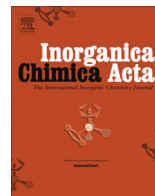




Contents lists available at ScienceDirect

Inorganica Chimica Acta

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Review

Detection of alkali and alkaline earth metal ions by fluorescence spectroscopy



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ARTICLE INFO

Article history:

Received 13 November 2013
 Received in revised form 1 March 2014
 Accepted 4 March 2014
 Available online 20 March 2014
 Metals In Supramolecular Chemistry Special Issue

Keywords:

Fluorescence signaling
 Alkali metal ions
 Alkaline earth metals
 Fluorophores
 Receptors

ABSTRACT

Alkali and alkaline earth metal ions are important from biological perspectives. These ions play diverse roles in bio-systems and their concentration in extracellular as well as in intracellular fluids should be known to understand several physiological processes. Fluorescence spectroscopy being a sensitive and powerful analytical technique has been used to detect the presence of these ions. The fluorescence signaling systems comprise of fluorophore and receptor moieties that may be separated through spacers or integrated into one unit. The receptor unit is designed to bind a particular metal ion in presence of others. A large number of receptors are designed and connected to different fluorophores for signaling the presence of alkali and alkaline earth metal ions.

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1. Introduction

Fluorescence sensors allow the event of binding of an analyte to a receptor to be conveniently transmitted to the macroscopic world via emission/quenching of fluorescence [1–5]. Since the fluorescence technique is highly sensitive, very small amount of an analyte can be detected. This is of crucial importance in biological systems where metal ions playing crucial roles often exist in μM quantities [6]. For practical applications, specially to detect a metal ion and its concentration in biological fluids, fluorescence enhancement rather than quenching is of importance. Also, the emphasis should be on the discrete and stoichiometric binding of an analyte although non-stoichiometric binding such as solvation can potentially afford useful information. The present review does not give an exhaustive list of sensors and we apologize if we have missed to refer to any important systems.

2. Design principles

Fluorescence signaling systems essentially comprises of a fluorophore and a receptor moieties that can either be separated through a spacer or integrated into one system (Scheme 1).

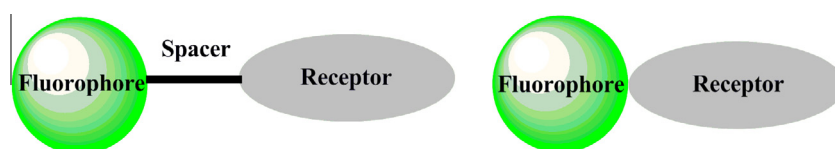
Fluorescence signaling systems where the fluorophore and the receptor are connected through a spacer are easier to design and synthesize compared to the ones where they are integrated. The spacer can act as a signal transducer and hence its length as well as nature is of utmost importance. The fluorophore should be chosen keeping in mind its excitation and emission wavelengths, quantum yield of emission, photo and chemical stability, easy availability and amenability of derivatization to integrate into the whole system. While fluorophores showing emission across the visible spectrum can be used, for biological work it is better to use fluorophores that emit at wavelengths longer than 600 nm [7]. The receptor design also requires a lot of attention. An ideal receptor should have high selective power in favor of a particular analyte in presence of many others that may be present in large excess. Besides, the receptor should bind the analyte strongly enough such that it is not replaced by solvent molecules under high dilution conditions that usually prevail in fluorescence measurements [8].

Finally, for biological studies, cell viability of the fluorescent complex and the solvent are two important parameters. It is highly preferred that the metal complex of the signaling system be soluble in water or aqueous alcoholic solvents for live cell imaging studies as other organic solvents may not be cell-viable. Obviously, design of the fluorophore as well as the receptor assumes great importance.

3. Sensors for Li⁺

Lithium-containing drug preparations are used in the treatment of manic-depressive psychosis [9,10]. The patients are required to take a drug for several months or years depending upon the conditions. However, the concentration of Li⁺ in blood after drug intake should be in the narrow range of 0.6–1.2 mM for its effective and safe use. This means a rapid and reliable determination of the ion in blood is of crucial importance for its safe therapeutic use. Apart from this, spatial distribution of the ion in lithium batteries can be studied by fluorescence spectroscopy to study Li⁺ ion transport in lithium batteries.

The fluoroionophore **1** and its polymer immobilizable derivative **2** have been designed and synthesized [11]. The tetramethyl-14-crown-4 shows excellent selectivity towards Li⁺ ($\log k_{\text{Li}^+,\text{Na}^+} = -2.6$) as the tetramethyl substituents do not allow two ionophores to come closer to form sandwich complexes with larger alkali metal ions. Besides, the crown ether contains no proton ionizable groups to ensure pH-independent binding of the Li⁺ ion. A coumarin is integrated into the ionophore as it shows bright emission over a wide pH range. In aqueous methanol (1:99 v/v), **1** exhibits an intense ICT band at 426 nm which is blue-shifted upon addition of Li⁺ ion due to stabilization of the ground state. With increasing concentration of Li⁺ ion, this band at 426 nm is quenched along with an enhancement of the shoulder at 380 nm. The appearance of the shoulder allows ratiometric processing of the intensity data at two wavelengths. While other ions such as Na⁺, K⁺, Mg²⁺ and Ca²⁺ do not interfere, the low solubility in a 100% aqueous medium considerably limits its analytical applicability. To surmount this problem, sensor **2** has been designed incorporating an unsaturated alkyl chain as the immobilizing site to a hydrophilic polymer optode membrane. The system can sense Li⁺ ion in aqueous



Scheme 1.

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