



A novel fluorescent nano-chemosensor for cesium ions based on naphthalene macrocyclic derivative



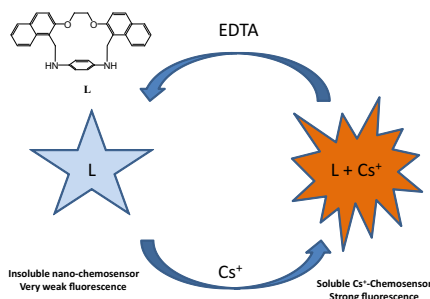
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HIGHLIGHTS

- The fluorescent nano-chemosensor with size about 40 nm was prepared by nanoprecipitation method.
- The nano-chemosensor exhibits a significant fluorescent enhancement toward Cs⁺ in aqueous buffer solution.
- The mechanism of fluorescence was based on the due to the photo-induced electron transfer (PET).

GRAPHICAL ABSTRACT



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ABSTRACT

A new macrocyclic nano-chemosensor (L) was synthesized and characterized by common spectroscopic methods. Spectral properties of fluorescent macrocycle L were studied either as solution in ethanol or as insoluble nanoparticles in aqueous buffer solution. The nano-chemosensors with size about 40 nm were prepared by nanoprecipitation method. The influence of metal cations such as Na⁺, K⁺, Cs⁺, Mg²⁺, Ba²⁺, Al³⁺, Pb²⁺, Cr³⁺, Mn²⁺, Fe³⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺ and Ag⁺ on the spectroscopic properties of the chemosensor in aqueous buffer solution were investigated by means of emission spectrophotometry. The macrocycle was found to be as an effective fluorescence sensor for Cs⁺ ions.

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Introduction

Selective detection of Cs⁺ ions in water samples is of great importance due to toxicity of cesium and its ability to displace potassium from muscles and red blood cells. Nuclear power provides about 11% of the world's electricity, and 21% of electricity in OECD countries. The spent nuclear fuel is reprocessed to recover the uranium and plutonium. Safe storage/disposal of radioactive wastes, generated in this process [1] is an important issue. In nuclear waste management, ¹³⁷Cs, one of the most abundant fission products, is a major radionuclide responsible for MANREM

problems. For this, the extent of removal of ¹³⁷Cs needs to be ascertained by measuring the concentration of Cs. While radioactivity counting techniques based on gamma spectrometry offer a very sensitive measurement option, they cannot be deployed for measuring stable isotopes of Cs. Also measurement of the radioactivity may not also be possible to all researchers. The other sensitive techniques such as atomic absorption spectroscopy (AAS) and polymeric membrane ion selective electrodes (ISEs) used to determine Cs⁺ ions involves expensive instrumentation and cost of operation. It would be ideal to have a measurement technique which is reasonably sensitive and at the same time can be applicable to measurement of stable cesium also. One method that offers rapid analysis and reliable measurements in aqueous environments is fluorescence spectroscopy by using fluorescent probes.

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Among the many reported fluorescent chemosensors for metal ions, only a few cases have been explored for Cs(I) [2–5]. However, most of the reported fluorescent chemosensors for recognition of Cs⁺ ion are based on crown ethers [2–5]. Dabestani et al. [2–4] developed a first-generation Cs⁺-selective fluorescence chemosensor based on a calix [4]arene derivative. This elegant chemosensor, while sensitive to the presence of Cs⁺, also binds other alkali metal ions with reasonably high affinity. As a result, there is a need to develop other Cs⁺ chemosensors that have higher selectivity. Less attention has been focused on the cesium-chemosensors that their receptors are oxoaza ligands. We herein report a cesium-chemosensor with oxoaza ligand as receptor.

Nanotechnology is a rapidly expanding area of research that utilizes nanoparticles in the development of imperative applications such as drug delivery, imaging, catalysis, chemical and biochemical sensing [6–20]. Nanoparticles have been used extensively as sensors with tremendous selectivity and sensitivity. Common nano-chemosensors are generally made up of incorporation of receptors or chemosensors on the surface of the nanoparticles. Our research team introduced a new type of nano-chemosensors that made up from organic nanoparticles [21,22].

Herein, we report a new nano-chemosensor for the cesium ions using organic nanoparticles (ONPs). The optical sensing ability of the chemosensor L was studied either as solution in ethanol or as insoluble nanoparticles in aqueous buffer solution. The chemosensor exhibits high sensitivity and selectivity to cesium ions when used as insoluble nanoparticles in aqueous buffer solution.

Experimental

Materials and apparatus

All chemicals, reagents, and solvents were the purest commercially available and used without further purification. Benzene-1,4-diamine was obtained from Merck. 2-[2-(2-Formylnaphthoxy)ethoxy]naphthaldehyde was prepared using the literature method [23]. NMR spectra were obtained using a Bruker A V300 MHz spectrometer. Infrared spectra were recorded as KBr pellets using a BIO-RAD FTS-40A spectrophotometer (400–4000 cm⁻¹). The fluorescence spectra were recorded on a Varian spectrofluorimeter. Both excitation and emission bands were set at 5 nm. The samples were characterized by a scanning electron microscope (SEM) (Phillips XL 30 and S-4160) with gold coating. Mass spectra were recorded on a JEOL JMS-SX102A.

Synthesis

Macrocycle of L

2-[2-(2-Formylnaphthoxy)ethoxy]naphthaldehyde (0.370 g, 1 mmol) was dissolved in ethanol (80 mL), and benzene-1,4-diamine (0.108 g, 1 mmol) was added. The reaction mixture was stirred and refluxed for 2 days. The solution was then allowed to cool to room temperature after which Sodium borohydride (0.83 g, 0.02 mol) was added in small portions and the solution was stirred over 10 min. Water (5000 mL) was added to the solution and the pH was adjusted to 11 with potassium hydroxide. The solution was extracted with chloroform (×2). The chloroform extracts were combined and dried over anhydrous sodium sulfate. The dried extracts were then reduced to a small volume on a rotary evaporator. The product formed as white crystals on letting this solution stand; (yield: 70%). Anal. Calcd. For C₃₀H₂₆N₂O₂: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.73; H, 5.84; N, 6.32%; FT-IR (KBr), cm⁻¹: 3391 (ν NH). ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 3.51 (b, 2H, NH), 4.57 (s, 4H, N-CH₂-Ar), 4.77 (s, 4H, O-CH₂-CH₂-O), 6.78–8.04 (m, 16H, Ar). ¹³C NMR (CDCl₃, 300 MHz) δ (ppm):

49.33, 69.87, 114.67, 123.24, 123.78, 127.79, 129.12, 128.42, 129.27, 129.44, 130.42, 132.65, 136.88 and 154.52. The mass spectrum shows peak at *m/z* = 446 corresponding to the [1+1] macrocycle.

Nanoparticle synthesis

A saturated solution of L was prepared by adding 0.1 g of L to 10 mL of DMF in room temperature. The solution was pumped from a small orifice (a sharp needle was arranged at the front of the orifice) into 100 mL of the antisolvent (water) which was placed in an ultrasonic bath at 180 W for 30 min and continuously stirred. The suspension was centrifuged at 5000 g for 15 min, and the supernatant was withdrawn and filtered through 0.2 μm pore size syringe filter [21].

Theoretical calculations

The geometry of macrocycle L were fully optimized at DFT [24,25] levels of theory using the GAUSSIAN 03 program [26], on a Pentium-PC computer with a 4000 MHz processor. A starting semi-empirical structure was optimized using the HYPERCHEM 5.02 series of programs [27].

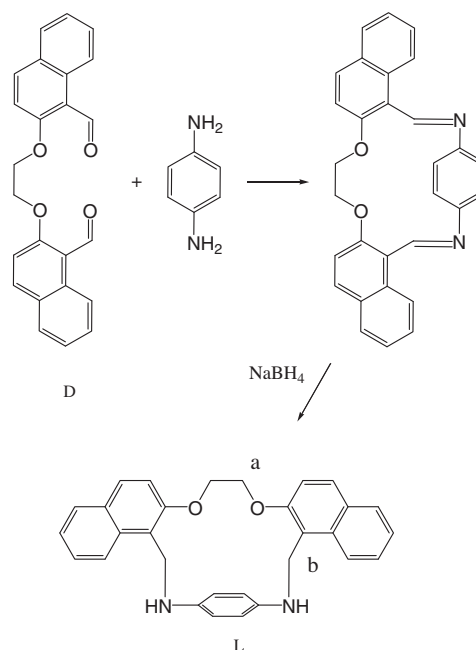
Results and discussion

Synthesis and characterization

The synthetic route for the macrocycle L was shown in Scheme 1. Macrocycle of L was prepared by direct cyclocondensation between dialdehyde D [21] and benzene-1,4-diamine in ethanol, followed by reduction with NaBH₄. Macrocycle of L was characterized by microanalysis, mass spectrometry, IR and NMR studies. The macrocycle is soluble in polar solvents such as chloroform and ethanol and was hydrolytically stable under both basic and acidic conditions.

NMR studies

The ¹H NMR spectrum of the L dissolved in chloroform exhibited a broad signal at ca. 3.51 ppm attributed to secondary



Scheme 1. The synthetic route of L.

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