



Contents lists available at ScienceDirect

# Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: [www.elsevier.com/locate/saa](http://www.elsevier.com/locate/saa)

## Spectroscopic study on the reactions of *bis*-salophen with uranyl and then with fructose 1,6-bisphosphate and the analytical application



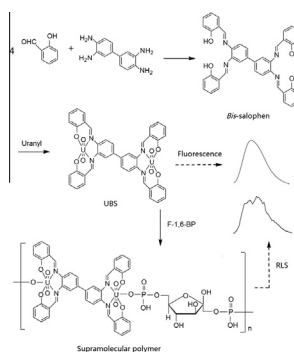
Xing Shen, Lifu Liao\*, Lin Chen, Yunfei He, Canhui Xu, Xilin Xiao, Yingwu Lin, Changming Nie

College of Chemistry and Chemical Engineering, University of South China, Hengyang, Hunan 421001, China

### HIGHLIGHTS

- *Bis*-salophen reacts with uranyl to form binuclear complex uranyl-*bis*-salophen (UBS).
- UBS reacts with fructose 1,6-bisphosphate (F-1,6-BP) to form supramolecular polymer.
- The two reactions were studied by fluorescence and RLS spectroscopy, respectively.
- Based on the reactions a fluorescence method for detecting U (VI) was established.
- A RLS method for detecting F-1,6-BP was also established.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Article history:

Received 3 August 2013

Received in revised form 16 November 2013

Accepted 5 December 2013

Available online 18 December 2013

#### Keywords:

*Bis*-salophen

Uranyl

Fructose 1,6-bisphosphate

Fluorescence

Resonance light scattering

### ABSTRACT

The chelating reaction of *bis*-salophen with uranyl to form binuclear complex uranyl-*bis*-salophen (UBS) was studied by fluorescence spectroscopy. The coordination reaction of UBS with fructose 1,6-bisphosphate (F-1,6-BP) to form supramolecular polymer was then studied by resonance light scattering (RLS) spectroscopy. The reaction of *bis*-salophen with uranyl results in a remarkable enhancement of fluorescence intensity. The maximum emission wavelength of the fluorescence is at 471 nm. The reaction of UBS with F-1,6-BP results in a remarkable enhancement of RLS intensity. The maximum scattering wavelength of the RLS is at 460 nm. The two reactions were used to establish fluorescence method for the determination of uranium (VI) and RLS method for the determination of F-1,6-BP, respectively. Under optimum conditions, the linear ranges for the detection of uranium (VI) and F-1,6-BP are 0.003–0.35 nmol/mL and 0.05–5.0 nmol/mL, respectively. The detection limits are 0.0017 nmol/mL and 0.020 nmol/mL, respectively. The proposed fluorescence method has been successfully applied for the determination of uranium (VI) in environmental water samples with the recoveries of 97.0–104.0%. The proposed RLS method has also been successfully applied for the determination of F-1,6-BP in medicine injection samples with the recoveries of 98.5–102.3%.

© 2013 Elsevier B.V. All rights reserved.

### Introduction

The reactions of ditopic ligands with metal ions to form binuclear complexes and their metallo supramolecular polymers have become of increasing interest in the last ten years. These reactions offer possibilities for the use in various fields due to produced var-

ious properties. The examples of applications include the use in optical [1,2], luminescent [3,4], molecular recognition and sensing [5,6] fields. At present, a few of ditopic terdentate ligands and several metal ions have been studied for the reactions of forming corresponding complexes and polymers [7–11]. However, up to date, ditopic tetradentate ligands and ditopic monodentate ligands as well as uranyl ion are hardly studied for reactions of forming binuclear complexes and their supramolecular polymers.

\* Corresponding author. Tel.: +86 734 8280649; fax: +86 734 8282375.

E-mail address: [llfcxllc@163.com](mailto:llfcxllc@163.com) (L. Liao).

Uranium is an important element and has been widely used as nuclear fuel. It is also high toxic and can severely damage human health and environment. Therefore, it is very important to study proper analytical method for the detection of uranium in water and environment [12–15]. Uranium can also be used in other fields due to its special advantages in structure and property, such as used as catalysts, analytical reagents and high density material [16–19]. Nevertheless, exploiting new application of uranium is still an interesting research field. Utilizing the reactions of uranyl with ditopic ligands to form uranyl-based binuclear complexes and supramolecular polymers can provide the possibility for the research of new application of uranium as well as new uranium analytical method.

Salophen is a tetradentate Schiff base ligand. It can combine uranyl cation to form stable uranyl-salophen complex [20]. Hence salophen is an excellent reagent used for recognition of uranium [21]. Since uranyl cation typically adopts a pentacoordinate environment, a tetradentate salophen ligand in uranyl-salophen complex leaves one site open for coordination to another molecule [22,23]. Thus, a uranyl-salophen complex is easily to bind a monodentate ligand to form a stable sandwich-type supramolecule: salophen-uranyl-monodentate ligand. Previous study demonstrated that the monodentate ligands can be phosphate and its derivatives such as adenosine triphosphate, and uranyl-salophen complex has strong ability to recognize these monodentate ligands with high affinity and high selectivity [24–27]. Therefore, it is possible to utilize the coordination reactions of salophen to uranyl and uranyl-salophen complex to monodentate ligands for the construction of binuclear uranyl complexes and corresponding metallo-supramolecular polymers.

Fructose 1,6-bisphosphate (F-1,6-BP) is a ditopic monodentate ligand containing two phosphate groups. It is an important substrate in living organisms and involved in many diseases for the treatment and diagnosis [28–30]. The detection of F-1,6-BP is of importance in pharmaceutical analysis, clinical diagnosis and biochemical study [31–33].

Here, for the first time, we have studied the chelating reaction of *bis*-salophen, which is a ditopic tetradentate ligand, with uranyl to form binuclear complex uranyl-*bis*-salophen (UBS) by fluorescence spectroscopy, and then studied the coordination reaction of UBS with F-1,6-BP to form supramolecular polymer by resonance light scattering (RLS) spectroscopy. Based on the two reactions, we have established a fluorescence method for the determination of uranium (VI) and a RLS method for the determination of F-1,6-BP. The two proposed methods have been successfully applied for the analysis of real samples with satisfactory results.

## Experimental

### Materials and apparatuses

Salicylaldehyde and 3,3',4,4'-tetraminobiphenyl were purchased from Aladdin (Shanghai, China). Uranyl nitrate hexahydrate was obtained from Aldrich (Milwaukee, WI, USA). Fructose 1,6-bisphosphate, trisodium salt (F-1,6-BP) was purchased from Sigma (Oakville, ON, USA). Other chemicals were purchased from Merck and Aldrich. All chemicals used were of analytical grade.

Fluorescent spectra and RLS spectra were recorded on a Hitachi 4500 spectrofluorometer. <sup>1</sup>H NMR spectra were obtained from a Bruker 300-MHz NMR spectrometer. FT-IR spectra were taken on a Shimadzu IR Prestige-21 FTIR spectrophotometer in the range of 4000–400 cm<sup>-1</sup>. Elemental analyses were carried out with a Thermo Finnigan EA 1112 elemental analyzer.

### Preparation of *bis*-salophen

The ditopic tetradentate Schiff base ligand, or *bis*-salophen, was prepared according to the procedure involving Schiff base condensation of tetramine with hydroxyaldehyde. Salicylaldehyde (1.05 g, 10 mmol) and 3,3',4,4'-tetraminobiphenyl (0.535 g, 2.5 mmol) were dissolved in 25 mL of methanol. The mixture was stirred for 1 h under reflux and then cooled to room temperature. The resulting yellow solid mass, *N', N'', N'''*-tetrasalicylidene-3, 3'-diaminobenzidine (*bis*-salophen), was filtered, and the product was recrystallized from THF and dried under vacuum. The preparing reaction and chemical structure of *bis*-salophen is shown in Fig. 1.

The ligand was characterized by analytical and spectral data. For elemental analysis of C<sub>40</sub>H<sub>30</sub>N<sub>4</sub>O<sub>4</sub>, calculated results are the following: C 76.19, H 4.76, N 8.88; found: C 75.82, H 4.85, N 8.67. For <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ results are the following: 13.01 (s, 4H, OH), 8.66 (s, 4H, imino bond), 7.45–6.95 (m, 22H, ArH). For FT-IR (KBr pellet, ν (cm<sup>-1</sup>)), absorption results are the following: 3452 (O–H stretching), 1616 (C=N stretching), 1408 (C–O stretching), 1097 (C–N stretching), 619 (C–H deformation). The presence of imino bonds indicated by <sup>1</sup>H NMR and IR spectroscopy demonstrates the formation of the ditopic tetradentate Schiff base ligand.

*Bis*-salophen solution (5.0 nmol/mL) used for the detection of uranium (VI) was prepared by dissolving the obtained *bis*-salophen in water containing 5% (v/v) DMSO.

### Preparation of binuclear uranyl Schiff base complex UBS

The complex was prepared by the following procedure. *Bis*-salophen (0.158 g, 0.25 mmol) and uranyl nitrate hexahydrate (0.251 g, 0.5 mmol) were dissolved in 25 mL of DMF. The mixture was stirred for the chelating reaction. After completion of the reaction, the solution was removed under reduced pressure. The obtained solid mass was purified by using a silica gel column, and eluted with chloroform-acetone mixture. Evaporation of solvent under reduced pressure afforded the solid binuclear uranyl *bis*-salophen complex. The preparing reaction and chemical structure of UBS is also shown in Fig. 1.

The binuclear uranyl complex was characterized by <sup>1</sup>H NMR and IR spectral data. For <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ results are the following: 9.60 (s, 4H, imino bond), 7.8–6.7 (m, 22H, ArH). For FT-IR (KBr pellet, ν (cm<sup>-1</sup>)), absorption results are the following: 1608 (C=N stretching), 1382 (C–O stretching), 1103 (C–N stretching), 891 (U=O stretching), 619 (C–H deformation). The chemical shift signal of OH groups at δ13.01 which is present in the <sup>1</sup>H NMR spectrum of *bis*-salophen disappears upon complexation. The absorption band of OH groups in the region 3500–3400 cm<sup>-1</sup> which is present in the IR spectrum of *bis*-salophen also disappears upon complexation. These results indicate the formation of the binuclear complex.

UBS solution (0.1 μmol/mL) used for the detection of F-1,6-BP was prepared by dissolving the obtained UBS in water containing 20% (v/v) DMSO.

### Procedure of uranium detection by fluorescence method

An appropriate amount of uranium (VI) calibration solution or sample solution, 1.0 mL of pH 6.0 2-(*N*-morpholino) ethane sulfonic acid (MES) buffer solution and 1.0 mL of Diethylene triamine pentaacetic acid (DTPA) masking agent solution were added into a 10 mL volumetric flask. The solution volume was fixed at 9 mL with water. Then under stirring 1.0 mL of *bis*-salophen solution was dropped into the uranium (VI) solution containing MES and DTPA with a total dropping time of 10 min. After *bis*-salophen was dropped, the fluorescence spectra of the system were recorded on the spectrofluorometer. A calibration curve of the emission

Download English Version:

<https://daneshyari.com/en/article/1232826>

Download Persian Version:

<https://daneshyari.com/article/1232826>

[Daneshyari.com](https://daneshyari.com)