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A new and highly selective turn-on fluorescent sensor with fast response time for the monitoring of cadmium ions in cosmetic, and health product samples

Rouhollah Khani, Ebrahim Ghiamati *, Ramin Boroujerdi, Abdolreza Rezaeifard, Mohadeseh Hosseinpour Zaryabi

Department of Chemistry, Faculty of Science, University of Birjand, P.O. Box 414, Birjand, Iran

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ABSTRACT

Cadmium (Cd) which is an extremely toxic could be found in many products like plastics, fossil fuel combustion, cosmetics, water resources, and wastewaters. It is capable of causing serious environmental and health problems such as lung, prostate, renal cancers and the other disorders. So, the development of a sensor to continually monitor cadmium is considerably demanding. Tetrakis(4-nitrophenyl)porphyrin, T(4-NO_2-P)P, was synthesized and used as a new and highly selective fluorescent probe for monitoring cadmium ions in the "turn-on" mode. There was a linear relationship between fluorescence intensity and the concentration of Cd(II) in the range of 1.0×10^{-6} to 1.0×10^{-5} mol L^{-1} with a detection limit of 0.276 μM. To examine the most important parameters involved and their interactions in the sensor optimization procedure, a four-factor central composite design (CCD) combined with response surface modeling (RSM) was implemented. The practical applicability of the developed sensor was investigated using real cosmetic, and personal care samples.

1. Introduction

Heavy metals, are one of the main sources of pollution in environment, especially because of their significant effects on biological systems. The importance of heavy metals determination at trace levels is due to their rapid diffusion as environmental contaminants [1,2] to the surroundings. Cadmium is toxic even at low levels and has influence on various biological processes [3–7]. Cadmium is a naturally occurring non-essential trace element and has a tendency to bioaccumulates in living organisms, raising environmental concerns [8,9]. Cadmium is ranked seventh in priority list of top 275 hazardous material on Comprehensive Environmental Response, Compensation, and Liability Act in USA [10,11]. Furthermore, the accumulation of cadmium in the human body can damage important internal organs like liver, lung, kidneys, central nervous system and bones [12,13]. Epidemiological studies conducted in general human populations have shown that Cd increases the risk of developing breast, prostate, and endometrial cancers [14–17].

Many attempts have been made during the last two decades to develop different methods for detecting cadmium, including electrochemical methods such as differential pulse anodic stripping voltammetry [18, 19], optical spectroscopic methods like flame atomic absorption spectrometry [7,20], and inductively coupled plasma mass spectrometry [21]. The problems with these techniques are the requirements for expensive instrumentation, specialized operator, and long analysis time. Spectrofluorometric and spectrophotometric methods, like Dual-Signaling Fluorescent (DSF) [22] were used to detect trace amount of metal ions, too. Fluorescent and colorimetric-based chemosensors are widely utilized for measuring the amount of cadmium ions in solutions [23–36].

Due to unique properties of fluorescence techniques, many detection methods have been emerged for speciation of analytes, such as heavy metal ions, mostly by studying the emission spectra like peak shifting [37], quenching [38,39], or enhancement [40–42]. The development of optical sensing approaches in designing sensors and biosensors for the detection of environmentally and biologically important species, such as toxic heavy metal ions, has been an inevitable task. A fluorescence-based optical sensor is one of the most practical application of these endeavors, because of its intrinsic sensitivity, high selectivity, specificity, real-time monitoring with fast response time and undamaging effects on the analytes [43–45].

On the other hand, the porphyrins are macrocyclic compounds constituting 1:1 complexes almost with all the metal ions. Mg(II), Cd(II) and Zn(II) in their porphyrin complexes, readily combine with one more ligand to form pentacoordinated complexes with square-pyramidal structure [46]. Porphyrins reactions with large metal ions like Cd(II), are relatively fast, because they cannot fit into the porphyrin nucleus and just sit on top of the molecule [47]. Porphyrin based sensory

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* Corresponding author.
E-mail address: eghiamati@birjand.ac.ir (E. Ghiamati).

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Table 1
Experimental factors and levels in the central composite design.

Factors	Unit	Notation	Range and levels				
			$-\alpha$	-1	0	$+1$	$+\alpha$
Conc. T(4-NO_2-P)P	mol L^{-1}	A	4.5×10^{-6}	8.0×10^{-6}	1.15×10^{-5}	1.5×10^{-5}	1.85×10^{-5}
Temperature	K	B	288	298	308	318	328
Time	min	C	15	25	35	45	55
Conc.Zn(II)	mol L^{-1}	D	2.5×10^{-5}	5.0×10^{-5}	7.5×10^{-5}	1.0×10^{-4}	1.25×10^{-4}

methods were widely used during the past decade because of their ability to interact with metal ions. Many of the newly developed Cd turn-on sensors capable of detecting Cd and Zn are unable to function selectively only for cadmium [48–52]. In this work T(4-NO_2-P)P was employed as a specific turn-on fluorescent probe to quantify cadmium ions in real samples. The influence of important variables such as temperature, time of response, the amount of the reagent and the concentration of zinc on function of the sensor were investigated. The optimization was carried out via a 2^4 full factorial central composite design (CCD) combined with response surface methodology (RSM) to maximize sensor efficiency of the target analyte. In this methodology, the interactions of two or more variables could be studied simultaneously, resulting in higher percentage yields, reduced process variability, closer confirmation of the output response to nominal and target achievement, and less treatment time with minimum costs [53].

2. Experimental

2.1. Reagents

2.1.1. Chemicals

All chemicals were purchased from Merck (Darmstadt, Germany) and were of analytical reagent grade. Absolute ethanol (Merck) was used for preparing the respective solutions. The metal ions stock solutions were made up of their nitrate and chloride salts. The Hg (II) ions were of its acetate salt. Double distilled deionized water was used for solutions dilution.

Table 2
Design matrix and the results of the central composite full factorial design.

Run	A	B	C	D	Flu. intensity
1	1.50×10^{-5}	318	25	5.00×10^{-5}	118.977
2	8.00×10^{-6}	298	25	1.00×10^{-4}	285.082
3	1.50×10^{-5}	318	45	1.00×10^{-4}	113.6
4	1.50×10^{-5}	318	45	5.00×10^{-5}	128.227
5	1.15×10^{-5}	308	35	7.50×10^{-5}	171.294
6	8.00×10^{-6}	298	45	5.00×10^{-5}	414.188
7	8.00×10^{-6}	298	25	5.00×10^{-5}	442.174
8	8.00×10^{-6}	298	45	1.00×10^{-4}	292.779
9	8.00×10^{-6}	318	25	1.00×10^{-4}	408.215
10	8.00×10^{-6}	318	45	1.00×10^{-4}	420.925
11	1.15×10^{-5}	308	35	7.50×10^{-5}	180.963
12	8.00×10^{-6}	318	45	5.00×10^{-5}	430.758
13	1.15×10^{-5}	308	35	7.50×10^{-5}	230.978
14	1.50×10^{-5}	298	45	5.00×10^{-5}	154.016
15	1.50×10^{-5}	298	25	1.00×10^{-4}	110.308
16	1.50×10^{-5}	298	25	5.00×10^{-5}	160.232
17	8.00×10^{-6}	318	25	5.00×10^{-5}	446.408
18	1.50×10^{-5}	298	45	1.00×10^{-4}	118.992
19	1.50×10^{-5}	318	25	1.00×10^{-4}	122.971
20	1.15×10^{-5}	308	35	7.50×10^{-5}	206.156
21	1.15×10^{-5}	308	15	7.50×10^{-5}	212.131
22	1.15×10^{-5}	308	35	2.50×10^{-5}	205.16
23	1.15×10^{-5}	308	35	1.25×10^{-4}	190.786
24	4.50×10^{-6}	308	35	7.50×10^{-5}	561.963
25	1.85×10^{-5}	308	35	7.50×10^{-5}	114.496
26	1.15×10^{-5}	308	35	7.50×10^{-5}	220.285
27	1.15×10^{-5}	308	55	7.50×10^{-5}	217.414
28	1.15×10^{-5}	288	35	7.50×10^{-5}	384.688
29	1.15×10^{-5}	328	35	7.50×10^{-5}	190.079
30	1.15×10^{-5}	308	35	7.50×10^{-5}	230.409

2.1.2. Real samples

Three real samples were chosen, i) A Kiss Beauty pink-purple lipstick; ii) An Atusa brown hair color from Sabzgolsar Co. under the supervision of Jos. H. Lowenstein, USA; and iii) My Lang Anhaltendes liquid foundation make up cream manufactured by ACT Cosmetics Co. (under the license of Kahl & Co, Germany).

2.2. Instrumentation and software

Photoluminescence (PL) spectra were obtained using a Shimadzu RF-5301PC spectrofluorometer (Japan) at room temperature (298 ± 2 K). UV–Visible spectra were acquired by A-160 Shimadzu UV–Vis equipped with a photomultiplier tube (PMT) detector. AA-6300 Shimadzu (Japan) atomic absorption spectrometer (AAS) equipped with a deuterium lamp background correction and cadmium hollow cathode lamp was used as a source for determination of cadmium. The lamp was operated at optimum condition expressed by the manufacture. For centrifugation, Hettich Zentrifugen Model EBA 200 was used. Wisettir model MSH-20D was utilized for magnetic stirring of the solutions.

2.3. Software

The Design-Expert, a statistical package software version 9.0 (Stat-Ease Inc., Minneapolis, MN, USA) was used for experimental design analysis and subsequent regression analysis of the experimental data. The proposed three dimensional molecular structure was drawn using Chem & BioDraw Ultra version 11.0 of Cambridge Soft products.

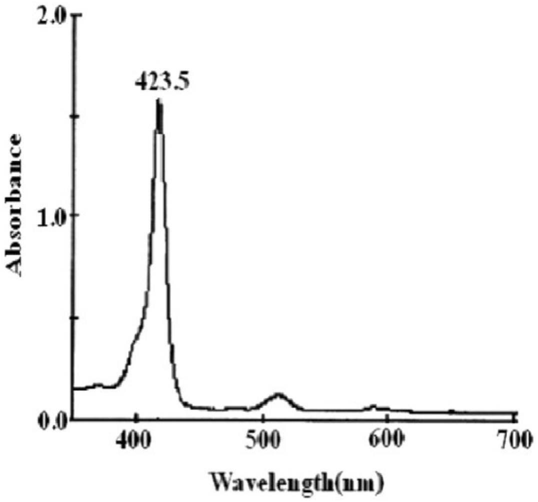

Fig. 1. UV–Vis spectrum of synthesized T(4-NO_2-P)P, [T(4-NO_2-P)P] = 1×10^{-4} mol L^{-1} in chloroform.