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# A review of recent developments in fluorescent sensors for the selective detection of palladium ions



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#### ABSTRACT

Palladium is one of the important elements used in various industries, such as fuel cells, automobile, dental crowns and catalysts in drug synthesis. Its extensive use and waste produced have raised pollution emissions to water sources and soils, and have severe effects on plants, animals and humans. As a result, many methods have been developed to assess the levels of palladium in drug chemicals, food and crops. The dietary intake per person is limited to <15  $\mu$ g day<sup>-1</sup>, as reported by the World Health Organization (WHO). This issue has led many researchers developing optical probes, hereafter fluorescent sensors, for the sensitive and selective detection of palladium, especially in the environmental and biological settings. The design of functionalized receptors that serve as palladium-selective chemosensors has gained great interest despite the difficulties associated with the similarities among the same group elements (especially platinum). This review provides a general overview of the recent research developments in fluorescent sensors, emphasizing on the structural features for designing fluorescent sensors for the selective detection of palladium ions. Because the number of chemosensors for palladium detection has grown in the past few years, this review was written to provide a comprehensive discussion of these types of sensors reported from 2000 to the present day. This review categorizes the palladium probes based on their sensing mechanisms or mode of interaction towards palladium ions, such as coordination, deallylation, depropargylation, hydrolysis, palladium induced aggregation, photo-induced electron transfer, Claisen rearrangement, C-CN bond cleavage, oxidative cyclization and cross coupling reactions. The basic principles involved in the design of chemosensors for the selective analysis of palladium, problems and challenges in the field as well as possible future research directions are presented.

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#### 1. Introduction

Palladium, denoted as 106.42Pd<sup>46</sup>, is a rare silver white metal belonging to the platinum group along with platinum, rhodium, ruthenium, osmium and iridium. The industrial demand for Pd is high and was ~316 metric tons in 2016 [1]. Pd is used in automobile catalytic converters for reduction in pollutant emissions (nitrogen oxide, carbon monoxide and hydrocarbons) from automobile exhausts and is also used in the electric and electronic equipment industry for the production of diodes, industrial circuits and semiconductors [2]. Through three different oxidation states (Pd<sup>0</sup>, Pd<sup>2+</sup> and Pd<sup>4+</sup>), Pd reveals highly catalytic effects in hydrogenation, dehydrogenation, oxygenation and hydrogenolysis reactions [3]. Therefore, Pd is widely used as a catalyst in chemical and petroleum industries, such as the oxidative conversion of alcohols to aldehydes [4,5], synthesis of drugs like rofecoxib and cefprozil [6,7], C-H functionalization [8–10], the Nazarov-type cyclisation reaction [11], the Suzuki-Miyaura reaction, the Buchwald-Hartwig amination reaction and the Sonogashira reaction [12,13]. Pd catalysts are also employed in carbon-carbon bond formation and play an indispensable role in the synthesis of complex structures, such as natural products, pharmaceuticals, functional materials, polymers and supermolecules [14–16]. Because Pd can absorb huge quantities of hydrogen, almost 900 times its own volume at ambient temperature and pressure, this opens up the possibilities of using Pd for the purification and storage of hydrogen and its use in fuel cells [17]. In the healthcare and medicine sector, Pd is being used in dental alloys and in surgical instruments. Such widespread use has increased Pd pollution in medicines caused by process containment and the environment due to the release from wastes, thus resulting in increased health risks.

Pd is known to have high mobility among the platinum group metals and its transfer coefficient into plants is over 0.1. It is also highly soluble in rain water from dust compared to platinum [18]. The concentration of Pd in contaminated soil has been reported to be 440 ng/g [19]. Pd in contaminated soils and aquatic ecosystems can be transferred to biological systems and undergo biogeochemical transformations, which increases its bioavailability and poses serious health threats [20]. The Pd byproducts obtained during organic molecule synthesis are transported into living organisms via a divalent metal transporter (DMT1), and are hazardous to human health and the environment [21,22]. For example, Pd could destroy DNA, coordinate with thiol containing amino acids, bind to vitamin B6, trigger protein denaturation and damage several cellular processes [23–25]. Due to strong bonding with organic ligands. Pd can interact with macromolecules like proteins and DNA, intensify hydroxyl radical damage, interfere with mitochondrial functions and inhibit the activities of many enzymes [26,27], which disturb cellular functions and equilibria in cellular environments [28]. Therefore, Pd is believed to be cytotoxic, causing cellular damage which could be sometimes lethal to the cell itself [29–31]. Pd is a known irritant and sensitizer, and continuous exposure can cause contact dermatitis [32]. It is also known to cause stomatitis and periodontal gum disease [33–35]. Pd can also leach from dental alloys and accumulate, specifically in the liver and kidneys in humans. The final threshold for Pd in end products is strictly limited, with set governmental restrictions (no more than 5–10 ppm) and there is a proposed maximum dietary intake of palladium (as a crude estimate) of less than 2  $\mu$ g per person per day [36]. As a result, knowledge of how to detect the concentration and distribution of Pd inside biological systems is an important issue.

Several analytical techniques with high sensitivity for the detection of Pd, such as atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), solid-phase micro extraction coupled with high-performance liquid chromatography (SPME-HPLC) and X-ray fluorescence (XRF) have been investigated [37,38]. However, expensive/sophisticated instrumentation, requirement of laborious sample-preparation steps, rigorous experimental conditions and highly skilled operational personnel are generally required during these processes. Especially, they are not suitable for application in living systems. With a biological outlook, as a complement to the above techniques, it is important to define the chemical form or speciation of metal ions in biological samples and the distribution of free hydrated ions, loosely bound ions, and tightly bound inaccessible ions. Nowadays, there is no single technique available that measures all of the different species in the specimen at one time. Yet there are certain other techniques that permit measurement of different subsets of these ion pools, for example, the use of a fluorescent sensor. Thus, a combination of complementary methods will be required for a comprehensive view of cellular metal regulation. The application of fluorescent sensors and fluorescence microscopy, in combination with other analytical techniques for mapping total metal content, permits the visualization of an object of interest in unicellular organisms, individual cells from multicellular organisms, cells encapsulated in 3D matrices, organotypic cultures, ex vivo models and whole organisms (bacteria, yeast, plants, flies, worms, fish and mice) [39]. Therefore, the development of superior fluorescent sensors for heavy metal ions are highly required and such demand has made this a hot research topic in recent years. From a chemistry perspective, fluorescent methods offer the advantages of simplicity, rapid response, sensitivity, low cost, non-destructive methodology, real-time monitoring and high spatial resolution via microscopic imaging [40–42]. Therefore, current research has focused on fluorescence based methods, in which the optical probe (colorimetric and fluorescent probe) has the characteristics of good selectivity, high sensitivity and convenient operating methods [43,44]. Additionally, it does not require expensive facilities and can be used in biological detection.

A number of reviews are available in literature related to fluorescent chemosensors for the selective detection of anions, including cyanates [45–48], phosphates [47,49–54], acetates [49,55] and fluoride ions [47,51,52,56], and metal cations including  $Cu^{2+}$  [57– 60], Fe<sup>3+</sup> [39,61], Hg<sup>2+</sup> [58,62–65], Cr<sup>3+</sup> [61,66], Pb<sup>2+</sup> [60,67] and Zn<sup>2+</sup> [39,58,61,64,68]. However, to the best of our knowledge, currently there is no review on chemosensors for the detection of Pd ions. Only few reports attempt to compile Pd sensors, which covered very few reports and especially focused on the pioneering work of Kazunori Koide's research group during the years of 2004–2008 [69]. Up until now, there have been no updates on the compilation and analysis of Pd chemosensors. This review deals with the compilation from fundamental concepts to recent Download English Version:

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