



Review

Addressing of multiple-metal ions on a single platform



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ABSTRACT

Multi-stimuli responsive “smart molecules” exhibit measurable responses in the presence of external stimuli. The output signal can be measured by exploiting one or more than one physical characteristics of the molecule-stimulus couple. Distinct responses by smart molecules after interaction with different metal ions at low concentration allow selective multiple-metal sensing. The focus of this review will be on the basic design principles of multi-metal responsive molecular systems, the broad array of their potential applications and further challenges to be accomplished in this rapidly developing area. In particular, addressing of multi-metal ions at single platform has been described with two aspects: (i) access of differential responses through a single channel or (ii) access of wide-ranging sensor-stimulus interactions through multiple channels. These state-of-the-art methodologies demonstrate the large scope and diversity in terms of metal ion screening, combinatorial approach to address the sensor characteristics, activation mechanism and utilization of multiple techniques for sensing prospects.

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1. Introduction

Stimuli responsive molecules show great potential as they may be used in many fields, including supramolecular chemistry, biochemistry, physical and organic chemistry, nanotechnology and material sciences. Recent developments in this interdisciplinary research area have established that these molecular systems show considerable promise as a result of their diverse utilization in

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molecular recognition, molecular switching, molecular logic, drug delivery, molecular data-storage *etc.* These molecules respond to external stimuli (*i.e.*, light, heat, electric field, chemicals, cations, anions, pH, and/or solvent polarity) and generate coherent mechanical signals that can be measured or interpreted.

A major exploitation of such characteristics has been intended for the development of chemosensors, thus, opening the door to the qualitative as well as quantitative analysis of various species, metal ions or small molecules in different environments. The working principles of chemosensors are based on “bind-transport-release” or “reversible grip-and-tell” mechanisms [1]. The desired properties of a chemical sensor include application-dependent sensitivity, a large effective range, high selectivity or specificity to a target analyte, low cross-sensitivity to interferences, near perfect reversibility of the physicochemical detection or sensing process (short sensor recovery and response times), speed and long-term stability of the sensor and sensing material [2]. They should demonstrate real-time and real-space response by consuming minimal power and volume, while being fabricated from inexpensive materials using economical batch methods. However, perfect selectivity and reversibility are ambiguous to a significant degree as only the stronger and less reversible binding process enhances the selectivity by making the interaction between the chemically sensitive interface and an analyte more specific [3,4].

Over the years, the development of metal ion responsive molecular systems has become of great interest. Many metal ions play indispensable roles in biological processes such as; transmission of nerve impulses, muscle contraction, regulation of cellular activity and the working of metalloenzymes *etc.* The amount of these metal ions has to be controlled in the body as they can turn out to be toxic if present in unrestrained amounts. In addition, there are several other environmental concerns regarding heavy metal ions such as mercury, cadmium and lead due to their deleterious effects on organisms. Therefore, their early detection and/or screening in the environment and biological system is desirable [5–7]. Several strategies were developed by Prodi [6], Anslyn [8], de Silva [9], Reinhoudt [10] and others to devise efficient sensor systems for metal ions coherent with the major sensor requirements. There is great success in addressing most of the sensor parameters using “single sensor for single metal ion”. However, addressing of more than one metal ion on a single platform remains a challenging task.

The array-based multi-analyte sensing is a new and burgeoning area of research as it entails simultaneous detection of many chemical targets which might lead to increased efficiency in applications as diverse as cell physiology and environmental monitoring of industrial waste [11]. The present review is a comprehensive analysis about signaling of multiple metal ions simultaneously by a single molecular sensor. It compiles the ingenious work on all the chemosensors reported so far, which could recognize more than one metal ion allowing access to output signals either *via* differential responses or *via* multiple-channels. In general, the probes discussed herein are highly selective and exclusively detect specific metal ions in the matrix containing all other interfering cations.

2. Designing modes for chemosensors

Chemosensors are multicomponent systems of abiotic origin comprising receptors, signaling units and a communication channel conjoined with each other. A receptor is the metal-ion binding site and a signaling subunit is a term generally used for the moiety which expresses the after-effects of the binding process (“recognition event”) by transducing the chemical information at the molecular level into quantifiable signals (“signaling event”). The receptors are responsible for the selectivity and efficiency of the binding process. They can further be customized for various

analytes by adroitly manipulating their properties to meet sensor requirements. The whole course of recognition event depends upon the basic features such as receptor topology, characteristics of the cationic radius, charge, coordination number, hardness and nature of the solvent. The interaction of the analyte with the receptor site should be well-communicated to the signaling unit with the help of a spacer. The spacer may change the geometry of the system and turn on the electronic interaction between the associated moieties; in order to record the concomitant perturbations in the immediate environment of the system [12] (see Section 5.2). Thus, all the components should work in coherence to make a viable chemosensor.

Two chemosensor protocols are followed based on the type of attachment of the receptor and the signaling unit. The two units may or may not be covalently attached to each other. The general design principle is based on the reversibility of the events. Additionally, irreversible reactions can also be considered while discussing metal ion sensing. In this context, chemosensors are termed as “chemodosimeters”. The present review also takes into account of the few advances in the field of multi-receptive chemodosimeters.

2.1. Covalent approach

The covalent approach has been the most widely used approach for the association of the receptor with the signaling unit in the development of many chemosensors. The coordination site (receptor) binds to the cation and brings about changes in the properties of signaling subunit (photophysical or electrochemical). The cation recognition groups have extensively used macrocyclic compounds as the ionophores. For say, crown ethers and calixarenes are excellent cation encapsulating units based on their unique ability to retain void inside their network, modifying the properties of the attached signaling group. The signaling units are sensitive to the subtle variations in the microenvironment of the molecule and thus, may show changes in its properties (color, absorption, emission, redox shifts *etc.*).

2.2. Displacement approach

This approach relies upon the formation of a molecular ensemble between the signaling unit and the binding site. As the analyte is added, it binds to the binding site and there occurs a “displacement reaction” resulting in the consequent release of the signaling subunit which thus, retrieves back to its native state. If the characteristics of the signaling unit are different in coordinated state as compared to its naive state, then the recognition event gets coupled with the signaling event [13,14].

2.3. Chemodosimeter approach

A dosimeter is a device which progressively accumulates the dose, each time adding up the signal, and which after extended use, has to be discarded, while a chemosensor requires quick reversibility and potential reutilization. Therefore, the term chemodosimeter describes an abiotic molecule which recognizes the analyte through transduction of irreversible chemical reactions into human observable signals. Thus, the approach reveals cumulative response of significant chemical transformations involving both breaking and formation of covalent bonds. The chemodosimeters are based on displacement methodology. The induced irreversible reactions generate products which are chemically different from the starting molecule. The core idea of these irreversible systems is to take advantage of the specific reactivity that certain analytes may exhibit [14,15].

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