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a=4.977(7) Å
	b=5.552(3) Å
	c=17.790(14) Å
	α=81.33(3)°
	β=88.25(9)°
	γ=82.49(4)°
Volume	483.7(8) Å^3
Z	1
Density (calculated)	1.388 Mg/m^3
Absorption coefficient	0.11 mm^{-1}
F(0 0 0)	214
Crystal size	0.15 × 0.08 × 0.01 mm^3
Theta range for data collection	3.5–26.0°
Index ranges	$-6 \le h \le 6$, $-6 \le k \le 6$,
	$-21 \le l \le 31$
Reflections collected	6061
Independent reflections	3140 [R(int)=0.051]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3514/0/287
Goodness-of-fit on F^2	1.08
R indices (all data)	R1=0.067, wR2=0.186
Largest difference in peak and hole (e Å^{-3})	0.31 and −0.50

2.4. Stoichiometry determination

Sequentially, to determine the stoichiometry of the receptor **5**·Ni^{2+} complexation, solutions of receptor **5** and Ni^{2+} ion were prepared at ratios of 1:9, 2:8, 3:7, 4:6, 5:5, 6:4, 7:3, 8:2, and 9:1. These solutions were allowed to stand for 1 h with frequent shaking. The fluorescence spectra were recorded with each solution. The plot of [HG] versus [H]/([H]+[G]) was used to determine the stoichiometry of the complex formed. The fluorescence intensity of emission peak maxima at 629 nm was used for stoichiometry

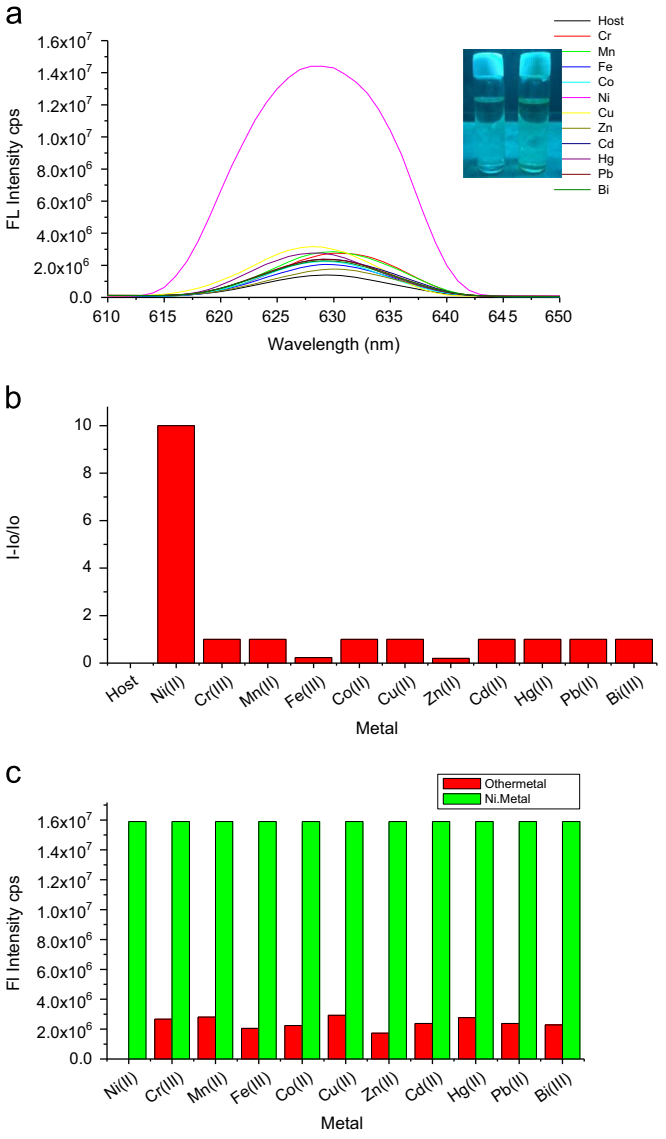

Fig. 2. (a) Changes in fluorescent intensity of receptor **5** upon the addition of a particular metal salts in DMSO/H_2O (1:1, v/v) solvent system, (b) fluorescence ratiometric response of receptor **5** upon the addition of a particular metal salts in DMSO/H_2O (1:1, v/v) solvent system, and (c) respective interference of metals at the time of Ni^{2+} ion detection.