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Selectively light scattering spectrometric detection of copper (II) based on a new synthesized oxamide ligand

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ABSTRACT

Light scattering (LS) signals have been applied for analytical detections, but the selectivity is poor. In order to improve the selectivity, pre-separation or new machines are generally considered. Differing from these methods, we synthesized a highly selective oxamide ligand, N′,N′-bis (2-aminophenyl) oxamide (NAPO). It was found that the LS signals of NAPO, measured with a common spectrofluorometer, could be selectively enhanced by copper ion in neutral medium. Thus, a new highly selective detection method for copper ion could be developed over the range of 0.9–31.0 μM with the limit of determination of 97.6 nM (3σ). Foreign ions including Cd(II), Al(III) could be allowed even if present at the level of 7-fold more than that of Cu^{2+}, avoiding pre-separation procedures from complicated samples such as real wastewater samples. Mechanism studies showed that the reaction between NAPO and copper ion could form some kinds of clusters and induce the enhanced LS signals.

1. Introduction

It was known that greatly enhanced resonance light scattering (RLS) signals could be detected with a common spectrofluoremeter when the assemblies or aggregation species of the solution was excited with the wavelength of the light beam close to their absorption bands [1,2]. It has proved that these enhanced signals could be applied for analytical purpose with high sensitivity [3–12]. One of the drawbacks of these RLS signals-based technique, however, suffers from poor selectivity. Although the selectivity could be improved with the newly developed totally internally reflected RLS and the back RLS techniques, new accessory matched with the spectrofluorometer must be designed [13,14]. Therefore, extensively finding or artificially synthesizing a new selective probe is a good way to improve the selectivity of the light scattering (LS) technique. With this aim, herein we designed and synthesized a new reagent (N′,N′-bis (2-aminophenyl) oxamide (NAPO) according to the coordination property of oxamide ligand [15,16], which can coordinate with copper ion selectively, causing the enhanced LS signals.

Copper is an important element, it plays a complex role in most living organisms, and it has received attention in physiology, clinic studies and environmental toxicity. For example, cardiovascular disease has been found closely related to the copper-deficiency in human body [17], while copper poisoning occurs if it excessively accumulates in human body [18]. In order to assess its deficiency or physiological accumulation in

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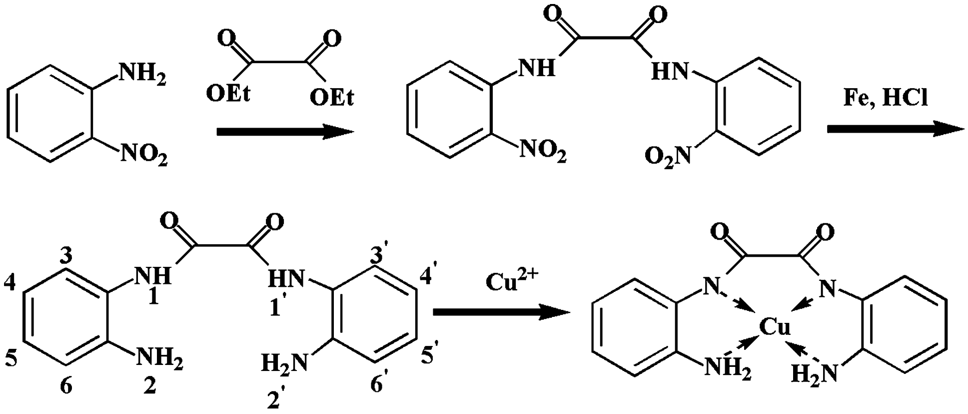

Fig. 1 – The synthesis process of NAPO and its reaction with copper ion.

biological or environmental bodies, many quantitative methods have been proposed including inductively-coupled plasma (ICP) emission spectrometry [19], surface plasmon resonance (SPR) spectroscopy [20], UV spectrophotometry [21], atomic absorption spectrometry (AAS) [22], ion-selective electrode [23], chemiluminescence technique [24], and flow injection detection [25]. In real samples, however, copper ion is separated commonly from complicate matrices before detection [25], to avoid the strong interferences from contaminants of the samples. Therefore, it is desirable to develop a simple method, which needs not to separate the copper ion from the complicated samples before detection.

It was found that our new synthesized NAPO could react with copper ion selectively in neutral medium, displaying strongly enhanced LS signals characterized at the wavelength of 451.8 nm. With these enhanced LS signals, a new rapid and selective method for copper ion detection has been proposed without the process of pre-separation, even for complicated wastewater samples. The results for the real sample measurements have been identified using the atomic absorption spectrometry and a portable laser turbidimeter method.

2. Experiment

2.1. Apparatus

LS measurements were made with a Hitachi F-4500 spectrofluorometer (Tokyo, Japan) and a quartz cell (1 cm × 1 cm). Absorption spectra were measured by a Hitachi U-3010 spectrophotometer (Tokyo, Japan). A PerkinElmer 2400 model element analysis instrument (PerkinElmer, USA) was used for detecting the element content of C, H, and N. Spectrumgx spectrophotometer (PerkinElmer, USA) was used for recording IR. An API 2000 mass spectrometer (PerkinElmer, USA) was used for detecting the mass of NAPO. An AV-300 NMR spectrometer (Bruker, Germany) was used for ^{1}H NMR measurements. For comparison, an Analyst 100 atomic absorption spectrophotometer (PerkinElmer, USA) and a portable laser turbidimeter (College of Physics, Southwest University, China) were used to detect the copper ion contents in real samples. A pHS-3C digital pH meter (Leici, Shanghai) was used to detect the pH values of the aqueous solutions. Size determination was conducted with a N5 submicron particles size analyzer (Beckman coulter, USA) based on dynamic light scattering (DLS) measurements with 90° scattering angle and at room temperature. A Nikon coolpix-4500 digital camera was used to detect the images of the aqueous solutions. A portable laser pointer of 450 nm with 0.5 mW light emitting diode (LED) and one of 653 nm with 2.0 mW were used as the light source in semi-quantitative detection. An MVS-1 vortex mixer (Beide Scientific Instrumental Ltd, Beijing) was used to blend the solutions in the volumetric flasks.

2.2. *Syntheses of N′,N′-bis (2-aminophenyl) oxamide (NAPO)*

Fig. 1 displays the synthesis procedure of NAPO. Under nitrogen protection, 56.0 g (about 0.4 mol) 2-nitro-aniline in a 250 mL four-neck-flask was heated to 190 °C. Subsequently, 33.0 mL oxalic acid diethyl ester was slowly added at magnetic force stirring, and the temperature of the reaction system gradually increased to the range of 200–220 °C. After stirring at 200–220 °C for 2 h, a yellow needle crystal could be obtained, and the mixture was cooled to the room temperature before 150.0 mL ether was added. At the end, the mixture was filtered and washed three times with 50% ethanol–H_2O (v/v), the product was dried in vacuum, and then the intermediate product of N′,N′-bis (2-nitro-phenyl) oxamide (NNPO) was obtained with the yield of 81% (mp 251–253 °C) referred to 2-nitro-aniline.

3.0 g NNPO, 12.0 g deoxidized iron powder, and 150.0 mL ethanol–H_2O (75%, v/v) were added to a 250 mL three-neck-flask, the solution was stirred with the mechanism and heated with water bath. When the solution started circulation reflux, 0.5 mL 6.0 mol L^{-1} hydrochloric acid was added and the reaction was kept circulation reflux for 2 h. After that, the pH of the solution was adjusted to 8.0–10.0, and the reaction system was filtrated under vacuum immediately. The product was washed three times with 50 % ethanol–H_2O (v/v) and dried in vacuum, then, NAPO was obtained with the yield of 26% (mp 241–242 °C) referred to NNPO. The molecular structure of NAPO has been identified by elemental analysis, mass spectrum, IR, and NMR. The result of elemental analysis is 62.19% C, 5.01% H, and 21.72% N, which is identical to the calculated values of 62.20% C, 5.22% H, and 20.73% N. Mass spectrum