Journal of Molecular Structure 1041 (2013) 175–182

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

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

Synthesis and spectral properties of pyrene based calix[4]arene

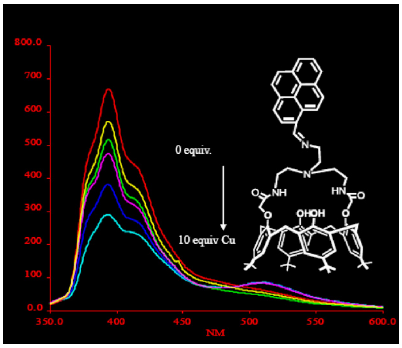
Ozlem Sahin *

Selcuk University, Department of Chemistry, 42031 Konya, Turkey

HIGHLIGHTS

- The novel Schiff base derivative of calix[4]arene was synthesized in the present study.
- The Schiff base derivative of calix[4]arene was characterized using spectroscopic techniques.
- This compound was examined for its fluorescent properties towards different metal ions and anions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 January 2013
Received in revised form 6 March 2013
Accepted 6 March 2013
Available online 19 March 2013

Keywords:
Calix[4]arene
Pyrene
Fluorescence
Metal

ABSTRACT

A new pyrene-based calix[4]arene was synthesized. This compound (**4**) was examined for its fluorescent properties towards different metal ions (Mg^{2+}, Ni^{2+}, Ba^{2+}, Ca^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}) and anions (F^-, Cl^-, Br^-, $H_2PO_4^-$, NO_3^-, HSO_4^-, CH_3COO^-) by UV, NMR and fluorescence spectroscopy. Fluorescence spectroscopy demonstrated that **4** exhibited high affinity for Cu^{2+} and low affinity for Pb^{2+}, Mg^{2+}, F^-. Quenching constant and stability constants for complexation of **4** with Cu^{2+} and F^- have been determined according to literature.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

There is a wide interest in the development of molecular sensors that can selectively detect metal ions even in low concentrations. Among the various techniques used for this purpose fluorescence-based methods have gained importance due to their sensitivity [1–8]. These methods depend upon the change of fluorescence intensity and/or a shift in the fluorescence band of the sensor upon interaction with the metal ion [9].

In recent years there has been considerable research interest in the area of molecular sensors, which can detect cations (or anions) with a high degree of specificity even at low concentrations [10–15].

The sensors often show the same design principle: a chelating ligand is attached to a fluorophore, the fluorescence of which is strongly affected by coordination of the metal ion [16].

The metal ion binding event can be transformed into a significant fluorescent signal by designing a good receptor containing a suitable fluorophore and ion-binding sites [17]. The fluorophore acts as a signaling moiety since it converts the recognition event into an optical signal via the perturbation of various photoinduced processes such as electron transfer, charge transfer, excimer formation, energy transfer or chelation-enhanced fluorescence (CHEF) effect upon cation complexation [18].

One of the essential trace elements [19] of transition metals is copper, which serves as a cofactor by taking an active part in a

---

* Tel.: +90 332 2233862; fax: +90 332 2410520.
E-mail address: oediz40@gmail.com

0022-2860/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molstruc.2013.03.016

large variety of enzymes [20–23]. Copper is the third most abundant essential trace element in the human body and is commonly found as Cu(II) in natural water, however, excessive uptake of copper causes liver or kidney damage [24–26]. Most of the reported fluorescent chemosensors for Cu^{2+} ions operate under fluorescence quenching mode because Cu^{2+} ion shows an inherent fluorescence quenching nature as a paramagnetic species [27].

Anions are ubiquitous and play important roles in many biological and chemical systems. There is an increasing interest in the design and development of receptors that selectively recognize specific anions [28,29]. For instance, considerable effort has been devoted to studies of F^- receptors because of the serious effects of F^- in the human body [30–35].

Ionophore is an important component in designing molecular sensors, its donor atoms, conformation, size, steric hindrance etc. determines selectivity [36–39]. Among various ionophores, calixarenes are an important class of macrocyclic compounds [40,41] and also an ideal platform for the development of complexing agents for heavy and transition metal ions [42–45].

We report herein the synthesis and fluorescent properties of fluorogenic pyrenyl calix[4]arenes chemosensors **4**. The perchlorate salts of Ca^{2+}, Cu^{2+}, Mg^{2+}, Ba^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} ions and tetrabutylammonium salts of F^-, Cl^-, Br^-, $H_2PO_4^-$, NO_3^-, HSO_4^-, CH_3COO^- ions were used to evaluate the metal ion binding properties of compound **4** in CH_2Cl_2:CH_3CN (1:1 v/v). When excited at 325 nm, **4** revealed emission at 392 nm. Pb^{2+}, Mg^{2+}, Cu^{2+} metal ions and F^- anion quenched the fluorescence of **4**.

2. Experimental

2.1. General

All starting materials and reagents used were of standard analytical grade from Fluka, Merck as well as from Aldrich and used without further purification. Other commercial grade solvents were distilled, and then stored over molecular sieves. The drying agent employed was anhydrous $MgSO_4$. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli Q Plus water purification system. ^1H and ^{13}C NMR spectra were recorded with a Varian 400 MHz spectrometer in. FT-IR spectra was recorded with a PerkinElmer spectrum 100. UV–Visible spectra were obtained on a Perkin Elmer UV–Visible recording spectrophotometer. Fluorescence spectra were recorded on a Perkin Elmer LS 55 spectrometer. Thin layer chromatography (TLC) was performed using silica gel on glass TLC plates (silica gel H, type 60, Merck).

2.2. Absorption and fluorescence measurements

Absorption spectra of ligands (1×10^{-6} M for fluorescence measurements and 1×10^{-4} M for absorption measurements) in CH_3CN:CH_2Cl_2 solutions containing 10 equiv. of the appropriate metal perchlorate salt were measured using a 1 cm absorption cell. Fluorescence spectra of the same solutions were measured with a 1 cm quartz cell. The excitation wavelength was 325 nm for **4**. Fluorescence emission spectra were recorded in the range 200–800 nm with a slit width of 1.0 nm. The stoichiometries of the complexes and their stability constants were determined according to a literature procedure.

2.3. Synthesis

The compounds **1**, **2** and **3** were synthesized according to the literature [46,47] procedures and the other compounds (**4**) employed in this work as illustrated in Scheme 1 were synthesized according to the procedure are given in the supporting information.

3. Results and discussion

3.1. Synthetic routes

The preparation receptor **4** is observed in Scheme 1. Compounds **1** [46], **2** [46] and **3** [47], were prepared according to the published procedures. First, *tert*-butylcalix[4]arene **1** was reacted with methyl bromoacetate in the presence of acetone to give **2**. To give the amide derivative of calix[4]arene **3, 2** was treated with tris(2-aminoethyl)amine. Then **3** was reacted with 1-pyrenecarbaldehyde to give the receptor **4**.

The structures of compound **4** were confirmed from their spectroscopic and analytical data. The IR spectra of compound **4** showed a stretching band 1662 and 1632 cm^{-1} due to C=O and C=N groups, respectively.

Figs. 1 and 2 illustrate the assignment of the ^1H NMR and NMR COSY spectrum.

The ^1H NMR spectrum of **4**, exhibited two singlets (18H each) for tert-butyl protons at δ 0.99 and 1.25 ppm, four broad singlets for NCH_2 protons δ 2.72, 2.83, 3.60, 3.06 ppm. The NMR COSY spectrum of **4,** a correlation peak that appeared for the coupling of two broad singlet at δ 3.06 and at δ 2.72 could be assigned to Hd and He protons. A correlation peak that appeared for the coupling of a broad singlet at δ 2.84 and a broad singlet at δ 3.60 could be assigned to Hb and Hc protons. The methylene bridge ($ArCH_2Ar$) protons appeared as an AB pattern for **4** at δ 3.40 and 4.20 ppm. The other correlation peak that appeared for the coupling of a dublet at δ 3.40 and a dublet at δ 4.20 could be assigned to $ArCH_2Ar$ protons. Two singlets (4H each) for aromatic protons (ArH) of **4** appeared at δ 6.88 and 7.07 ppm. Two dublet and two multiplet (9H) for pyrene protons and (1H) imino proton apeared at δ 8.47, 9.45, 8.07–8.13 and 7.23–8.36 ppm. The coupling of the doublet and multiplet at δ 9.47 and at δ 8.34 gave a cross correlation peak which indicated that these signals corresponded to the aromatic protons of pyrene unit of the molecule. Similarly the other correlation peak that appeared for the coupling of two multiplet at δ 8.48 and δ 8.28, at 8.27 and δ at 8.13 for the aromatic protons indicated that these signals correspond to the aromatic protons of pyrene unit. One triplet (2H) for amide protons seemed at δ 9.10 ppm. A correlation peak that appeared for the coupling of a triplet at δ 9.10 and a broad singlet at δ 3.60 could be assigned to Ha of amide protons and Hb of CH_2 protons.

3.2. Absorption spectrum

The cation binding properties of compound **4** were investigated by UV–vis and fluorescence spectroscopy. The titration experiments were carried out in CH_2Cl_2:CH_3CN (1:1 v/v) by adding of Pb^{2+}, Mg^{2+} and Cu^{2+} ions. The UV–vis absorption spectra of the compound **4** exhibit typical pyrene absorption bands at 360 nm for compound **4** (Fig. 3). Upon addition of increasing amounts Pb^{2+}, Mg^{2+} and Cu^{2+} ions (0–10 equiv) to a solution of **4**, it was observed that intensity of the absorption peak changed at 453 and 290 nm.

3.3. Fluorescence spectra

The fluorescence spectrum of compound **4** gave an emission at 392 nm by excitation of the pyrene moiety of **4** at 325 nm. There was highly selective fluorescence quenching effect in its emission with Cu^{2+}, Pb^{2+} and Mg^{2+} among the metal ions examined. (Fig. 4).

Download English Version:

https://daneshyari.com/en/article/1408862

Download Persian Version:

https://daneshyari.com/article/1408862

Daneshyari.com