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Research paper

Synthesis and characterization of a new organic nanoparticle as fluorescent chemosensor for aluminum ions

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ABSTRACT

A new macrocyclic ligand (L) was synthesized and characterized with spectroscopic techniques. Its nanoparticles were prepared by nanoprecipitation method. The averaged size of the synthesized nanoparticles in the optimized conditions was about 50 nm. The nanoparticles exhibit an "off–on" type mode with high selectivity in the presence of Al^{3+} ions. The organic nanoparticles (L) could be used as Al^{3+} chemosensor in aqueous media. Upon binding of Al^{3+} with the nanoparticles, a significant fluorescence enhancement with a turn-on ratio over 15-fold was triggered. However, other metal ions had no such significant effect on the nano-chemosensor. The detection limit of nanoparticles L for Al^{3+} was as low as 2.8×10^{-7} M. Application of the nano-chemosensor (L) was also studied as molecular logic gate.

1. Introduction

In the Earth's crust, aluminum is the most abundant (8.3% by weight) metallic element. It is highly used in many industries to make millions of different products and highly important for the world economy. It has been found that Al^{3+} ions exerted several neurotoxic effects in organisms a long time ago. For example, Al^{3+} has an important role in Alzheimer's disease, Parkinson's disease, bone softening, chronic renal failure and smoking related diseases. Since there is a close association between Al^{3+} and human health, the investigation of Al^{3+} detection attracts more and more attention [1–8]. In recent decades, fluorescent chemosensors for various metal ions have attracted much interest because of their potential applications in environmental detection, molecular catalysis, and biological fluorescence imaging, etc [9–15]. The lack of spectroscopic characteristics and poor coordination ability of Al^{3+} are two main obstacles in the development of an Al^{3+} selective fluorescent chemosensor [16–22]. The macrocycles are an important class of compounds to design of chemosensors. macrocycle-based receptors have been well studied as effective systems showing high selectivity and affinity for environment and biological cations. With the progress of nanotechnology and the application of nanometre sensing devices, the capacity to smartly design new analytical platforms for target species has been greatly expanded [23–25]. By using organic nanoparticles, the chemodetection selectivity and sensitivity to analytes was demonstrated [26,27].

Herein, we report a nano-chemosensor as a fluorescence "turn-on" sensor for distinct detection of Al^{3+} ions in aqueous solutions. The chemosensor has been chosen as macrocylic compound for high selectivity and low detection limit. Selective fluorescence enhancement by Al^{3+} could be due to the effective coordination of Al^{3+} with L over other metal ions. This restricts the photoinduced electron transfer (PET) process and enhances the fluorescence output of L via chelation enhanced fluorescence (CHEF) effect. This new fluorescent sensor **L** displayed an extreme selectivity for Al^{3+} compared with other metal ions examined.

2. Experimental

2.1. Materials

All chemicals were of reagent–grade from Merck chemical companie. The nitrate and chloride salts of all the used cations were of the highest purity available and used without any further purification. *N*-(3-aminopropyl)propane-1,3-diamine also purchased from Merck Company. Dialdehyde (D) was prepared according to the literature method [27].

2.2. Instruments and spectroscopic measurements

The infrared spectra (KBr pellet) were recorded using FTS165 Bio-Rad FTIR spectrophotometer in the range 4000–450 cm^{-1}.

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SEM analysis was performed on a Philips XL-30 field-emission scanning electron microscope operated at 16 kV. ^{1}H, ^{13}C, COSY, DEPT and HMQC ^{1}H, ^{13}C NMR spectra were recorded on a Bruker AMX-500 spectrometer and DMSO was used as the solvent in all cases. Fluorescence measurements were done in a Varian spectrofluorimeter. Mass spectra were recorded on a JEOL JMS-SX102A,

2.3. Synthesis of macrocycle L and its nanoparticles

Synthesis of L was based on the following method (Scheme 1): an ethanol solution (300 mL) of *N*-(3-aminopropyl)propane-1,3-diamine (0.13 g, 1 mmol) was added dropwise to a solution (400 mL) of D (0.370 g, 1 mmol) in ethanol. The solution was stirred for 48 h under reflux. After the solution has come to room temperature, Sodium borohydride (0.83 g, 0.02 mol) was added and the solution was stirred at this temperature for 10 min. Distilled water (5000 mL) was added to the solution and the pH was adjusted to 11 using potassium hydroxide. The solution was extracted with chloroform (×2). The chloroform extracts were dried over 5 g anhydrous sodium sulfate. The dried extracts were then reduced under reduced pressure by a rotary evaporator. Finally, the product formed as white crystals on letting this solution stand; (yield: 70%). Anal. Calcd. For $C_{36}H_{39}N_3O_2$: C, 79.23; H, 7.20; N, 7.70. Found: C, 79.45; H, 6.98; N, 7.72 %; FT-IR (KBr), cm^{-1}: 3273 (ν NH). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 5.51 (s, 4H, H_a), 4.20 (s, 4H, H_b), 2.70 (b, 4H, H_c), 2.51 (b, 4H, He), 1.66 (b, 4H, H_d), 7.28–8.02 (m, 16H, Ar). ^{13}C NMR ($CDCl_3$, 300 MHz) δ (ppm): 27.56, 43.03, 48.01, 69.48, 114.36, 121.28, 122.86, 123.74, 127.09, 128.48, 128.56, 128.94, 129.30, 133.21, 135.06, and 153.95. The mass spectrum shows peak at m/z = 545.7 corresponding to the [1+1] macrocycle (S.1).

The nanoprecipitation technique for nanoparticle manufacture was first developed and patented by Fessi and co-workers [28]. This technique presents numerous advantages, in that it is a straightforward technique, rapid and easy to perform. The nanoparticle formation is instantaneous and the entire procedure is carried out in only one step. Briefly, it requires two solvents that are miscible. Nanoprecipitation occurs by a rapid desolvation of the compound when the compound solution is added to the antisolvent. Indeed, as soon as the compound-containing solvent has diffused into the dispersing medium, the compound precipitates.

Nanoprecipitation often enables the production of small nanoparticles. Nanoprecipition is an efficient technique for the preparation of versatile organic nanoparticles. Nanoparticles of L with mean size in the range 50–60 nm were prepared as shown in Fig. 1. The molecular states of the bulk and nanosized L were studied by means of FT-IR. Fig. 2 shows the FT-IR spectrum of the L in the range of 400–4000 cm^{-1}. The spectrum of the L is characterized by the bending vibration of NH (1624 cm^{-1}) and stretching vibration of NH (3423 cm^{-1}). The close agreement between the FT-IR spectra of the raw and nanosized L suggested that there were no changes in the L molecular structure caused by the nanoprecipitation process (Fig. 2).

2.4. Density functional theory calculation

It has been shown that DFT calculations give a good description of geometry and other properties of this type of compounds. Therefore quantum chemical calculations at DFT level of theory have been carried out to obtain the possible structure of L.

3. Results and discussion

As shown in Scheme 1, a novel N_3O_2 macrocycle (L) was easily synthesized by reacting dialdehyde D with *N*-(3-aminopropyl)propane-1,3-diamine through cyclocondensation reaction in refluxed absolute ethanol. The structure of compound L was characterized by ^{1}H NMR,^{13}C NMR, ^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and DEPT and MS, and the results are in good agreement with the structure presented in Scheme 1 (Figs. S2–S5 in the Supporting Information).

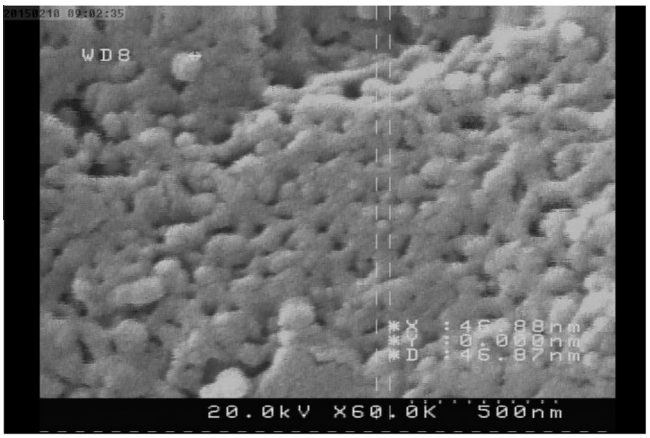
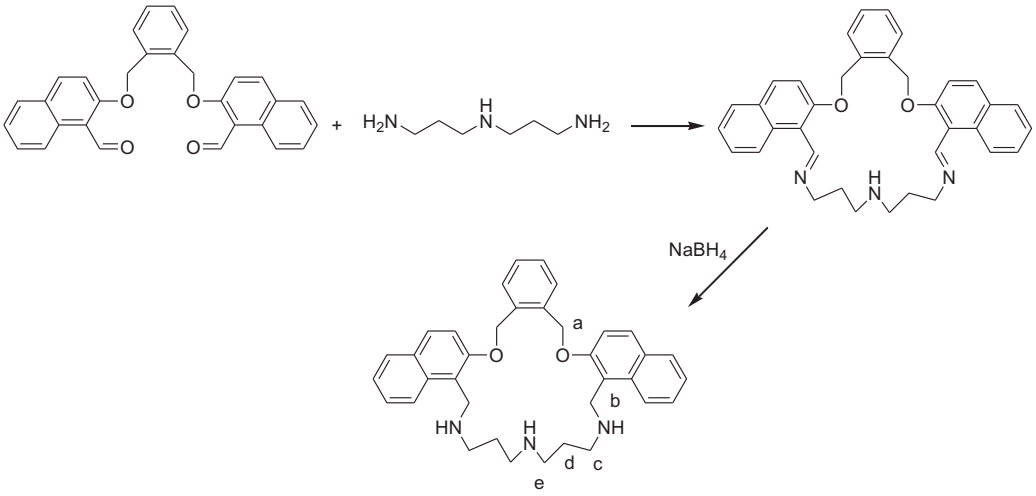


Fig. 1. FT SEM image of nanoparticles L.



Scheme 1. The synthetic route to prepare of L.