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ARTICLE

Dual Responsive Salen-type Schiff Bases for the Effective Detection of L-Arginine *via* Static Quenching Mechanism.

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L-Arginine is one of the most important amino acid and plays a key role in diagnostic studies. Herein we report four Salen-type Schiff base fluorimetric/colorimetric sensors for the rapid detection of L-arginine. Substituents play a major role in the sensing mechanism of the probes with the nitro-substituent bearing probe showing the highest efficiency. Evidence of a 1:2 complexation between all the probes and the analyte was evidenced from the absorption titrations; and the fluorescence studies revealed quenching phenomenon occurring during complex formation. From the life time measurements, the nature of quenching was found to be static and the formation of a ground state complex was confirmed. DFT calculations done at B3LYP/TZVP level of theory corroborated the experimental findings and further established the proton transfer happening from probe to the analyte during the complex formation.

Introduction

L-Arginine is the most propitious, naturally occurring amino acid among the non-thiol containing amino acids. The most inimitable property of Arginine among the rest of the natural amino acids is the high basicity of one of its terminal position *i.e*. guanidine part.[1] Its pKa value is found to be 13.8 and is a conditionally essential amino acid.[2] It is also found in cerebral system in 14µM concentration and has the highest isoelectric point[3]. Studies especially sensing appertaining to the detection of L-Arginine(L-Ar) has inordinate importance in the scientific community as well as in the medical and biological fields[4]. Arginine is one of the most important diagnostic indicator for some of the human diseases like hypertension, renal damage and also the varying concentration of Arginine or its derivatives cause many health issues that can even lead to death.[5, 6] Administration of L-Ar orally on patients with preeclampsia was found to accelerate foetal gain and improve biophysical profile.[7] Arginine also plays a pivotal role in the pathophysiology of hyperammonemia disorders and astrocytes of aggregating neural cell culture.[8]

Biological functions of Arginine include secretion of certain hormones such as insulin growth hormone, glucagon and prolactin.[9] It also has a vital role in cell division, healing of wounds *etc*. Nitric oxide which has many biological functions is also produced from the conversion of L-Arginine into Citrulline.[10] Besides these, some cell-cell, signalling molecules are also generated from Arginine in the presence of oxygen. Owing to its ability to attain different charge states, Arginine is involved in a large number of crucial biochemical process which includes some steps of metabolic pathways, trans-membrane transport *etc*. Also, Arginine is essential for the quantum chemical study of the interactions involved in proton transfer and other selective binding processes.[1, 2]

Extensive methods are available in the literature for the selective detection of Arginine. Apart from the voluminous data of detecting Arginine using methods like HPLC, mass spectrometry *etc*. Reports are there in the literature for the detection of thiol-containing amino acids using fluorescent probes. Fluorescent sensors for the detection and sensing of amino acids other than thiol-based ones are limited in number and still limited when it comes to colorimetric as well as fluorescent sensors.[11-13]

Among the reported sensors colorimetric detection are mainly reported in the field of gold based nano particles, which again has a limitation *i.e.* incorporation of costly Au particles.[9, 14, 15] Works including fluorescent, electrochemical and surface plasmon resonance detection of Arginine were reported but the sensor or probe used for this purpose are mainly of macrocyclic type like crown ether and quantum dots (QDs).[3, 16-18] These methods also bear some unavoidable limitations such as poor solubility, advanced experimental set up, sophisticated characterization methods and the use of costly metals. Recently colorimetric as well as fluorescent probes were

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IR, UV-VIS ^{1}H-NMR spectra, GC-MS data, crystal data refinement table and, hydrogen bonding interactions, Jobs plots, life-time data, K_{SV} value and Stern-Volmer plot, fluorimetric response times. CCDC 1845374 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.] [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x