



A new metallo-supramolecular sensor for recognition of sulfide ions



Har Mohindra Chawla*, Preeti Goel, Priyanka Munjal

Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

ARTICLE INFO

Article history:

Received 18 October 2014

Revised 9 December 2014

Accepted 10 December 2014

Available online 16 December 2014

Keywords:

Calixarenes

Copper ion

Metallosupramolecular complex

Sulfide ions

Recognition

ABSTRACT

A hydroxynaphthyl hydrazine linked calix[4]arene derivative (**4**) has been designed, synthesized and evaluated for multi ion recognition. **4** not only recognizes copper ions selectively through a change in color, UV–Vis and fluorescence spectrum but the resultant metallo-supramolecular complex (**4**·Cu²⁺) emulates specific recognition of S²⁻ ions as well.

© 2014 Elsevier Ltd. All rights reserved.

During recent years, there has been an upsurge in research activity in the design, synthesis and evaluation of molecular receptors for anions.¹ This is partly due to the academic challenges involved and the utility of anion recognition in numerous biological, chemical and environmental processes.² Simple anions like fluoride, cyanide, sulfide, arsenate, phosphate, nitrate, chloride, sulfate, chlorate, and chromate are often considered as critical anions due to their importance in drinking water and consequent onset of diseases when they are present in higher concentrations.³ The studies are also very useful for effluent treatments and in ensuring a green environment. Besides mentioned inorganic anions, molecular receptors are also being investigated for the recognition of organic anions like citrate, tartrate and aliphatic and aromatic carboxylates.⁴

Major difficulties encountered in the design of molecular receptors for anions⁵ are due to their larger size and charge spread in comparison to those in cations. Their shape (which may vary from linear to octahedral), smaller window for manipulation of pH of the medium as well as stiff competition from electron donor solvents further complicate investigations on receptors for anions. The approaches used for the design of target molecular receptors have been based upon complementarity of charge, shape, size or through the electron deficient nature of the functional group appendages. In this connection, the use of metal ions with expandable valence shells (e.g., use of ferrocene, boron trifluoride residues attached to the organic molecular scaffolds)⁶ have proven useful

for recognition of anions. Recently secondary supramolecular forces have been deployed for anion recognition.^{7,8,19}

Molecular scaffolds generally employed for the target purpose are hydrophobic cavity containing organic macrocycles or pseudo molecular macrocycles such as calixarenes,¹⁰ resorcinarenes,¹¹ cyclodextrins,¹² steroids,¹³ molecular tweezers,¹⁴ and clefts¹⁵ which provide templates for assembling efficient platforms for anion recognition.

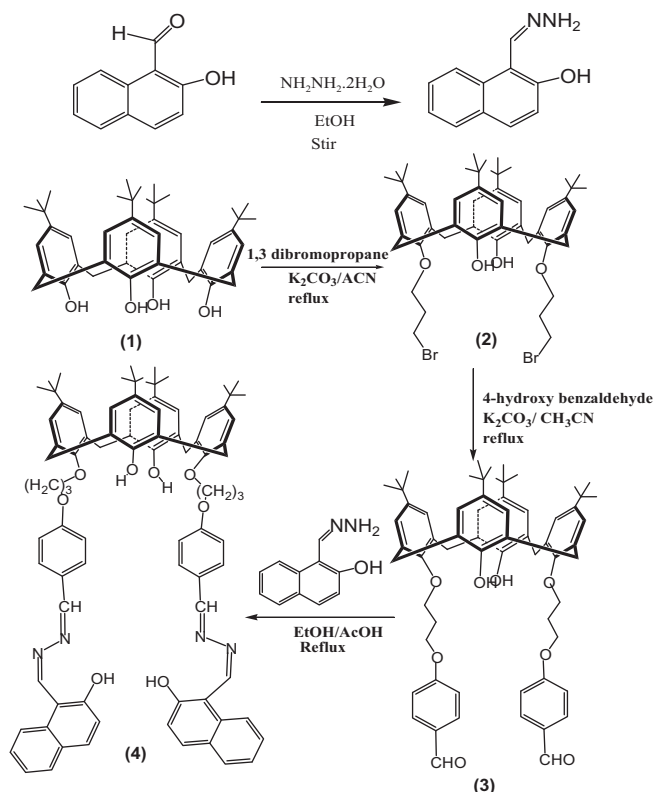
In the family of active anions, sulfide is known to strongly interfere in numerous biological processes. Continuous exposure to sulfide can cause gradual and cumulative damage that include loss of consciousness, irritation of mucous membranes, and suffocation.^{16,17} Once protonated, sulfide ions become more toxic and caustic. Some of the strategies evolved for recognition of S²⁻ at low concentrations include spectroscopic and electrochemical titrations,¹⁸ metal anion affinity,^{7–9,19} ion chromatography,²⁰ and chemo luminescence measurements.²¹ In this Letter we have focused our attention to the design of reversible sensors for sulfide ions by using its known affinity for copper ions to make a stable copper sulfide complex.

The synthesis and evaluation of a molecular Schiff base molecular probe **4** reveals that it is not only capable of detecting copper ion but the formed supramolecular metallo receptor **4**·Cu²⁺ could be further used for selective and specific detection of sulfide ions from among various related anions via colorimetric and fluorescence protocols.

Calix[4]arene with a naphthalene moiety attached at the lower rim was synthesized by adopting a reaction sequence given in Scheme 1.^{22,23} Bis(4-formylphenylpropyloxy)-*p*-*tert*-butylcalix[4]arene (**3**) was prepared by the method reported earlier.²⁴ It was

* Corresponding author. Tel.: +91 11 26591517; fax: +91 11 26581 102.

E-mail addresses: hmchawla@chemistry.iitd.ac.in, hmchawla@chemistry.iitd.ac.in, ernet.in (H.M. Chawla).

Scheme 1. Synthesis of molecular receptor **4**.

refluxed with 2-hydroxy-1-naphthaldehyde hydrazone in the presence of glacial acetic acid in ethanol to yield a product which when washed with methanol gave a novel calixarene derivative **4** in good yield (83%). The identity of all the intermediates and the target molecular receptor **4** was established by IR, ^1H and ^{13}C NMR as well as by ESI-MS analysis (ESI, Fig. S1). The synthesized molecular receptor **4** showed a $>\text{C}=\text{N}-$ signal at 1603 cm^{-1} and a sharp pair of doublets at a δ 3.36 and δ 4.29 for axial and equatorial protons, respectively, in the ^1H NMR spectrum. A distinct signal at δ 31.02 for the methylene carbons in its ^{13}C NMR spectrum revealed its symmetric cone conformation for the calix[4]arene scaffold. It was further confirmed by observing D_2O exchangeable singlets at δ 13.03 which could be assigned to the $-\text{OH}$ protons. Non deuterable singlets at δ 9.69 and 8.29 for the azo-methine proton ($-\text{N}=\text{CH}$) confirmed the depicted structure for **4** (Scheme 1).

The sensing ability of naphthalene based molecular receptor **4** for cations was examined in CH_3CN by naked eye color change, UV–Vis absorption and fluorescence spectroscopy.

On gradual addition of metal cations such as Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ , Ca^{2+} , Mn^{2+} , Co^{2+} , Cd^{2+} , Pb^{2+} , Fe^{2+} , Ni^{2+} , Zn^{2+} , and Cu^{2+} as their perchlorate salts in CH_3CN , a color change from light yellow to dark yellow was observed only in the presence of copper ions. ESI-MS of the **4** showed a molecular-ion peak $[\text{M}+\text{Na}]^+$ at m/z 1331.5334 and at m/z 1371.7741 (ESI, Fig. S5) due to the presence of $[\text{4}+\text{Cu}^{2+}]$. Other metal ions did not produce any noticeable change in color even on adding higher concentrations.

Following our observations based on color change, cation sensing ability of receptor **4** in CH_3CN was further monitored by UV–Vis absorption spectroscopy. UV–Vis spectra of **4** was characterized by two peaks (337 nm and 405 nm) with $\epsilon = 6.4 \times 10^4\text{ M}^{-1}\text{ cm}^{-1}$. Addition of different cations as perchlorates, led to no change in the absorption spectra of **4** except copper perchlorate.

On addition of Cu^{2+} ions, there was considerable change in the absorption spectra of synthesized calixarene derivative. To further

comprehend the Cu^{2+} binding nature of **4**, quantitative UV–Vis titration of **4** ($20\text{ }\mu\text{M}$) was carried out with increasing equivalents of Cu^{2+} ions (0–1.45 equiv). It was determined that gradual addition of Cu^{2+} ions to the receptor **4** led to a decrease and a shift in absorbance at 405 nm to 430 nm (Fig. 1) accompanied by a color change of the solution of receptor.

Fluorescence emission spectra of **4** ($20\text{ }\mu\text{M}$) in CH_3CN was recorded after excitation at 337 nm. It was determined that on addition of Cu^{2+} ions a prompt change in the intensity of fluorescence emission of **4** was observed to yield more than 90% quenching of the emission maxima at 505 nm. To learn more about the properties of **4**– Cu^{2+} complex formation, a titration of the receptor was performed with increasing concentration of Cu^{2+} ions. The fluorescence intensity of a $20\text{ }\mu\text{M}$ solution of **4** decreased with an increase in the concentration of copper perchlorate to reach saturation levels after addition of 1.5 equiv of Cu^{2+} ions (Fig. 2). Though analysis of the vibronic spectrum is outside the scope of this study, it appears that the fluorophore gets excited to its S_1 state in the absence of metal ions to result in higher intensity emission band due to $S_1 \rightarrow S_0$ state. However in the presence of copper ions, specific complexation leads to intersystem cross over from S_1 to T_1 state to usher a much decreased intensity of fluorescence and deactivation by bimolecular non radiative processes. Analysis of the infrared spectrum of the compound and its complex with Cu^{2+} reveals that a significant shift (26 cm^{-1}) in $\nu(\text{OH})$ of the

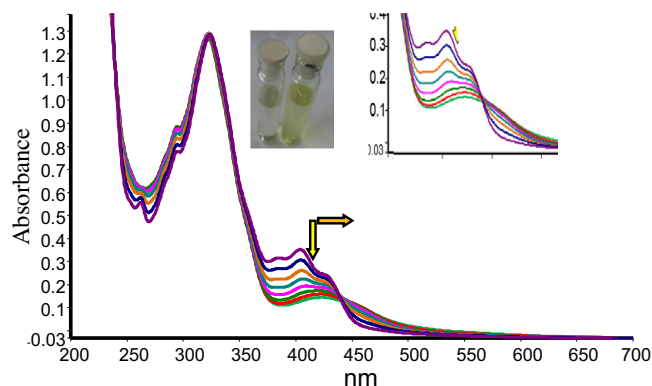


Figure 1. Change in the UV–Vis spectra of **4** ($20\text{ }\mu\text{M}$) upon addition of Cu^{2+} (0–28 μM) in CH_3CN ; inset: color change upon addition of Cu^{2+} to the solution of molecular receptor **4**.

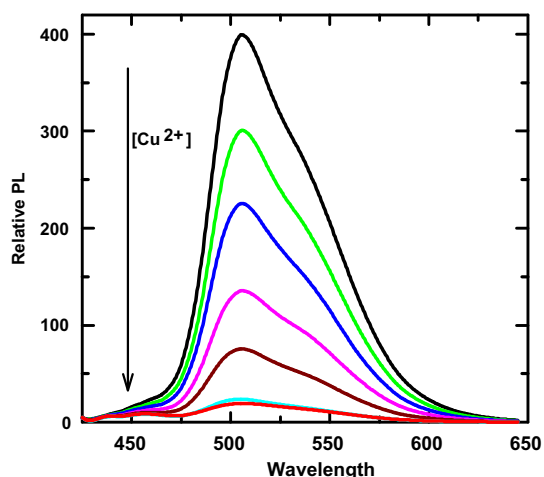


Figure 2. Quenching in the fluorescence intensity of **4** ($20\text{ }\mu\text{M}$) in CH_3CN in the presence of Cu^{2+} (0–29 μM).

Download English Version:

<https://daneshyari.com/en/article/5263461>

Download Persian Version:

<https://daneshyari.com/article/5263461>

[Daneshyari.com](https://daneshyari.com)