



Review

Potentially toxic elements and environmentally-related pollutants recognition using colorimetric and ratiometric fluorescent probes



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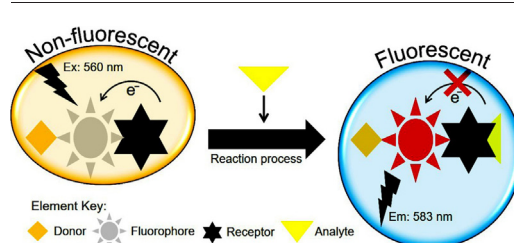
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HIGHLIGHTS

- Various signaling pathways and working scheme of fluorescent sensors are discussed.
- Low-cost interventions and a framework to detect heavy metal ions are highlighted.
- In-vitro detection via bio-imaging against cancerous cell lines is presented.
- Major consequences and adverse effects of heavy metal ions are presented.
- Ecotoxicology of toxic heavy metal ions require further research.

GRAPHICAL ABSTRACT



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ABSTRACT

A safer detection or sensing of toxic pollutants is one among several environmental contamination issues, across the globe. The ever-increasing industrial practices and controlled or uncontrolled release of toxic pollutants from various industrial sectors is a key source of this environmental problem. Significant research efforts have been or being made to tackle this problematic issue to fulfill the growing needs of the modern world. Despite many useful aspects, heavy metals are posing noteworthy toxicological concerns and human-health related issues at various levels of the ecosystem. In this context, notable efforts from various regulatory authorities, the increase in the concentration of these toxic heavy metals in the environment is of serious concern, so real-time monitoring is urgently required. Herein, we reviewed fluorescent sensor based models and their potentialities to address the detection fate of hazardous pollutants including chromium, manganese, cobalt, nickel, copper, and zinc as model elements. The novel aspects of turn-on/off fluorescent sensors have also been discussed from a state of the art viewpoint. In summary, comprehensive literature regarding fluorescent sensor based models and their potentialities to detect various types of toxic pollutants is reviewed.

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## 1. Introduction

The widespread occurrence of various environmentally-related pollutants including toxic heavy metals and other emerging hazardous contaminants is a serious concern (Bilal et al., 2018; Hernandez-Vargas et al., 2018). The dissolution of such polluting agents is a leading cause of environmental pollution of all key spheres including the hydrosphere, lithosphere, and biosphere, among others (Bilal et al., 2018). Transition metals are known as trace elements, as some are present at very low extent in nature, some of them play their vital role in the living systems (Rai, 2008). On the other hand, excessive buildup of transition metal ions can cause harmful effects on biotic life including cancer, heart disease and neuron degradation (Bilal et al., 2018; Rasheed et al., 2018a, 2018b). The determination of metal ion contents from in and out of the cell becomes highly necessary for biological and disease-related risk evaluations. Therefore, many efforts have been made to engineer numerous types of sensitive and selective methods to detect the concentration of toxic heavy metals in an abiotic cell or industrial wastes (Kim et al., 2013; Rasheed et al., 2018a). Based on scientific literature, several strategies have been introduced to determine the low concentration of transition metal ions. Among them, biosensors have gained special interest due to their notable potentialities including highly specific recognition sites as compared to traditional chromatography-based methods (Rodriguez-Mozaz et al., 2005). Among existing electrochemical biosensors, optical class of biosensors at large and fluorescent, in particular, have various advantages over other types of sensors, such as allowing real-time monitoring, miniaturization and the enhancement of selectivity and sensitivity. Molecular setups that transform the chemical input to a meaningful output in the form of signals (optical, electrical, magnetic or electronic) are called chemical sensors (Bell and

Hext, 2004). Also, as electrochemical reactions deliver electronic signals, it is not necessary to use complex signaling elements. This facilitates the support towards the development of portable systems for clinical testing and on-site environmental monitoring (Arduini et al., 2017). Since the first report on fluorescent sensors in 1990, several reports on metal ions recognition using numerous types of fluorescent sensors have been published. Design and synthesis of some recently reported fluorescent sensors for the selective detection of potentially toxic heavy elements are summarized in Table 1. Major milestones and/or noteworthy achievements in fluorescence science are shown in Fig. 1.

In an earlier work (Rasheed et al., 2018a), we have reviewed fluorescent sensor based models and their potentialities to address the sensing strategies of hazardous heavy metals with particular reference to lead, cadmium, and mercury and thus are not the focus of present work. Also, the photoinduced electron transfer (PET) mechanism, chelation enhancement fluorescence (CHEF) effect and spirocyclic ring opening mechanism insights are also discussed in an earlier review (Rasheed et al., 2018a). Herein, we reviewed different fluorescence-based sensors for the detection of potentially toxic elements including, chromium, manganese, cobalt, nickel, copper, and zinc as model elements. Depending upon the response to specific analyte fluorescent sensors can be divided into three kinds, turn on (enhanced), turn-off (quenched) and ratiometric (change/shift in wavelength). This review also presents various colorimetric and ratiometric fluorescent probes according to their analytes and working mechanisms for potentially toxic elements recognition.

### Fluorescent probes – opportunities.

Fluorescent probes are composed of small organic molecules or fluorescent dyes and are considered to be molecular devices for the transformation of chemical information to analytical signals (Bell and Hext,

**Table 1**

Design and synthesis of some recently reported fluorescent sensors for the selective detection of potentially toxic heavy elements.

Sensor type	Analyte	Solvent system	Association constant	Limit of detection	Reference
Rhodamine based	Cu <sup>2+</sup> , Al <sup>3+</sup>	H <sub>2</sub> O:CH <sub>3</sub> CN (3:7, v/v, HEPES buffer, pH 7.4)	6.2 × 10 <sup>4</sup> M <sup>-1</sup> 1.4 × 10 <sup>4</sup> M <sup>-1</sup>	321 nM 572 nM	Rai et al. (2018)
Rhodamine based	Cu <sup>2+</sup> , Hg <sup>2+</sup>	CH <sub>3</sub> CN:H <sub>2</sub> O(4:1 v/v, pH 7.2 10 mM, HEPES buffer)	3.37 × 10 <sup>5</sup> M <sup>-1</sup> 7.6 × 10 <sup>5</sup> M <sup>-1</sup>	3.9 nM, 2.36 nM	Rasheed et al. (2018b)
Pyrene based	Ni <sup>2+</sup>	CH <sub>3</sub> CN	–	2.5 × 10 <sup>-7</sup> M	Khan et al. (2018)
Naphthalimide rhodamine	Cu <sup>2+</sup>	DMF/HEPES (1: 9, v/v, pH = 7.4, 10 mM)	–	49 nM	Zhang et al. (2017)
Quinoline turn-on, CHEF induced FRET	Au(III)	Ethanol: water, 7:3 (v/v), 0.1 MHEPES buffer, pH 7.4.	–	0.5 nM	Adhikari et al. (2015)
Rhodamine-based	Au(III)	1:1 CH <sub>3</sub> CN–HEPES, pH 7.0	–	0.6 ppm	Chinapang et al. (2015)
Rhodamine and coumarine	Cu <sup>2+</sup>	Aqueous media	–	–	Song et al. (2014)
FRET-based 1,8-naphthalimide and rhodamine	Cr <sup>3+</sup>	CH <sub>3</sub> CN–HEPES buffer solution	4.51 × 10 <sup>4</sup> M <sup>-1</sup>	–	Hu et al. (2014)
PET–FRET based	Cr <sup>3+</sup>	(2/1, v/v, 0.5 mM, pH = 7.4)	–	–	Barba-Bon et al. (2014)
BODIPY-based on-off	–	water-CH <sub>3</sub> CN (40/60 v/v)	–	0.19 μM	Goswami et al. (2014)
BODIPY-based	Au(III), HgII	1:1 phosphate buffer EtOH, (0.1 M)/pH 7.0.	–	44 nM	Karakuş et al. (2014)
Rhodamine/BODIPY	Au(III)	1:1 CH <sub>3</sub> CN/HEPES buffer (pH 7.0)	–	65 nM	Emrullohoğlu et al. (2013)
Fluorescein-based	Ni <sup>2+</sup> , Co <sup>2+</sup>	DMSO	2.1 × 10 <sup>4</sup> M <sup>-1</sup> ,	–	Kumar et al. (2011a)
Turn on	–	in aqueous solution buffer solution (7/3, v/v, pH 7.4)	4.5 × 10 <sup>3</sup> M <sup>-1</sup>	–	–

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