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## A mercuric ensemble based on a cycloruthenated complex as a visual probe for iodide in aqueous solution



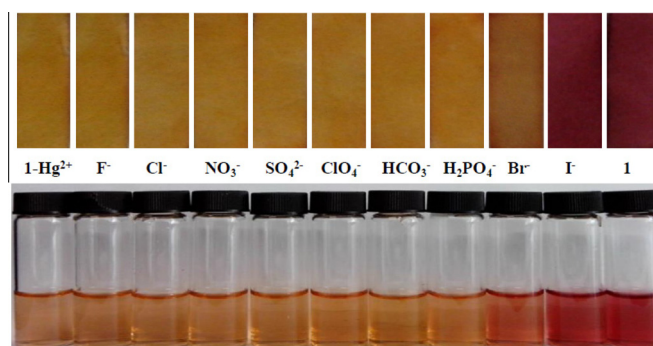
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### HIGHLIGHTS

- A mercuric ensemble based on a cycloruthenated complex was obtained for detecting  $I^-$  in water.
- It exhibit remarkable color change from yellow to red with the detection limit of 0.77  $\mu M$ .
- The test strips with the ensemble for tracing  $I^-$  were practically realized.

### GRAPHICAL ABSTRACT



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### ABSTRACT

A new water-soluble cycloruthenated complex  $Ru(bthiq)(dcbpy)_2^2+$  (**1**, Hbthiq = 1-(2-benzo[b]thiophenyl)isoquinoline, dcbpy = 4,4'-dicarboxylate-2,2'-bipyridine) was designed and synthesized to form its mercuric ensemble (**1**- $Hg^{2+}$ ) to achieve visual detection of iodide anions. The binding constant of **1**- $Hg^{2+}$  is calculated to be  $2.40 \times 10^4 M^{-1}$ , which is lower than that of  $HgI_2$ . Therefore, the addition of  $I^-$  to the aqueous solution of **1**- $Hg^{2+}$  lead to significant color changes from yellow to deep-red by the release of **1**. The results showed that iodide anions could be easily detected by the naked eyes. The detection limit of iodide anion is calculated as 0.77  $\mu M$ . In addition, an easily-prepared test strip of **1**- $Hg^{2+}$  was obtained successfully to detect iodide anions.

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## 1. Introduction

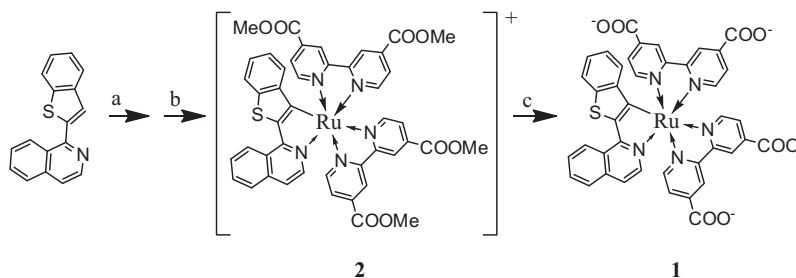
Iodine is an essential microelement to humans, which plays a key role in several biological activities such as brain functions, cell growth, neurological activity and thyroid function [1–4]. Moreover, elemental iodine has been frequently used in chemistry, biology and food fields [5,6]. Therefore, the development of technology for the detection of iodide is very important. It is worthy to note that several methods such as chemiluminescence [7–9], ion

chromatography [10–12], ion-selective electrode [2,13], diffuse reflectance spectroscopy [14] and inductively coupled plasma mass spectrometry (ICP-MS) [1,15] have been conducted for the determination of trace amount of iodine and iodide. However, complicated procedures and expensive equipments are required in these methods.

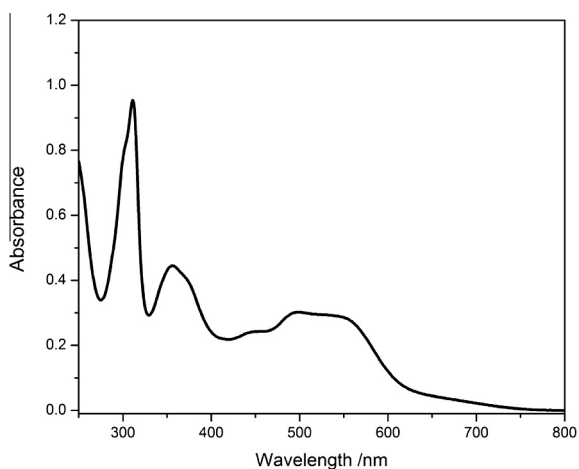
Recently, chromogenic and fluorescent recognition of iodide anions has received much attention because of the high sensitivity, low cost, good potential efficiency, and easy operation. Unfortunately, the similar chemical properties of halogen elements make them difficult to distinguish from each other [4]. Moreover, iodide anion has large anionic radius, low charge density, and

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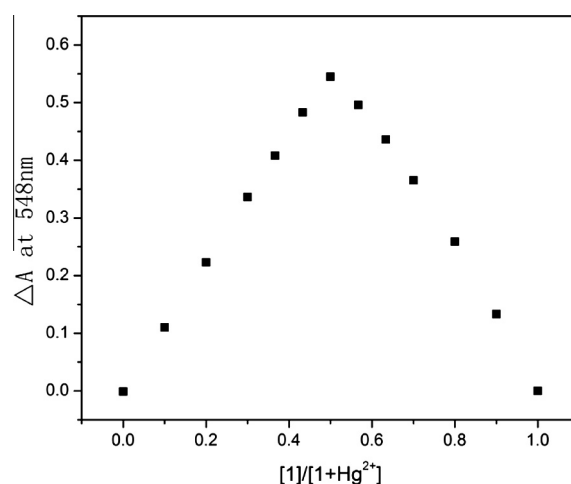
E-mail address: [lixhchem@mail.scuec.edu.cn](mailto:lixhchem@mail.scuec.edu.cn) (X. Li).



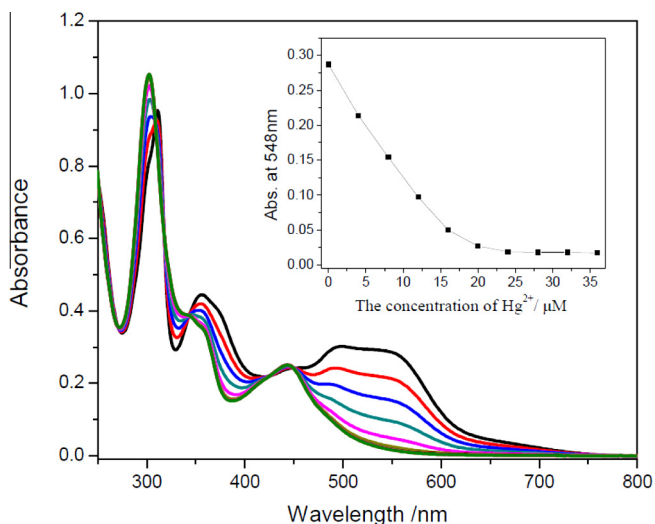
**Scheme 1.** Synthetic route of cyclometallated ruthenium complex **1**. (a) NaOH, KPF<sub>6</sub>, [Ru(cycme)Cl<sub>2</sub>]<sub>2</sub>, CH<sub>3</sub>CN, 50 °C; (b) 4,4'-dimethylester-2,2'-bipyridine, CH<sub>3</sub>OH, reflux; (c) NaOH, CH<sub>3</sub>CH<sub>2</sub>OH, 25 °C.



**Fig. 1.** The UV-Vis spectrum of **1** in HEPES (20 mM, pH = 7.00) solution.



**Fig. 3.** Job's plot for  $[1] + [\text{Hg}^{2+}] = 8.0 \times 10^{-5}$  mol/L in HEPES solution (20 mM, pH = 7.00).



**Fig. 2.** The absorption spectra changes of **1** (20 μM) in HEPES solution (20 mM, pH = 7.00) with increasing amounts of mercury metal ions. Inset: UV-Vis titration curve of **1** with Hg<sup>2+</sup>.

low hydrogen-bonding ability [16–20]. All these make the probes for iodide anions rarely shown [21–30]. Up to now, most of these reported probes respond to iodide anions with changes only in fluorescent intensity, which can also be caused by many other poor quantified or variable factors such as the sample environment and probe concentration in practical application and lead to signal fluctuations. Wang has recently developed an iodide anions probe with a red-shift in the absorption and fluorescent emission

maxima [21]. However, the probe is insoluble in water and THF/H<sub>2</sub>O (4/1, v/v) is needed. As is well known, water solubility is important for the probes in practical application because the iodide anions widely exist in aqueous systems in nature. Nevertheless, most of the probes for iodide anions are incompatible with aqueous systems. On the other hand, in order to increase the selectivity and sensitivity, the appreciable color change in absorption or emission will be useful for rapid visual sensing [23,26]. Therefore, the design of the novel water-soluble probes attracts our attention, which can detect iodide anions selectively with simultaneous changes of spectra and solution color.

By contrast, the colorimetric technology is a good tool for sensing iodide owing to its simplicity, short responsive time and visualization without aids of instruments [23,26]. In view of long-wavelength absorptions of cyclometallated ruthenium complexes [31–34] for easy visualization, a new water soluble cycloruthenated complex Ru(bthiq)(dcbpy)<sub>2</sub> (**1**, Hbthiq = 1-(2-benzo[b]thiophenyl)isoquinoline, dcbpy = 4,4'-dicarboxylate-2,2'-bipyridine) was designed to form its mercuric(II) ensemble (**1**-Hg<sup>2+</sup>) (Scheme 1). Subsequently, **1**-Hg<sup>2+</sup> was further used to recognize iodide visually in aqueous solutions, which resulted in an apparent color change from yellow to deep-red. Therefore, it can be used as a colorimetric chemo-sensor for I<sup>-</sup> in water.

## 2. Experimental

### 2.1. Materials and instruments

All chemicals were commercially available and used without further purification unless specified. Acetonitrile was freshly

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