Functionalized Calix[4]Pyrrole For Selective and sensitive detection of lead ions

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Abstract:

The synthesis of metal ion sensors by eco-friendly synthetic methods is very important aspects in the field of suparamolecular chemistry and a wide variety of applications in the field of molecular sensors, biotechnology, biomedical science and organic chemistry. In this study, we reported quick, easy and complete green route for the detection of lead ions in a very low concentration in aqueous solution. Glycine derived acetyle benzaldehyde functionalized Calix[4]Pyrrole - (GABCP) were synthesized and it is tested with the variety of metal ions like Cu^{+2}, Ni^{+2}, Fe^{+2},Cr^{+2}, Cd^{+2}, Co^{+2}, Hg^{+2}*and* Pb^{+2}.*We found that this GABCP is very selective and sensitive fluorescent sensor for the quick and rapid detection of lead ion as it shows fluorescence enhancement only with lead ions even at a very low concentration* 10^{-7} *M. The method has been very successfully applied for the determination of lead ions in ground water and Industrial effluents and Waste water.*

Keywords: *Calix[4]Pyrrole, Fluorescent 'turn – on' sensor, Lead*

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1. Introduction

The field of suparamolecular chemistry has blossomed over the last twenty years and need for nanotechnology will only increase as miniaturization becomes very important in area of computing [1], sensors[2], biomedical applications[3], material science and organic chemistry for their function as molecular markers, catalysts and diagnostic properties[4]. It is highly challenging to do a selective and effective functionalization on a multifunction macrocylic unit bacause it requires a very efficient control in chemoselectivity, sterioselectivity and regioselectivity. Molecular Scaffolds which are prepared by some easy chemical synthesis, functionalization modification and designed recognization system makes Supramolecules as a very effective Molecular Receptos[5] that is a 'Host' molecule[6-8]. A variety of supramolecular organic receptors like crown-ethers, cryptands, spherands, calixarenes have been developed and synthesized that having a wide variety of application and further very fast growing in the area of research.

Calixarenes are the third generation supramolecules[9-11]. The term calixarene was first given by C. D. Gutsche in 1978. The word calixarene is derived from the greek word calix means vase or cone shape conformation. Calix[4]pyrrole, a white crystalline solid material was firstly synthesized by Bayer in 1886. Bayer obtained calix[4]pyrrole by the condensation reaction of pyrrole with acetone in the presence of hydrochloric acid as as acidic medium in a single step with high yield.

In 1990, Floriani and Co-workers by their considerable work on metallation and stimulate the synthetic chemistry of deprotonated calix[4]pyrrole[12-15]. Sessler et al. first reported the synthesis of meso-octamethyle calix[4]pyrrole act as a host molecule due to its cone structure and have a extraordinary binding capabilities with different anions[16], cations and neutral guest species[17] through the –NH group present in the pyrrole ring that acting as a multiple hydrogen bonding donor under different conditions[]. All these versatile properties of calix[4]pyrrole makes them a ground platform for the variety of further modification.

In present investigation we have reported the synthesis of Glycine derived Acetyle benzaldehyde functionalized Calix[4]Pyrrole (GABCP), characterization, absorption and fluorescence study with different metal ions like Cu^{+2}, Ni^{+2}, Fe^{+2},Cr^{+2}, Cd^{+2}, Co^{+2}, $Hg^{+2}$and Pb^{+2}. We observed that GABCP shows fluorescence enhancement only with lead ions even at a very low concentration of 10^{-7} M in aqueous solution of metal ion and having no any change in fluorescent intensity when treated with other metal ions. GABCP here therefore act as a Fluorescent “turn – on” sensor for the detection of lead ions which can only sense lead ions even in a very low concentration from ground water, Industrial effluents and waste water.

2. Experimental

2.1 Reagents and Solutions

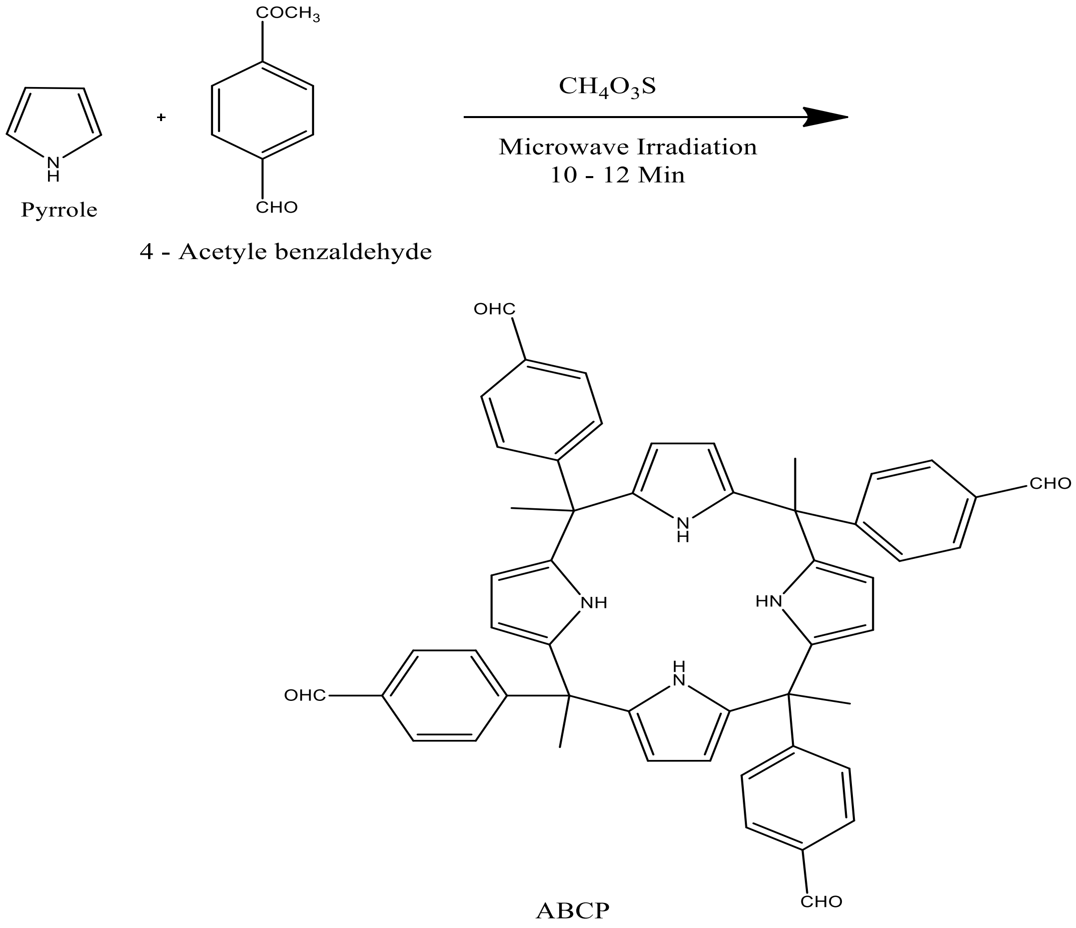
Experimental procedure follows the preparation of Calix[4]Pyrrole by reported method. All chemicals were of analytical grade and used as received without further purification. Metal nitrate and chloride salts, Pyrrole and other chemicals were obtained from Sigma-Aldrich and E. Merck. All aqueous solutions were prepared with quartz distilled deionized water. The stock solutions of metal ions were prepared from their nitrate and chloride salts in double distilled water.

2.2 Apparatus

VEEGO Model was used to obtain the melting points (uncorrected). KBr pallets were used for Samples preparation in infrared spectra. Tensor Bruker 27 (Ettlingen, Germany) spectra were used for recording and spectra were stated in cm-1. Elemental analysis of C, H and N was carried out by MICRO-Variant analyzer (Mt. Laurel, USA). Micromass Quarter 2 (Utah, USA) instrument was used for Electrospray ionization (ESI) mass spectra (MS). FT-NMR instruments (Ettlingen, Germany). Jasco spectrophotometer (Easton, US) was used for measuring UV-Vis spectra while Jasco spectrofluorimeter FP 8300 (xenon lamp headxe90) spectrometer (Livingston, US) was used for measuring fluoroscene spectra.

2.3 Synthesis of 4-Acetyle Benzaldehyde functionalized Calix [4]Pyrrole by Microwave irradiation technique

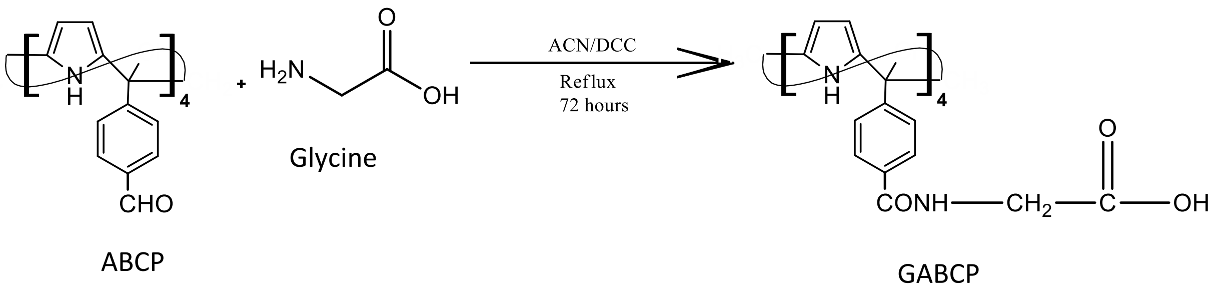
The Mixture of 1.0 ml Pyrrole (0.015 mole) and methane sulfonic acid (0.1 ml) is taken in methanol (10 ml) and then subjected to microwave irradiation for 10 min. A solution of 4-Acetyle benzaldehyde (2.22 gm, 0.015 mole) prepared in methanol (10 ml) was added to pyrrole reaction mixture and then subjected to microwave irradiation for 10 min with every two-minute break. Dark brown-black mixture was obtained after completion in reaction. The mixture was then decanted in cold water (50 ml) to obtain a precipitate of brown black colored residue. The residue was filtered, dried and further dissolved in solution of diethyl ether (25 ml x 2). Again, filtration was carried out to remove black tar. The residue obtained after evaporation was then recrystallized from a methanol mixture to get pure product for analysis. **(Scheme 1)**



Scheme 1. Synthesis of ABCP

2.4 Synthesis of Glycine Derived ABCP

1g ABCP (0.006 mole) is dissolved in 50 ml of acetonitrile is taken in roud bottom flask and a solution of 0.33 gm Glycine (0.0044mole) added into flask containing ABCP and 1 ml of N,N'-Dicyclohexylcarbodiimide (DCC) is added into the reaction mixture. The reaction mixture is then refluxed for about 72 hours and then cooled at room temperature and added into the cold water (50ml) to obtain residue. The residue were filtered and dried. Again the residue were dissolved in diethyle ether. The residue obtained after evoparation were then recrystallized from methenol to get pure product.**(Scheme 2)**



Scheme 2. Synthesis of Glycine derived ABCP (GABCP)

2.5 Characterization of Ligands

2.5.1 Characterization of ABCP

Dark Brown, Yield; 78%, Melting Point: 218 °C, Molecular Weight: 852.93, Elemental Analysis calc. ($C_{52}H_{44}N_4O_4$) (%) C, 79.16 ; H, 5.62 ; N, 7.10 ; O, 8.11, Found ; C,78.31 ; H, 5.08 ; N, 6.97 ; O, 8.00. FT-IR (KBr) (cm^{-1}) 1730 (Aromatic aldehyde), m/z, ESI-MS (M+1) 788.34 (100%).

2.5.2 Characterization of GABCP

Deep Brown Black, Yield: 70%, Melting Point: >300 °C, Molecular Weight: 1081.13, Elemental Analysis calc. ($C_{60}H_{56}N_8O_{12}$) (%) C, 66.66 ; H, 5.22 ; N, 10.36 ; O, 17.76, Found ; C, 65.67 ; H, 5.01 ; N, 10.12 ; O, 17.89. FT-IR (KBr) (cm^{-1}) 3150 (aliphatic carboxylic acid), m/z, ESI-MS, (M+1) 1080.40 (100%).

3. Result and Discussion

3.1 Absorption Study

Stock solution of the GABCP and that of the nitrate and Chloride salts of various cations Cu^{+2}, Ni^{+2}, Fe^{+2},Cr^{+2}, Cd^{+2}, Co^{+2}, Hg^{+2}and Pb^{+2} (2 x 10^{-4} M) were prepared in aqueous solution. Then 2 ml stock solution of the GABCP and 2 ml stock solution of each cations salt were taken in a 5 ml volumetric flask, so that the effective concentration of of cations are 1 x 10^{-4} M. The absorption spectra of the resulting solutions and that of the original GABCP were recorded with excitation at the absorption maxima (λmax) at 433 nm. SPR absorption maxima of GABCP, depicted in **Fig 1**., did not show any significant shift on interacting with all the other cations Cu^{+2}, Ni^{+2}, Fe^{+2},Cr^{+2}, Cd^{+2}, Co^{+2}and Hg^{+2}except Pb^{+2} However, 10 $^{-4}$ M of solution of Pb^{+2} caused a shift of 20 nm towards the lower wavelength region (blue shift). To study the effect in more detail, different concentrations of aqueous solutions of Pb^{+2} ranging from 10^{-9} M to 10^{-4} M were prepared and the SPR absorption was recorded. SPR absorption bands shifted proportionally from 428 nm to 408 nm with different concentrations of Pb^{+2} ion. The blue shift in the spectra was found to vary almost linearly with the concentration of Pb^{+2} ions.

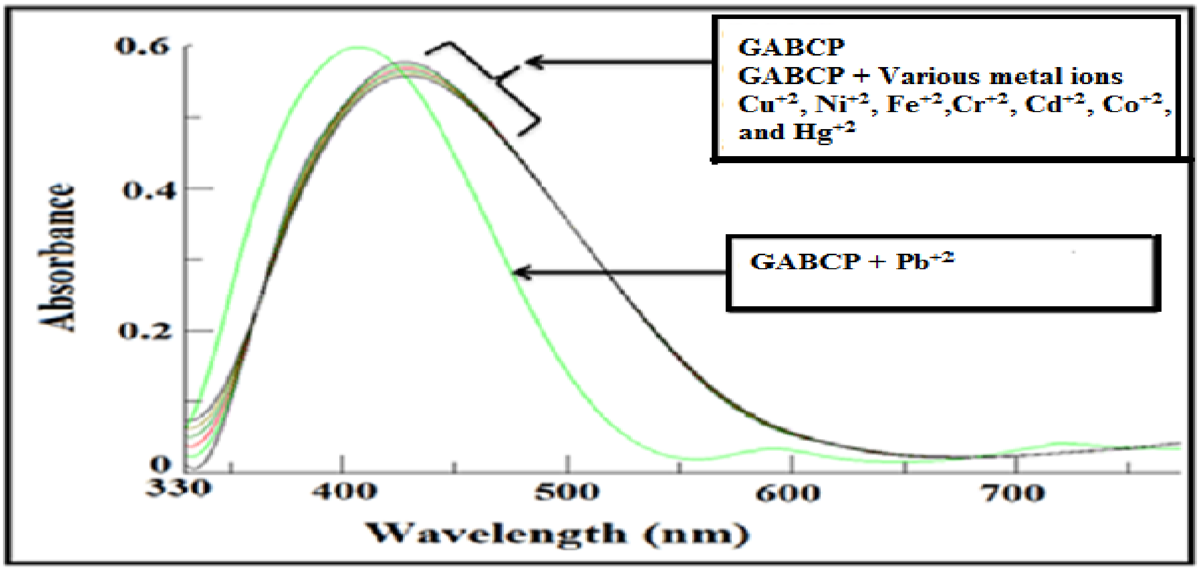


Fig. 1: Absorption Spectra of GABCP with Variuos Metal Ions

3.2 Fluorescence Study

Chemically synthesized GABCP shows a yellowish-brown color in aqueous solution The color recognition properties of the GABCP toward different metal ions were studied by the several methods such as the naked-eye experiment, the UV–Vis titration[18]. The response of the naked-eye experiment of GABCP toward a set of cations Cu^{+2}, Ni^{+2}, Fe^{+2},Cr^{+2}, Cd^{+2}, Co^{+2}, Hg^{+2}and Pb^{+2} was studied in aqueous solution. In these experiments, all the metal ions (10^{-4} M) do not show any color changes but only Pb^{+2} shows noticeable deep color change from yellow to colourless in the presence very low concentration (10^{-7} M)

We investigated the selectivity of our new approach for Pb^{+2} over other metal ions under the same conditions. The solution of GABCP after addition of other ions has fluorescence emissions at about 578 nm. Importantly, the fluorescence of the GABCP was enhance completely in the presence of Pb^{+2} ion, while fluorescence enhancement was not observed in the presence of other metal ions and the concentration of other ions was 10–100 times more higher than that of Pb^{+2} solution **(Figure 2)**. The results showed that the fluorescent intensity of GABCP was hardly affected by Pb^{+2} ions even up to the 120 times increase. The high selectivity of GABCP for Pb^{+2} with compared to the other metal ions should because of the strong coordination ability of Pb^{+2} then other metal ions.

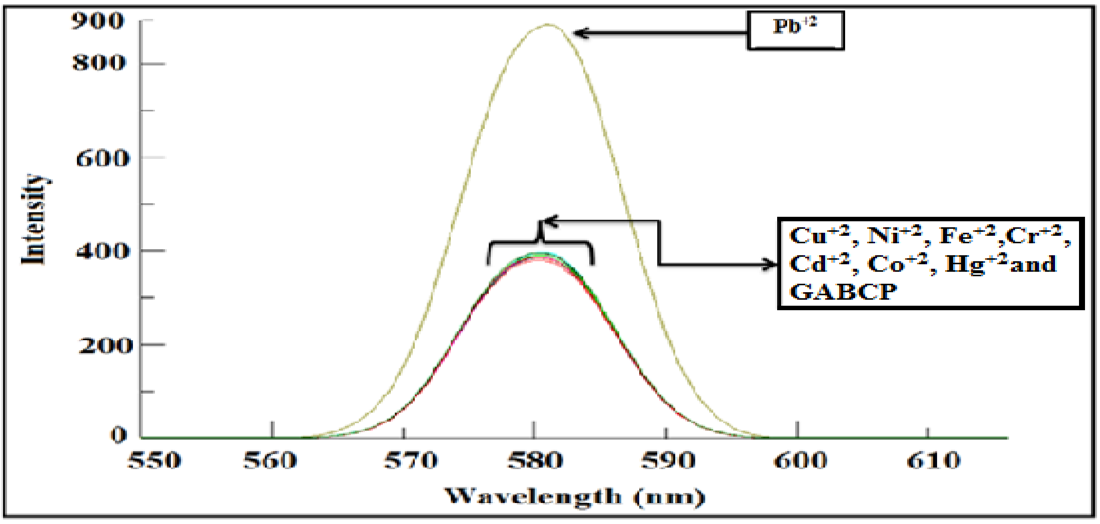


Fig. 2: Emission Spectra of GABCP with various metal ions

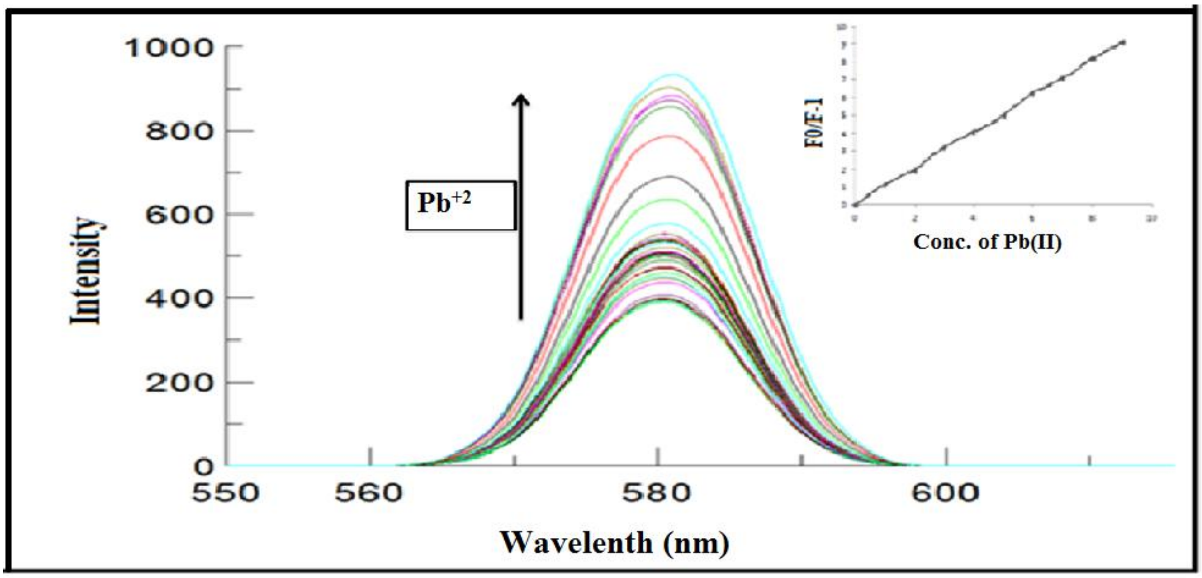


Fig. 3: Fluorescence responce of GABCP on addition with Pb^{+2} solution and inset shows stern-volmer plot

4. Conclusion

In conclusion, Glycine based Acetyle benzaldehyde functionallized Calix[4]Pyrrole were sucessfully synthesized. Absorption study indicates that there is no any change in absorption maxima observed with metal ions like Cu^{+2}, Ni^{+2}, Fe^{+2},Cr^{+2}, Cd^{+2}, Co^{+2}, Hg^{+2} but noticable blue shift is of 20nm is observed when GABCP solution is treated with Pb^{+2} even at a very low concentration of 10^{-4}M. The absorption band varies propotionally from 428nm to 408nm with different concentration of Pb^{+2} . Fluorescence study revels that this newly synthesized GABCP possess high selectivity for Pb^{+2} by showing enhancement in fluorescence intensity. Enhancement in fluorescence intensity suggests that GABACP could be act as a ‘turn-on’ fluorescent sensor for the detection of the Pb^{+2}. The results shows that Pb^{+2} can be detected very selectively and sensitively by GABCP in various samples like ground water, industrial effluents and waste water and this functionalized calix[4]pyrrole has a very potential application in the field of biolebaling, biosensing and many more. GABCP can also be explored for the use in the detection of Pb^{+2} in environental and biological samples.

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