



Novel calix[4]pyrrole assembly: Punctilious recognition of F⁻ and Cu⁺² ions



Keyur D. Bhatt ^{a,*}, Hemangini Shah ^b, Krunal M. Modi ^c, Anita Kongor ^c,
Manthan Panchal ^c, Vinod K. Jain ^c

^a Department of Chemistry, Ganpat University, Kherva 384012, India

^b Department of Chemistry, C. U. Shah University, Wadhwan-City 363030, India

^c Department of Chemistry School of Sciences, Gujarat University, Ahmedabad 380009, India

ARTICLE INFO

Article history:

Received 7 June 2017

Received in revised form

24 July 2017

Accepted 2 August 2017

Available online 3 August 2017

Keywords:

Calix[4]pyrrole

Colorimetric sensor

Spectrophotometric titration

Molecular docking

ABSTRACT

A new tetra hydroxyl methoxy substituted calix[4]pyrrole (HMCP) has been synthesized and found to form stable complex with F⁻ ions and Cu⁺² ions. The red-shift in absorption band of HMCP was observed due to the presence of both cation (Cu⁺²) and anion (F⁻). These results displayed that formation of the complex is mainly attributed to the charge–transfer interactions between HMCP with electron deficient pyrrole rings and the electron-rich guest ions. Molecular dynamics simulation predicts intermolecular H-bonds and van der Waals types of interaction for the complex formation of HMCP-Cu⁺² and HMCP-F⁻.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The field of ion binding chemistry, is one of the important frontiers in the generalized area of supramolecular chemistry and molecular recognition [1]. Anion and cation receptors are an important class of devices within supramolecular chemistry [2–6]. A number of different receptor systems are known to respond to cations [7,8] and anions [9,10], on pairs and some even give a colorimetric [11–14] response upon recognition of the targeted substrate. Calixpyrroles [15] are macrocyclic compounds that consist of pyrrole units linked through the pyrrolic 2 and 5 positions by sp³ hybridized carbon atoms. They are readily obtained by acid-catalyzed condensation of pyrrole with ketones. Calixpyrroles [16,17] have recently been studied as receptors for possible use in optical or electrochemical recognition of anions and HPLC supports for the separation of anions and neutral substrates [18,19]. The calix[4]pyrrole macrocycle tetramer represents one of the most successful chemoreceptors [20] so far developed by chemists for the spherical recognition of halide anions [21,22]. Calix[4]pyrroles as a representative class of neutral macrocycle receptors, first reported by Sessler and coworkers, are

capable of selective binding anions and neutral substrates [23] both in the solution and the solid states. These calix[4]pyrroles were strapped using flexible straps via 1,3-linkage to benzene derivatives and 2,5-heteroarenes having diester, diether and diamide based alkyl chains [24].

Calix[4]pyrrole is among such which holds a great promise in the fields of sensors, and their unique behaviour as sensors attributed due to its structural flexibility. Calix[4]pyrrole can be modulated by various structural modification [25] or change in solvent [26]. The meso-position or at β-pyrrolic positions of calix[4]pyrrole undergoes changes by introduction of electron-releasing and electron-withdrawing forming deep cavities and fixed walls which lead to increase selectivity and binding effects [27]. The modified calix[4]pyrrole shows tuneable modified binding property [28,29], high selectivity as well as sensitivity acting as punctilious recognition towards ions.

The interest in fluoride chemistry is escalating as a result of the importance of their role. Fluoride anions is currently used as a tool for dental caries control and prevention, it is now well-established that its uncontrolled use may cause odontogenesis disturbance and cytotoxicity on soft tissues.

Calix[4]pyrroles are macrocyclic species with an array of four N–H bonds that act as binding sites for anionic and electron-rich neutral guests in organic solvents. Interestingly, the anionic and

* Corresponding author.

E-mail address: drkdbhatt@outlook.com (K.D. Bhatt).

electron-rich neutral guests organize calix[4]pyrrole into a cone conformation, which provides an electron-rich cup that putatively binds cations. Copper is an important trace element for most organisms in all kingdoms. In humans, copper plays role as a cofactor for numerous enzymes, such as Cu/Zn-superoxide dismutase, cytochrome c oxidase, tyrosinase, ceruloplasmin and other proteins, crucial for respiration, iron transport and metabolism, cell growth, haemostasis. Copper forms stable complexes with drugs, amino acids [30] and fluorescence molecules [31]. Administration of copper in a form of organo-metallic complexes can be done in order to selectively deliver copper ions or radionuclides to diseased tissues, or to modify pharmacokinetics and/or pharmacodynamics of ligands [32].

This report describes the synthesis of novel hydroxyl methoxy substituted calix[4]pyrrole (HMCP).

In this paper we report the synthesis and characterization of novel hydroxyl methoxy substituted calix[4]pyrrole (HMCP). The interesting features of this ligand (HMCP) are that shows both cation and anion sensing properties at very low concentration. Ion binding, stoichiometric ratio, linearity and molecular docking study have been determined.

2. Experimental section

2.1. Chemicals and reagents

Tetra ammonium salts, metal nitrate salts and other chemicals were obtained from Sigma-Aldrich. Silica gel and fluorescence active TLC plates (F-2009) were purchased from the Merck. All aqueous solutions were prepared with quartz distilled deionized water, which was further purified by a Millipore Milli-Q water purification system. All the solvents employed for synthesis were commercially available and used as received without further purification.

2.2. Instruments

The melting points (uncorrected) were obtained from a VEEGO (Model; VMP-DS, (Mumbai, India). Samples for infrared spectra were prepared as KBr pellets, spectra were recorded on tensor Bruker 27 (Ettlingen, Germany) and expressed in cm^{-1} . Elemental analysis (C,H and N) was performed on varioMICRO-Variant elemental analyser (Mt. Laurel, USA). Electro-spray ionization (ESI) mass spectra (MS) were determined using Micromass Quarter2 (Utah, USA). NMR spectra were recorded on a model DPX 200 MHz and Avance II500 MHz Bruker FT-NMR instruments (Ettlingen,

Germany).UV–Vis spectra were recorded on a JASCO spectrophotometer (Easton, US).

2.3. Synthesis of HMCP

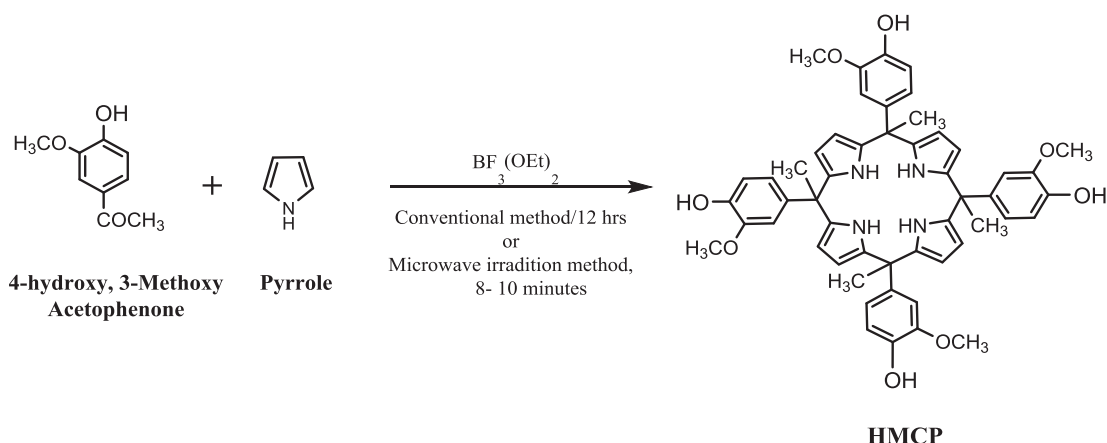
2.3.1. Conventional method

Parent 4-hydroxy, 3-methoxy-substituted calix[4]pyrrole skeleton was synthesized by the following general method of acid catalyzed condensation reaction of pyrrole (HMCP) and 4.0 gm (0.02 mol) of 4-hydroxy,3-methoxyacetophenone and 1.7 mL (0.02 mol) of freshly distilled pyrrole, were dissolved in 100 mL of MeOH. To the above solution 3.17 mL (0.025 mol) of $\text{BF}_3(\text{OEt})_2$ were added dropwise. The reaction mixture was stirred for 12 h at room temperature and there after it was quenched by the addition of 100 mL of water and 2.5 mL of triethylamine. The organic solvent was evaporated in vacuum and the resulting aqueous solution was extracted with diethyl ether (3×100 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure obtaining 6 gm of a solid residue. A precipitate was obtained, when trying to dissolve the solid residue in 10 mL of the eluent mixture before charging the column. Column chromatography on silica gel of the dissolved solid residue using a 1:1 mixture of ethyl acetate and Hexane containing 5% of acetic acid. Acetonitrile was used to recrystallize the compound HMCP.

2.3.2. Microwave irradiation method

A mixture of 2.23 gm (0.0146 mol) 4-hydroxy, 3-methoxy acetophenone and 1.0 mL (0.0146 mol) of freshly distilled pyrrole were dissolved in 30 mL of methanol. To the above solution 1.5 mL of $\text{BF}_3(\text{OEt})_2$ was added dropwise. The reaction mixture was subjected to microwave irradiation for approximately 8–10 min with a break of 1 min each, for the purpose of stirring, after regular interval of 2 min. After 8–10 min, the dark orange colour mixture was quenched in 200 mL of distilled water with constant stirring. Triethylamine was added dropwise to neutralize the acid. Light brown coloured precipitation was filtered quickly and made soluble in ethyl acetate or diethyl ether, dried over MgSO_4 concentrated to get Compound HMCP, which were further separated and purified by column chromatography to get white crystalline compound HMCP.

White solid (60% yield). M.P. 184°C . FT-IR (KBr disk): 3414, 1616 cm^{-1} . $^1\text{H-NMR}$ (500 MHz, $\text{DMSO}-d_6$): 1.83 (s, 12H), 3.71 (OCH_3 , d, 12H), 5.6–5.8 (d, 4H); 5.8–6.1 (d, 4H); 6.4–7.4 (m, 12H); 7.6 (m, 4H); 8.7 (s, 4H). $^{13}\text{C-NMR}$ (500 MHz, $\text{DMSO}-d_6$): 154.6, 149.2, 131.1, 128.74, 126.5, 119.3, 98.7, 54.7, 48.5, 46.5, 14.6. ESI-MS m/z : 862 $[\text{M} + 1]$.



Download English Version:

<https://daneshyari.com/en/article/5160000>

Download Persian Version:

<https://daneshyari.com/article/5160000>

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