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## Combined spectral experiment and theoretical calculation to study the interaction of 1,4-dihydroxyanthraquinone for metal ions in solution

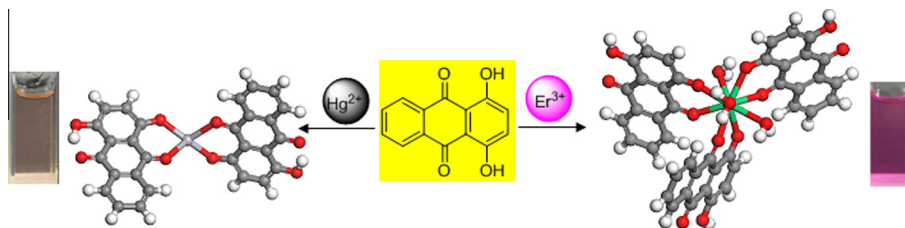
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### HIGHLIGHTS

- The interaction between 1,4-dihydroxyanthraquinone and metal ions in solution was studied in detailed.
- 1,4-Dihydroxyanthraquinone has better response for Hg<sup>2+</sup> and Er<sup>3+</sup> over other metal ions.
- 1,4-Dihydroxyanthraquinone has a potential application in the design of metal ions probe.

### GRAPHICAL ABSTRACT

The statement: Hg<sup>2+</sup> and Er<sup>3+</sup>, their reaction abilities for 1,4-DHA were studied by UV-Visible and fluorescence spectroscopies in solution. They all have better response for 1,4-DHA in the spectra with distinct and regular changes. And theoretical calculation concluded that Er<sup>3+</sup> easily react with 1,4-DHA over Hg<sup>2+</sup> attributed to the low reaction energy of Er<sup>3+</sup>-1,4-DHA than Hg<sup>2+</sup>-1,4-DHA.



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### ABSTRACT

The interaction between 1,4-dihydroxyanthraquinone (1,4-DHA) and metal ions was studied by UV-Visible and fluorescence spectroscopies in solution. Time-dependent density functional theory calculations confirmed complex structures. The investigation results showed 1,4-DHA can selectively respond some metal ions and can be monitored by UV-Vis, fluorescence spectra and naked-eye. So 1,4-DHA has a potential application in the design of metal ions probe. More, as typical metal ions, Hg<sup>2+</sup> and Er<sup>3+</sup>, their reaction abilities for 1,4-DHA were studied in detailed. Experimental results showed they have better response for 1,4-DHA. And theoretical calculation concluded that Er<sup>3+</sup> easily reacts with 1,4-DHA over Hg<sup>2+</sup> attributed to the low reaction energy of Er<sup>3+</sup>-1,4-DHA than Hg<sup>2+</sup>-1,4-DHA.

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### Introduction

Anthraquinone, also called anthracenedione or dioxoanthracene, is an aromatic organic compound with formula C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>. One specific isomer, 9,10-dioxoanthracene, wherein the keto groups are located on the central ring. It is a building block of many dyes and is used in bleaching pulp for papermaking. Dyes

anthraquinone derivatives generally have the biological activity and pharmacological effects, such as hemostatic, anti-bacterial and anti-cancer [1]. For example, red dye having an anthraquinone structure as a class of photosensitizers is ubiquitous in nature, and it is also a constituent part of a variety of anti-cancer drugs, these drugs target DNA and can damage DNA including physiological active molecules induced by visible light exhibiting photosensitive anti-cancer effects [2–7]. So, the biological and pharmaceutical science of anthraquinones has received significant attention, with derivatives showing a breadth of applicability (e.g., antibiotics

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and antitumor activity), the hydroxy-antraquinone unit has been identified as a key biologically active site in antitumor anthracyclines. As one of anthraquinone derivative, hydroxy-antraquinone is a naturally occurring genotoxic compound found in medicinal plants, including *Rubia tinctorium* L [8,9]. The extraction from *Scutia myrtina* has yielded three anthrone-antraquinone derivatives, a new bisanthrone-antraquinone and the known aloesapoin I [10]. Most of these compounds, as they possessing antimicrobial, antiviral and anticancer properties [11,12], were commonly used as biological fluorescent probes in cell imaging microscopy [13]. In the 1990s, studying for biological redox anticancer new drug AQ4N showed that the compounds combination with anthraquinone structure and aliphatic N-oxides have broad prospects in the creation of the anticancer compound. The 1,4-dihydroxyanthraquinone is critical structure in anthraquinone-based anticancer new drug including AQ4N, including AQ4N, doxorubicin [14–22]. It is well known that 1,4-dihydroxyanthraquinone (1,4-DHA), commonly known as quinone Sin, its space structure is very symmetry, and its color is obvious (when dissolved in different solvents, it then show different colors, along with a strong fluorescence change). Based on its characteristics, in recent years, 1,4-DHA can be used to synthesize various dyes and are common structural subunits of many biologically active quinonoids namely, anthracyclines, dynemicins, mitoxantrones, anthraquinonesteroid hybrids, and naphthacenedione organic dyes [23]. It also can be modified into synthetic dyes intermediates, 1,4-diamino anthraquinone. In addition, under certain condition, 1,4-dihydroxyanthraquinone can be induced to self-assembly to form a metallo-supramolecular coordination polymers [24–26] which demonstrate good selectivity and binding for planar aromatic guests, small organic molecules and transitional metal ions, such as methylene dichloride and iridium [27–30]. 1,4-dihydroxyanthraquinone with multi coordinating groups, can coordinate to many different metal ion (such as alkali metal, alkaline earth metal, the third main group metals and transition metal) [31]. In view of this, the fluorescent complexes between hydroxy-antraquinone and some rare earth ions in applying to the fluorescence method determination have been reported [32]. In this work, the interaction between 1,4-DHA and metal ions was studied by UV–Visible, fluorescence spectroscopies in solution. The results showed that  $\text{Hg}^{2+}$  and  $\text{Er}^{3+}$ , all have better response for 1,4-DHA in the spectra and color with distinct and regular changes. And theoretical calculation concluded that  $\text{Er}^{3+}$

easily reacts with 1,4-DHA over  $\text{Hg}^{2+}$  attributed to the low reaction energy of  $\text{Er}^{3+}$ -1,4-DHA than  $\text{Hg}^{2+}$ -1,4-DHA.

## Experimental

### Materials

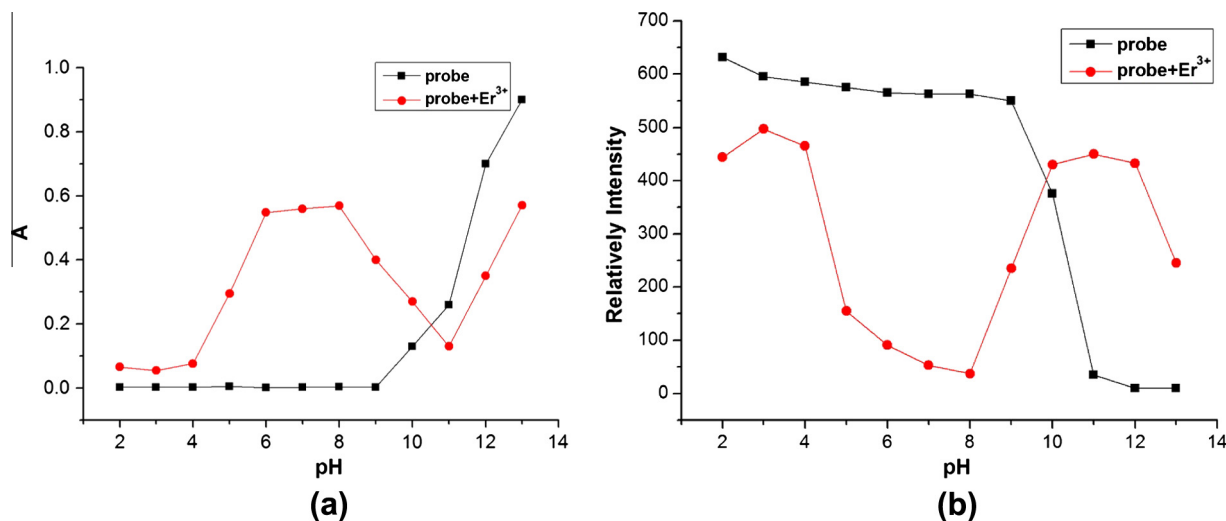
All chemicals and solvents were of analytical grade and bought from Sigma–Aldrich or Beijing City without further purification. Chromatography was carried out on silica gel (200–300 mesh). Thin layer chromatography (TLC) was carried out using silica gel GF<sub>254</sub> plates with a thickness of 0.20–0.25 mm. Deionized water was used to prepare all aqueous solutions. The solutions of  $\text{Hg}^{2+}$ ,  $\text{Er}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Eu}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Ho}^{3+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Ce}^{4+}$  and  $\text{Zr}^{3+}$  were prepared from their chloride salts. The solution of  $\text{Ag}^{+}$  was prepared from nitrate salt. The solution of  $\text{VO}^{2+}$  was prepared from their sulfate salt. All spectroscopic measurements were performed in HEPES (10 mmol/L, pH 7.0) buffer. HEPES buffer solutions were obtained by adding 1 mol/L NaOH solution into 10 mmol/L aqueous HEPES using a Mettler Toledo pH meter. 1,4-DHA was dissolved in absolute EtOH to prepare the stock solutions with concentrations of 2.0 mmol/L.

### Synthesis of the complex

To a stirred solution of phthalic anhydride (1 mmol) and boric acid (25 mmol), chlorophenol (1.2 mmol) (dissolved in 5%, 20 g sulfuric acid) was added dropwisely. Then the system was stirred 5 h at room temperature. The solution was poured into ice water (400 g), and then heated to 85 °C for another 30 min. The reaction mixture was filtered, and the solid was washed with water for several times until it became neutral. After drying in high vacuum, 0.21 g (0.88 mmol) pink powder was obtained in a yield of 90% (Fig. S1). The structure of complex was shown Fig. 1.

### Physical measurements

The UV–Visible spectra were recorded on a Cary 50 Bio UV–Visible spectrophotometer in a 4.5 mL (1 cm in diameter) cuvette with 2 mL solution. Fluorescence spectra were measured on Cary Eclipse fluorescence spectrophotometer. All data were treated with the



**Fig. 1.** (a) and (b) are UV–Vis absorbance values at 538 nm and fluorescence intensity at 532 nm of free 1,4-DHA (130  $\mu\text{mol/L}$ ) and 1,4-DHA (130  $\mu\text{mol/L}$ )- $\text{Er}^{3+}$  under different pH conditions, respectively.

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