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# Synthesis of fluorescent naphthalimide-functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticles and their application for the selective detection of Zn<sup>2+</sup> present in contaminated soil

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## ABSTRACT

A fluorescent dopamine–naphthalimide–dipicolylamine (DPA) was synthesized as a sensing receptor for Zn<sup>2+</sup>. Naphthalimide–DPA (**2**) was immobilized onto the surface of iron oxide nanoparticle to prepare a hybrid nanomagnet **1-Fe<sub>3</sub>O<sub>4</sub>**. Naphthalimide–DPA (**2**) and **1-Fe<sub>3</sub>O<sub>4</sub>** were observed to bind with Zn<sup>2+</sup>, leading to significant increase in fluorescence intensity at 527 nm. The fluorescence increases of **2** (10 μM) and **1-Fe<sub>3</sub>O<sub>4</sub>** (0.33 wt%) by addition of Zn<sup>2+</sup> were linear over the [Zn<sup>2+</sup>] range of 0–7 μM and 0–20 μM, respectively. These fluorescence changes were highly selective for Zn<sup>2+</sup>, which were readily monitored even in the presence of other competitive cations. In particular, **1-Fe<sub>3</sub>O<sub>4</sub>** exhibited an excellent limit of detection determined to be 0.0345 ppb. Furthermore, this system was found to be suitable for detecting Zn<sup>2+</sup> in a wide pH range of 3–11 and could be reused with the addition of ethylenediaminetetraacetic acid (EDTA). Moreover, nanomagnet **1-Fe<sub>3</sub>O<sub>4</sub>** was employed for the selective detection and removal of Zn<sup>2+</sup> from a soil sample. These results confirm that the use of **1-Fe<sub>3</sub>O<sub>4</sub>** is a novel and simple method for detecting Zn<sup>2+</sup> in environmental samples.

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## 1. Introduction

Particular attention has been focused on heavy and transition metal (HTM) ions and their detection methods. Exposure to HTM through diverse pathways can lead to accumulation in the human body, causing severe illness [1]. In particular, zinc is an indispensable element as it plays an essential role in biological processes (e.g., protein synthesis, neurotransmission, and signal transduction) [2]. However, the accumulation of zinc in the human body causes fatal organ failure, copper deficiency, stomach cramps, skin irritations, vomiting, nausea and anaemia [3,4]. Thus, the detection and removal of Zn<sup>2+</sup> in contaminated samples are of significant interest due to this cation's unique role in physiological functions and harmful effects to human body.

Currently, fluorescent sensors have been reported as powerful tools for detecting metal ions in water and biological samples,

attributed to their high sensitivity and selectivity, as well as ease of operation [5–15]. In particular, development of fluorescent sensors for Zn<sup>2+</sup> have engaged great attention, due to the biological significance of Zn<sup>2+</sup> ions. In general, fluorescent molecules are linked to Zn<sup>2+</sup>-chelators such as dipicolylamine (DPA), bipyridine, cyclic polyamines, and etc [16–22]. However, most of the sensors exhibit a poor selectivity for Zn<sup>2+</sup> ions over other metal ions. Specially, there is difficulty in distinguishing Cd<sup>2+</sup> and Zn<sup>2+</sup> ions, owing to their similar binding properties [23,24]. Recently, Yoon et al. reported a Zn<sup>2+</sup>-selective fluorescent sensor based on amide tautomerization of naphthalimide linked to DPA and this was used for detecting Zn<sup>2+</sup> ions in human cells and zebrafish [16].

Compared to the detection of HTM present in contaminated water, that of HTM present in contaminated soil is considerably more difficult. Soil demonstrates potential to buff the contamination level of groundwater and river [25]. HTM adsorbed on soil surfaces may leach into groundwater and stream water, which are important sources of drinking water [26]. Thus, it is necessary to investigate the contamination of zinc in soil.

Conventional analytical methods widely employed for detecting HTM in soil samples include atomic adsorption spectrometry [27],

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