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Ni^{2+} Ion Sensing by a Semicarbazone Derivative of Piperidin-4-one: A Spectrofluorimetric Study

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Nickel ions are toxic to the environment and they are also relevant in biology. Fluorescence sensing is a sensitive method and metal sensing can be carried out employing cheaper and easy-to-synthesize molecules that possess fluorescence emission. Therefore, the development of newer and simply-synthesized chemosensor molecules for nickel ions in aqueous media is required. We report, in this paper, a simple semicarbazone derivative of a piperidin-4-one as a nickel ion sensor in water. The compound forms a 1:1 stoichiometric complex with nickel ions. The association constant value is 4.04×10^4 mol^{-1} dm^3. The nickel ion-selectivity of the compound is explored employing UV-Vis and fluorescence spectroscopy. Ni^{2+} ion-chelation enhances the fluorescence of the chemosensor molecule. The Ni^{2+} detection limit of the chemosensor was 1×10^{-7} mol dm^{-3}. The compound also forms a 1:2 inclusion complex with β-cyclodextrin. The structure of the complex is proposed. Host: guest complex formation of β-cyclodextrin with the piperidin-4-one derivative results in the interference of the host molecule with the chelation of Ni^{2+} ions. As an extension of the application of the piperidin-4-one derivative, we demonstrate the Ni(II) ion filtration by incorporating the compound with a polysulfone film.

Keywords: Semicarbazone, Piperidone, Ni^{2+} sensing, Fluorescent chemosensor, β-Cyclodextrin, Host-guest complex

INTRODUCTION

Molecular recognition and chemosensing have earned much interest recently and the thrust for developing newer and cheaper metal ion sensors has grown dramatically. Overtaking amperometric [1], potentiometric [2], and surface techniques [3], the detection of cationic analytes using fluorescence chemosensors [4] comes to the forefront due to the sensitivity of the technique. The design and synthesis of fluorescent chemosensors is a major goal in achieving a sensitive and selective detection of metal ions [5]. Piperidones are simple and easy-to-synthesize compounds and their derivatives are reported abundantly in the literature [6-8]. They are generally non-toxic and possess biological importance [9,10].

A high level of Ni^{2+} ion-uptake leads to various diseases like pneumonitis, dermatitis, asthma, and lung cancer [11,12]. Nickel is present in compounds that are used for several commercial and industrial purposes *viz*., preparation of pigments, catalysts and electroplating [13,14]. Apart from

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this, nickel is a metal nutrient in biological system taking part in the biosynthesis and metabolism of some plants and microorganisms [15]. Therefore, a practical monitoring of nickel ion is crucial [16-20]. Based on the above reasons, we prepared a piperidin-4-one derivative for the sensing of Ni^{2+} ions in the solution.

Cyclodextrins are non-toxic bucket-shaped oligosaccharide molecules. The molecules possess a hydrophobic cavity and a hydrophilic exterior [21]. These cavity-containing molecules can accommodate a variety of molecules of appropriate size, forming host: guest complexes [22-24]. β-Cyclodextrin, which has seven α-D-glucopyranose units, is capable of influencing the metal ion sensing behavior of the guest fluorophore [25]. In addition, CD-complexes of organic fluorophores can be employed in metal sensing [26-29]. Therefore, we studied the metal ion sensing by the piperidone derivative in the presence of β-cyclodextrin. In addition, the chemosensor we report here is a structural variant of the simple piperidin-4-one reported by our research group [30]. Interestingly, the metal ion selectivity changes when the semicarbazone moiety is introduced in the structure (Cd^{2+} in the literature report and Ni^{2+} in the current report of the semicarbazone). Therefore, depending upon the necessity of specific metal ion sensing, a simple variation in the structure can be imparted by suitable substitution of groups in the molecule. This paper reports the Ni^{2+} ion-sensing by the synthesized piperidin-4-one derivative, its host-guest complex with β-cyclodextrin and the hindrance offered by the host molecule in metal ion sensing.

EXPERIMENTAL

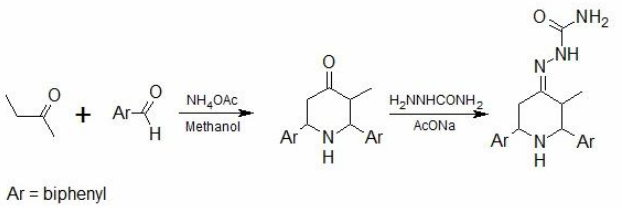
Materials and Instrumentation

Analytical grade salts of the metal cations (Na^{+}, K^{+}, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and $A1^{3+}$) were the products of Aldrich (India) and utilized as received. The precursors used for the synthesis of the chemosensor (Sigma, India) were also of analytical grade.

The FT Infra-Red spectrum was recorded on a Prestige 21 Shimadzu spectrometer (Japan), employing KBr discs. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer (USA). Deuterated DMSO and tetramethylsilane (TMS) were used as the solvent and internal standard respectively. 2-Dimensional Rotating-frame Overhauser Effect Spectrum was recorded on a Bruker Avance instrument under the spin-lock condition. The mixing time was 200 ms. The mass spectrum was recorded on a Finnigan mat 8280 mass spectrometer. UV-Vis spectra (Jasco V630, USA) were recorded using a Jasco V 630 spectrophotometer and employing 1 cm width quartz cells. A Jasco FP 8300 spectrofluorometer (USA) served the purpose of recording steady-state fluorescence spectra.

Synthesis of Semicarbazone of 2,6-Bis(biphenyl-4-yl)-3-methylpiperidin-4-one

2,6-Bis(biphenyl-4-yl)-3-methylpiperidin-4-semi-carbazide (receptor 1) was synthesized by (Scheme 1) the reaction between 2,6-bis(biphenyl-4-yl)-3-methylpiperidin-4-one (1 g) and semicarbazide hydrochloride (0. 2674 g) in ethanol (equimolar). The mixture was refluxed for 2 hours. The progress of the reaction was followed by thin layer chromatography. The product was recrystallized from ethanol (yield 80%, m. p.: 172 °C).



Scheme 1. Synthesis of receptor 1

Earlier, the 2,6-bis(biphenyl-4-yl)-3-methylpiperidin-4-one was prepared using a reported procedure [30]. 4-Phenylbenzaldehyde (2 mol, 2 g), butan-2-one (1 mol, 0.39 ml), and ammonium acetate (1 mol, 0.4230 g) were mixed in ethanol and heated at 70 °C for 7 h. The product was extracted with ether, dried, and recrystallized from ethanol (yield 82%, m. p.: 110 °C).

Preparation of Solutions

Owing to the poor solubility of receptor 1 in water, a stock solution was made in acetonitrile. The test solutions were obtained by an appropriate dilution of the stock solutions in deionized water. The final concentration of

acetonitrile in the test solutions was 1%. Typically, the test solutions were prepared by adding 0.1 ml of each metal ion into 10 ml standard measuring flasks. The spectra were recorded immediately after preparing the test solutions and shaking them well for a few seconds. The excitation wavelength set up for the fluorescence spectral measurements was 320 nm.

RESULTS AND DISCUSSION

Synthesis of the Receptor Molecule 1

Receptor 1 was synthesized in two steps, *viz*., (i) a simple Mannich reaction between 4-phenylbenzaldehyde and butan-2-one in the presence of ammonium acetate and (ii) treatment of semicarbazide hydrochloride with the piperidin-4-one synthesized in step (i). The characterization of 1 was carried out by IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry. The ^{1}H NMR and mass spectra are displayed in Figs. 1 and 2, respectively (For IR and ^{13}C NMR spectra, see SI 1 and 2 respectively, in the supporting information).

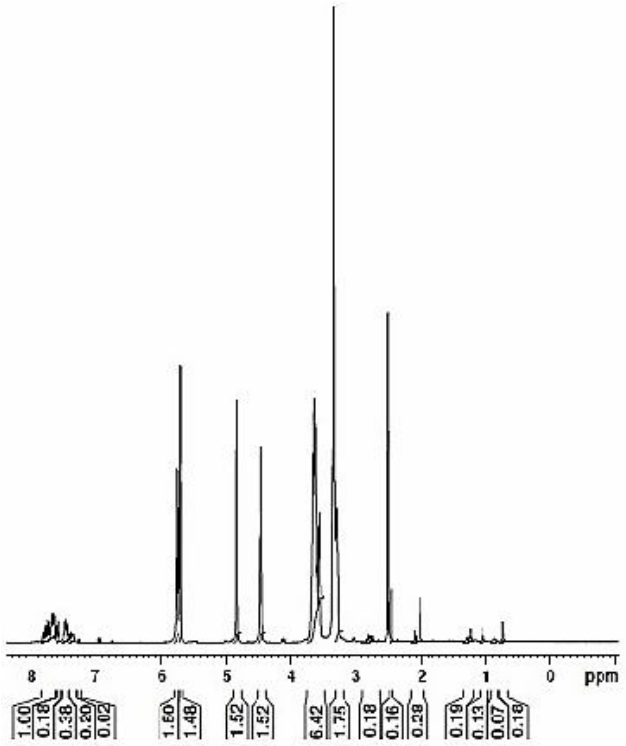


Fig. 1. ^{1}H NMR spectrum of 1.

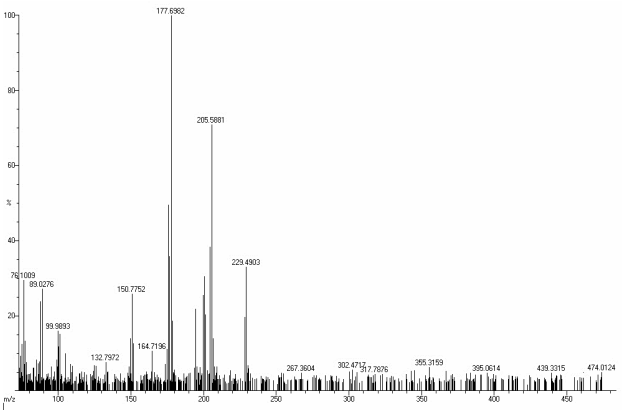


Fig. 2. Mass spectrum of 1.

Absorption and Fluorescence Spectral Studies of 1 in the Presence of Metal Ions

The cation sensing by 1 from the series of metal cations (Na^+, K^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and $A1^{3+}$) were studied employing UV-Vis absorption and fluorescence spectroscopy. Receptor 1 displayed a prominent absorption band at 260 nm and a shoulder at 320 nm. In the presence of metal ions, the absorption bands shift either hyperchromic or hypochromic (SI 3). Nevertheless, the differences are less than enough for any distinction between metal ions.

Unlike the UV-Vis spectrum, the fluorescence spectrum of 1 shows a vivid behavior on the addition of Ni^{2+} ions. When each of all the other metal ions is added, the emission spectral band of 1 (observed at 420 nm) shows quenching of fluorescence (Fig. 3a). When Ni^{2+} is added, the fluorescence of 1 gets enhanced. This is owing to the selective and preferential strong Ni^{2+} complex-formation of the receptor. For the other metal ions, it implies that there is the quenching of fluorescence due to the collision of the metal ions with the receptor. The fluorescence spectral titration shows that receptor 1 can act as a Ni^{2+} ion sensor since it shows Ni^{2+} ion selectivity. The binding of Ni^{2+} occurs due to the 'hard-acid nitrogens' of the semicarbazone moiety as Ni^{2+} has the tendency to complex with such groups [31]. This is as opposed to the unmodified piperidin-4-one reported earlier where the Cd^{2+} complexation occurs owing to the predominating oxophilicity of the carbonyl group [30]. The bar chart in Fig. 3b compares the intensities of fluorescence of 1 with various added metal ions. The Ni^{2+}

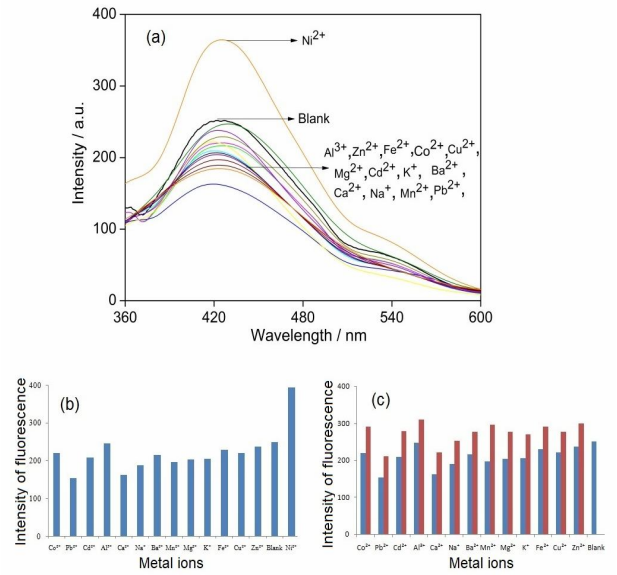


Fig. 3. (a) Fluorescence spectral response of 1 to various metal ions in aqueous medium. (b) Bar chart showing the intensities of fluorescence of various metal ion added 1. (c) Competitive binding of Ni^{2+} ion in the presence of other metal ions.

added-receptor 1 shows the most intense spectrum, shown by the tallest bar in the chart. The other bars stand shorter than the one corresponding to free 1, *i.e.*, without any metal ion added. Figure 3c shows the intensities of fluorescence of 1 when Ni^{2+} is added to the receptor having each of the other metal ions already added. The fluorescence gets enhanced in each case when Ni^{2+} is added to the metal-ion chelated 1. This result suggests that the Ni^{2+} ions bind to 1 in competition with other metal ions.

The stoichiometry and the association constant of the 1-Ni^{2+} complex in aqueous media were determined by doing respectively a Job's plot (SI 4 (a)) *i.e.*, the mole fraction of Ni^{2+} ions vs. intensity of fluorescence and a double reciprocal Benesi-Hildebrand plot of $1/[Ni^{2+}]$ *vs.* $1/[I'-I_0]$ (SI 4(b)). Here, I' represents the intensity of fluorescence of the 1-Ni^{2+} complex with the maximal amount of Ni^{2+} added, and I_0 is the fluorescence intensity of free receptor 1 (*i.e.*, without the metal ion added). The Job plot shows an inflection point at a mole fraction of 0.5, indicating that the stoichiometry of the 1-Ni^{2+} complex is 1:1. The association constant calculated from the Benesi-Hildebrand plot is 4.04×10^4 mol^{-1} dm^3. The detection limit of 1 for Ni^{2+} was determined to be 1×10^{-7} mol dm^{-3} and the corresponding plot made for the determinate of LDL (Lower detection limit) is provided in the supporting information (SI 5).

Formation of Host-guest Complex Receptor 1-β-Cyclodextrin

In order to understand the effect of β-CD on the metal ion sensing property of 1, the complex formation of 1 with β-CD was studied in solution. A binding titration was carried out between 1 and β-CD by keeping the concentration of 1 fixed (1×10^{-5} mol dm^{-3}) and adding β-CD stepwise. An increase in the concentration of β-CD led to the enhancement of the absorbance of 1 continuously up to the largest concentration. The spectra are shown in Fig. 4a.

This hyperchromic effect is accompanied by a 4 nm bathochromic shift, implying that the guest molecule (receptor 1) is accommodated by the host molecule (β-CD) with a portion of the former being outside the cavity of the latter, and hence interacting with the hydroxyl groups of the outer rim [32]. A fluorescence binding titration between 1

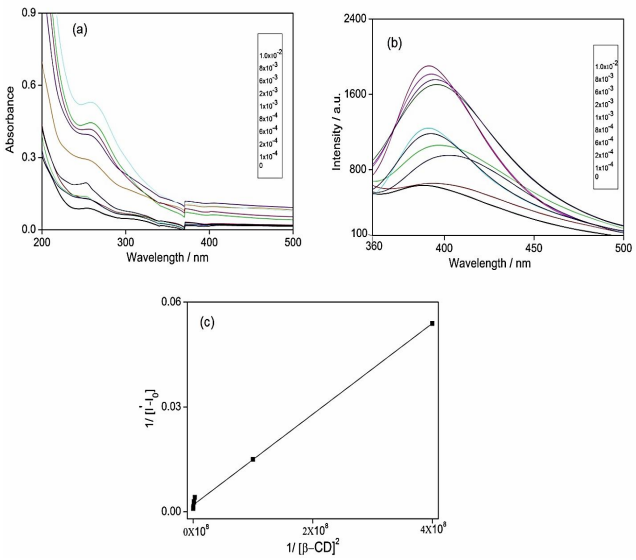


Fig. 4. (a) Absorption spectra and (b) fluorescence spectra of 1 at the addition of β-CD in stepwise increasing concentration. (c) Benesi-Hildebrand plot of the complex formation of 1 with β-CD.

and β-CD, carried out in a similar way gave further evidence for the formation of the host-guest complex. The fluorescence of 1 gets enhanced at each addition of β-CD (Fig. 4b) which suggests that a host-guest complex is formed. A 5 nm red shift is also observed. The fluorescence enhancement on β-CD complex formation is typical for a molecule having size of the moieties matching with that of the hydrophobic cavity of β-CD [33].

The stoichiometry and the binding constant of the 1-β-CD complex were determined from the double reciprocal Benesi-Hildebrand plot as shown in Fig. 4c. The plot reveals linearity when the reciprocal of the square of the concentration of β-CD is plotted along the X-axis. This result suggests that the stoichiometry of the complex is 1:2, formed by encapsulation of the 1 molecule by two β-CD molecules. A similar plot made using 1/[β-CD] in the X-axis gave a concave curve. The binding constant calculated applying the Benesi-Hildebrand equation is 7.24×10^5 M^{-2}.

The mode of binding of 1 with β-CD and the structure of the 1-β-CD complex was optimized by recording 2D ROESY Spectrum of the complex. Cross peaks pertaining to the protons of the guest molecules and those of the inner rim of β-CD would mean that the host-guest complex is formed and the corresponding part of the guest molecule is encapsulated. In the ROESY spectrum as seen in Fig. 5a the aromatic protons of 1 show cross-correlations with the H-3 and H-5 protons of β-CD.

Based on the above evidence from ROESY and from the 1:2 stoichiometry suggested by the fluorescence based binding titration, the structure of the 1-β-CD complex is suggested as shown in Fig. 5b. The structure implies that the aromatic groups are encapsulated by β-CD.

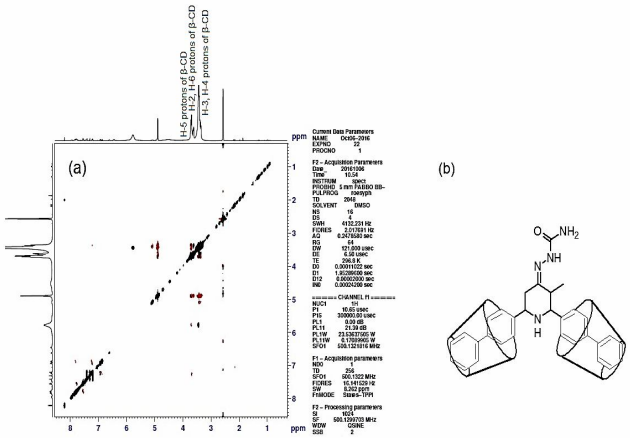


Fig. 5. (a) 2D ROESY spectrum of 1-β-CD complex. (b) Schematic representation of the host-guest complex.

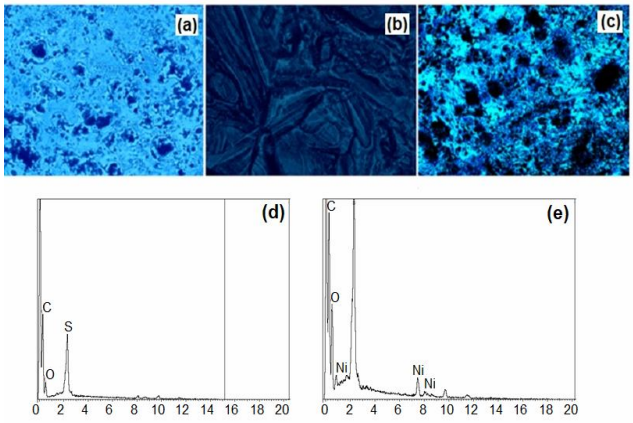


Fig. 6. Fluoresence images of (a) receptor 1, (b) nickel sulfate, and (c) receptor 1-Ni^{2+} ions. EDX spectra of the (d) as-prepared 1-polysulfone membrane and (e) metal ion filtered membrane.

Absorption and Fluorescence Spectral Studies of 1–β-CD in the Presence of Metal Ions

The absorption spectral titration of the interaction of 1-β-CD with various metal ions is shown in SI 6(a). The fluorescence spectral titration between the same species is shown in SI 6(b). Although the experimental conditions of this titration (pH 7.0, room temperature and concentration of the receptor and the added metal ions being 1×10^{-5} mol dm^{-3}) were the same as of the titrations in aqueous medium as discussed in the previous section 3.2, the spectra showed no significant change when Ni^{2+} was added.

Similarly, the spectrum of any of the other metal ions did not stand out, either in terms of intensity or wavelength shifts. This result means that the =N-NH-$CONH_2$ moiety, even though getting placed outside the cavity of β-CD in the 1:2 complex, has lesser availability for Ni^{2+} ion selectivity. Further, this may be due to the interaction of the above moiety with the outer rim of the β-CD molecules encapsulating the biphenyl rings as discussed in the absorption spectral shifts in the previous sections. In our previous work, we reported the enhanced sensing of Zn^{2+}

ions by a benzothiazole derivative due to β-CD complexation [25]. In that case, the metal ion chelating dihydroxyphenolic moiety was found to be located far away from the encapsulating β-CD molecule. In the present case (in receptor 1), the chelating moiety, even though being outside the β-CD cavity, does not show sensing of Ni^{2+} ions. Therefore, we conclude that the chelating group of the guest fluorophore molecule needs to be free from any weak interaction with β-CD in the host-guest complex in order to show sensing of metal ions. In addition, the steric effect due to the bulky β-CDs in the 1:2 complex is to be necessarily considered to influence the metal ion binding Nevertheless, it requires studies on several host-guest complexes to further extend insight into the influence of cyclodextrin on metal-ion sensing.

Filtration of Ni^{2+} Ions by Chemosensor Immobilized Polysulfone Film

Many industrial applications involve ion-exchange membranes. The mobility of a particle in the filtration membrane is governed by the interactions involved in the polymer, friction with water molecules, *etc*. [34]. Polysulfone membranes offer the ability to exchange ions in a controlled fashion. It is a material having good mechanical wet strength [35] and chemical stability. Therefore, we examined the filtration of Ni^{2+} ions by a polysulfone membrane having receptor 1 immobilized on it.

The polysulfone membrane immobilized with 1 was imaged before and after the filtration of Ni^{2+} ions through it. Due to the filtered Ni^{2+} ions, clear spots are seen in the latter case, suggesting that 1 chelates Ni^{2+} and facilitates the filtration of the ions (Fig. 6a-c). In order to further confirm that the Ni^{2+} ions are also adsorbed on the surface of 1-polysulfone membrane, energy-dispersive X-ray spectra (EDX) of the as-prepared polysulfone membrane and the membrane after the filtration of Ni^{2+} ions were recorded. The EDX spectrum of the as-prepared 1-polysulfone membrane (Fig. 6d) shows peaks corresponding to the elements C, O, and S, whereas the metal ion filtered membrane sample (Fig. 6e) shows peaks corresponding to the element Nickel apart for other peaks. Therefore, it is concluded that the 1-immobilized polysulfone membrane effectively filters the nickel ions from water samples.

CONCLUSIONS

We prepared a semicarbazone of 2,6-biphenyl-3-methylpiperidin-4-one. The compound selectivity recognizes Ni^{2+} in aqueous medium. The association constant of the Ni^{2+} complex is 4.04×10^4 mol^{-1} dm^3. The compound forms a host-guest complex with β-CD and two β-CD molecules encapsulate one guest molecule. The chelating unit of the compound, having a weak interaction with the exterior of cyclodextrin, binds Ni^{2+} ions weakly and does not show sensing of the metal ions. The synthesized compound when immobilized on polysulfone membrane is able to filter Ni^{2+} ions from water samples.

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