Coordination Chemistry Reviews 310 (2016) 1–15

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Chemically derived optical sensors for the detection of cesium ions

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Contents

ARTICLE INFO

Article history:
Received 14 August 2015
Accepted 20 November 2015
Available online 26 November 2015

Keywords:
Cesium ions
Cesium detection strategies
Optical detection
Calixcrowns
Fluorescent chemosensors

ABSTRACT

Cesium is an alkali metal of high reactivity, is used in photoelectric cells and atomic clocks, and also acts as a catalyst for promoting organic reactions. Although cesium is mildly toxic in nature, its radioactive counterparts have been considered as hazardous pollutants owing to their adverse health effects. Therefore, it is desirable to develop techniques for the rapid detection of cesium ions in environmental and biological systems. A variety of methods have contributed significantly toward the detection of cesium ions. However, the method based on chemically derived optical sensors has the advantages of being non-destructive, having high sensitivity, and having high applicability to biological systems. In this review, we mainly discuss fluorescent optical chemosensors that have been used for the detection of cesium ions with the particular aim to provide a general design strategy. Fluorescent molecular chemosensors provide easily assessable evident information (e.g., color/fluorescence change) about the targeted species, which in turn is indispensable for an efficient detection method.

1. Introduction

Metal ions are essential to perform a variety of functions in biological as well as environmental systems [1,2]. For example, alkali, alkaline earth, and some transition metal ions are abundant in biological systems and are associated with numerous physiological processes [3]. Although metal ions play significant roles, they have also been linked to adverse environmental and health effects [4–6]. In recent years, therefore, techniques for the identification of metal ions have been an emerging area of research [7–11]. Among various alkali and heavy metal ions, the investigation of cesium ions, particularly the radioactive counterparts, is very important owing to their negative health effects [12,13]. The abundance of cesium in nature is lower than that of other members of the same group, but cesium still has significant commercial applications [14]. Cesium, because of its strong affinity for oxygen, is used in oxygen removal [15]. The ability of cesium to convert solar energy into electrical energy makes feasible the use of cesium in photoelectric devices. Precise time measurement is possible with cesium-based atomic clocks [16]. In addition, cesium also has medical [17,18] and chemical [19] applications. Cesium, being of alkaline nature and because it has chemical and physical properties similar to those of potassium, when it enters the body is conveyed by membrane transport mechanisms into the cellular matrix [20]. Extensive investigations revealed that cesium can substitute for potassium during cell membrane transport, which may be a serious health problem [21,22]. Although the harmful effects of cesium are not as great as those of metals such as cadmium and mercury, its radioactive isotopes are regarded as notable environmental contaminants [23]. Of the most common radioisotopes of cesium – that is, ^{134}Cs and ^{137}Cs

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http://dx.doi.org/10.1016/j.ccr.2015.11.008

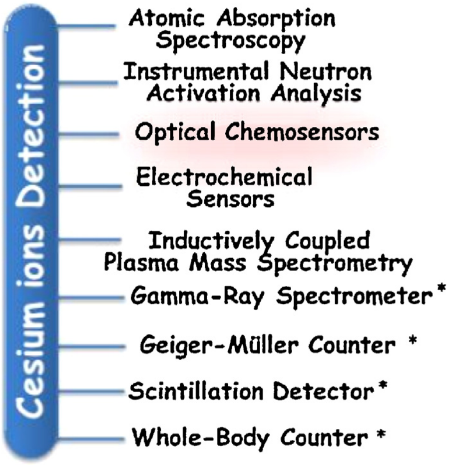

Fig. 1. Methods for the detection of Cs^+ ions (*for radioactive cesium).

– the latter is of serious environmental concern [24]. Radioactive ^{137}Cs is one of the important nuclear products produced by the fission of uranium, plutonium, and thorium [25]. Indeed, ^{137}Cs has industrial and medical applications as a source of gamma radiation. The major sources of ^{137}Cs contamination include radioactive material fallout during nuclear weapon testing, accidental nuclear leakage, and waste from nuclear plants [26–29]. The high reactivity and solubility of ^{137}Cs make possible its movement via the environment (air, water, and crops) to living systems, and its half-life of approximately 30 years means it persists for a long time. Exposure of living beings to radioactive cesium may occur through inhalation or ingestion and causes cell damage due to β-particle emission, resulting in cancer and cardiovascular, gastrointestinal, fetal, and neurological problems [30–34]. In addition, exposure to strong gamma radiation released from radioactive cesium may also occur through direct contact with nuclear waste and contaminated areas. Because of the environmental issues and hazards related to cesium, it is crucial to develop systems for the sensitive and rapid detection of cesium ions in environmental and biological systems. Information concerning cesium levels and the presence of cesium in the environment is important to understand its health effects and hazards, and acquisition of such information relies on the availability of detection techniques.

2. Methods for Cs^+ detection

In this section we provide a general discussion of the methods for the detection of cesium ions in environmental and biological systems. Selectivity, sensitivity, and a low limit of detection (LOD) are the properties that a detection approach must have for successful measurement. The harmful cesium (i.e., radioactive cesium) enters the environment via nuclear experiments or disasters, and thus its measurement is important at the site of fallout or in nearby areas. The presence of cesium can be identified by various analytical methods (Fig. 1). Approaches such as atomic absorption spectroscopy (LOD ≈ 1 μg/L) [35], optical chemosensors (LOD < 1 μg/L) [36], instrumental neutron activation analysis (LOD $\approx 1\text{–}1 \times 10^4$ μg/L) [37], electrochemical sensors (LOD ≤ 1 μg/L) [38], ion exchange (LOD ≈ 1 μg/L) [39], and inductively coupled plasma mass spectrometry (LOD < 1 ng/L) [40] are well applicable to the detection of cesium in environmental and biological samples. The radioactive isotopes of cesium, which release gamma radiation of a specific energy, can be identified by techniques based on the measurement of gamma radiation. The presence of gamma radiation can be monitored by gamma-ray spectrometers [41], a Geiger–Müller counter [42], and scintillation detectors [43], which in turn provide information regarding particular radioactive nuclei. The direct assessment of radioactive cesium within the body is possible with the gamma ray counting procedure known as whole-body counting [44]. The advantage of these techniques is that they can detect a number of gamma ray—releasing radionuclei in a single analysis. However, the application of such methods is restricted to measurement of only radioactive nuclei.

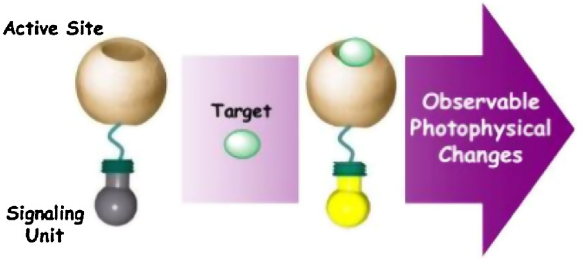

Fig. 2. Design strategy for the molecular chemosensors.

As discussed above, different types of techniques have been used for the detection of cesium ions, and have contributed significantly to their detection in different systems. However, the approach based on chemically derived optical sensors has the advantages of being nondestructive, having high sensitivity, and having high applicability to biological systems, providing important information about the species of interest [45,46]. Chemosensors, particularly those based on the fluorescence approach, are actively used for the detection of as well as to understand the physiological importance of ions of interest [47,48]. In general, a molecular chemosensor is the combination of an active site to interact with a target and a signaling unit, which must be able to identify the interaction between the active site and the target species via photophysical changes (Fig. 2). Photophysical changes offer measurable outputs such as color, emission, and intensity changes that are easily correlated to specific targets. A variety of photophysical approaches have been exploited for the development of molecular chemosensors [49,50]. The fundamental photophysical mechanisms have been discussed in detail in previous articles [51–55], but it is essential to summarize the mechanisms here. Chemosensors have been made with electron donor or acceptor parts to exhibit charge transfer, the so-called intramolecular charge transfer mechanism. This state is very sensitive, and the interaction with the target alters the charge–transfer and photophysical properties of the chemosensor. Charge transfer is one of the mechanisms observed in ratiometric measurements. In photoinduced electron transfer (PET)-based probes, quenching of fluorescence occurs because of the involvement of electron transfer to the excited fluorophore. The PET mechanism has been effectively used to design fluorescence off-on or on-off systems. In some cases the interactions (i.e., π–π and van der Waals) between aromatic molecules have been utilized for the formation of excited-state dimers, or excimers. Such dimers are frequently used in the development of fluorescent chemosensors. Another very common mechanism is resonance energy transfer, where energy transfer is possible nonradiatively between molecules either through space or through a bond. Resonance energy transfer is widely used to study biological mechanisms and for efficient detection. Recently, aggregation-induced emission has been exploited to develop sensing platforms [56]. In addition, spirocyclization [57] and a reaction-based approach [58] have used for sensing applications.

In this review, we will principally highlight the chemical sensors used for the optical detection of cesium ions in the past. The chemosensors have been categorized into different sections according to the use of the binding unit and the molecular scaffold.