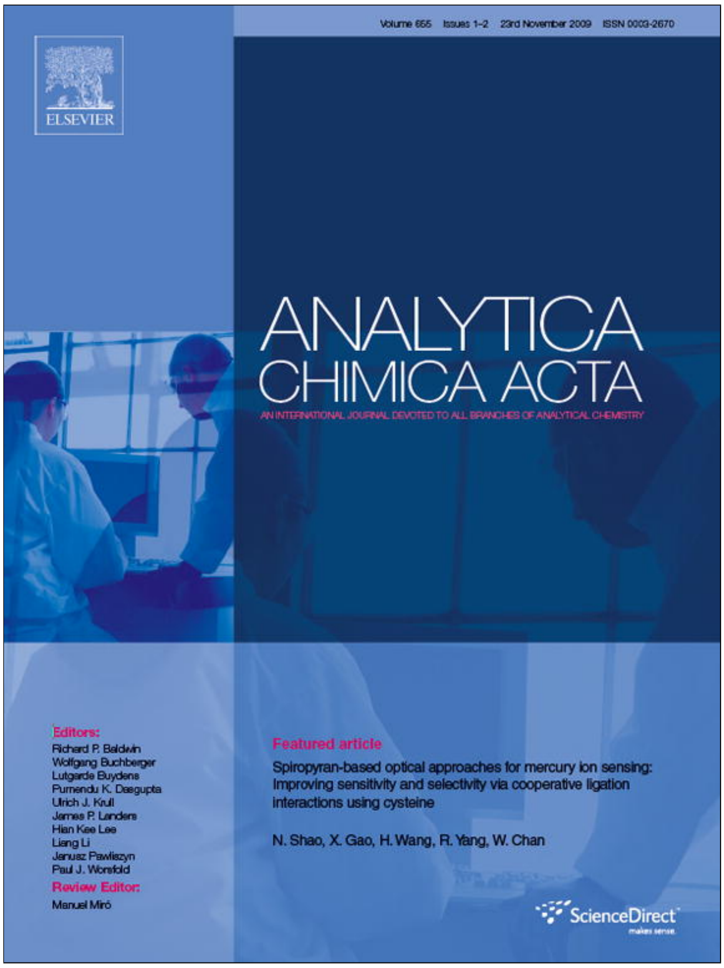
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Selective chemosensor for Hg(II) ions based on tris[2-(4-phenyldiazenyl)phenylaminoethoxy]cyclotriveratrylene in aqueous samples

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ABSTRACT

A novel chemosensor, based on tris[2-(4-phenyldiazenyl)phenylaminoethoxy]cyclotriveratrylene (TPPECTV) as chromophore, has been developed for the colorimetric determination and visual detection of Hg(II) ions. TPPECTV exhibits a pronounced chromogenic behavior toward Hg(II) ions by changing the color of the solution from yellow to red-orange upon its addition, which can be easily detected with the naked-eye. Based on this sensing scheme a colorimetric method was developed, where the absorbance linearly increases as a function of the Hg(II) concentration up to 2.0×10^{-4} M, with a detection limit of 0.5 μM. The visual detection, using TPPECTV absorbed on silica, provides a simple, rapid and sensitive method and was used for the detection of Hg(II) ions in water samples with a detection limit of 5.0 μM. The colorimetric results of the detection of Hg(II) ions in environmental water samples (river water) are in good agreement with those obtained by cold vapor atomic absorption spectrometry (CVAAS).

1. Introduction

Currently, there is an increasing demand to selectively sense heavy metal ions such as Hg(II), Pb(II) and Cu(II) because of their high toxicity [1,2]. Among the heavy metal ions, Hg(II) is one of the environmentally most important metal ions whose toxicity, even at very low concentrations, is already known for a long time and is a problem of primary concern [3]. Many analytical methods have been developed for its detection including atomic absorption spectrometry (AAS), ion selective electrode (ISE) and flame photometry [4]. However, these methods require a large amount of sample, are relatively expensive and do not allow continuous monitoring as well as on-site or in situ analysis of Hg(II) ions. Therefore, there is a need for analytical methods for the selective, sensitive, and rapid detection of Hg(II) ions. In this direction, chemosensors play an importance role, in particular employing molecular probes that generate and transduce an analytical signal as response to the binding event between the probe and the target analyte [5–8]. Currently, several examples of chemosensors for Hg(II) ions have been developed, such as redox-active [9], fluorogenic [10], and chromogenic ones [11]. In particular, fluorogenic and chromogenic systems have distinct advantages in term of their sensitivity, versatility, and ease of signal detection and visualization [5,8,12].

To take advantage of the favorable feature of chromogenic systems, we have designed a novel chromogenic compound that selectively binds Hg(II) ions. It concerns the attachment of three ligating sites to the cyclotriveratrylene platform to give the tripodal chromophore tris[2-(4-phenyldiazenyl)phenylaminoethoxy]cyclotriveratrylene (**1**, TPPECTV; Fig. 1). Its use as chemosensor will be demonstrated.

2. Experimental

2.1. Material and apparatus

All chemicals and solvents were of analytical grade purchased from Aldrich Chemical Co., unless otherwise stated and used as received. Chromogenic compound **1** was prepared by reacting 4-aminoazobenzene **2** with the *C*3 symmetric tris(acetyl chloride)cyclotriveratrylene **3**. Individual stock solutions of the metal ions (Na(I), K(I), Ca(II), Mg(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), Ag(I) and Hg(II), as anhydrous nitrate salts, were prepared in an acetate buffered (pH 7.0) aqueous solution and standardized with EDTA. ^{1}H NMR spectra were recorded on a Bruker AC300 MHz spectrometer in $CDCl_3$ solution with TMS as reference. Column chromatographic separation was carried out with Merck silica gel

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