



# Allosteric anion binding controlled by infrared irradiation: Light-triggered chromogenic sensing of iodide in aqueous solution



Qiong Qi, Ruolin Lin, Xiaoyu Chen, Shunhua Li\*

Department of Chemistry and the MOE Key Laboratory of Spectrochemical Analysis & Instrumentation, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

## ARTICLE INFO

### Article history:

Received 27 February 2015  
Received in revised form 16 August 2015  
Accepted 24 August 2015  
Available online 28 August 2015

### Keywords:

Allosterism  
Molecular recognition  
Iodide  
Sensors  
Colorimetric detection

## ABSTRACT

Allosteric molecular sensing, which makes a synthetic receptor work like a biological signal transduction system, is a challenging topic attracting intense research interest. In this manuscript, we report the first allosteric chemosensor that can be activated and controlled by infrared (IR) irradiation. As a very important structural element in the maintenance and regulation of protein function, disulfide bond (DSB) was employed as the photoactivatable hinge of a homotropic anion receptor based on disulfide-bridged binuclear silver(I) complexes. Because of the light-driven rotation of DSB, this biomimetically designed receptor shows a unique dynamic color response to iodide in aqueous solution under IR irradiation, which is distinctly different from what occurs in the dark. As a consequence, specific colorimetric detection of iodide in aqueous solution can be well established at the micromolar concentration level. Our study exemplifies a brand-new molecular sensing mode for anions. Furthermore, it opens a new way to operate disulfide bond as an optical switch, which may lead to important applications in chemical biology.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Precise regulation of the function of a protein by allosteric interaction between distinct active sites ubiquitously occurs in biological events [1–3]. Biomimetic design of allosteric molecular recognition systems offers an important strategy to regulate the complexation ability or catalytical activity of synthetic receptors and is therefore attracting much research interest [4–8]. An allosteric guest binding process enables possible high selectivity and sensitivity in molecular sensing. Furthermore, the resulting dynamic or multiple sensing responses are highly useful for establishing a reliable diagnosis. Although the photochemical control of molecular sensing and biological functions has motivated many researches because of its capability of probing in real time and real place [9–13], it remains challenging to manipulate allosteric molecular sensing by a similar external control. Herein, we report an allosteric anion receptor driven by IR irradiation and its application to chromogenic sensing of iodide in aqueous solution.

The synthetic receptor was designed to contain two anion binding sites linked by a disulfide bridge (Scheme 1). As a very important structural element in the maintenance and regulation of protein

function [14–19], DSB can be cleaved by reductants or ultraviolet (UV) irradiation and thus act as an allosteric trigger. Indeed, the photolysis of DSB has been successfully utilized to regulate the conformations and bioactivities of proteins or synthetic peptides [20–28]. In addition to the photolysis reactivity, the optical activity of disulfide compounds arising from the rotation-induced different dihedral angles over DSB has been well studied [29–32]. The fact that the low rotation energy barrier of DSB can be matched by IR irradiation opens another theoretically possible entry to the optical regulation of protein conformation. Compared with the UV photolysis, IR control means minimal damage and deeper penetration in biological applications. However, conformation regulation of DSB-containing species by IR irradiation has never been reported. In our design, DSB was employed as a photoactive hinge of a binuclear silver(I) complex (**1**), which displays a unique allosteric response to iodide anions under irradiation.

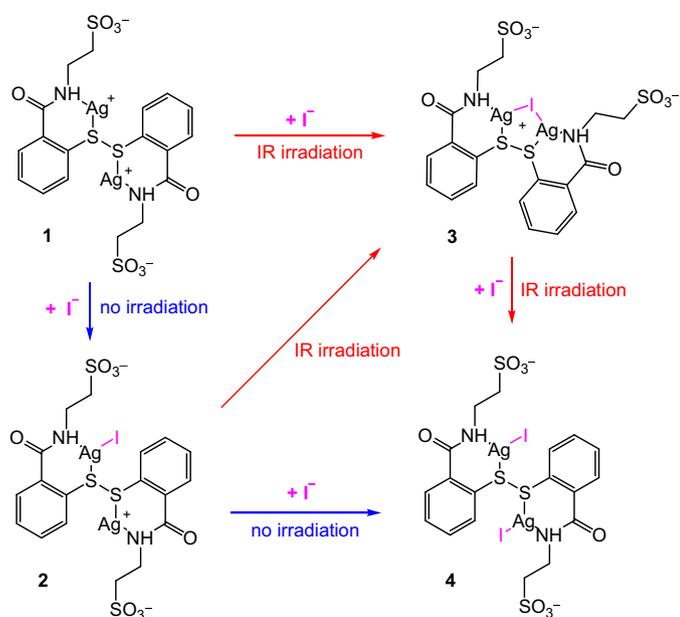
## 2. Materials and methods

### 2.1. Reagents and apparatus

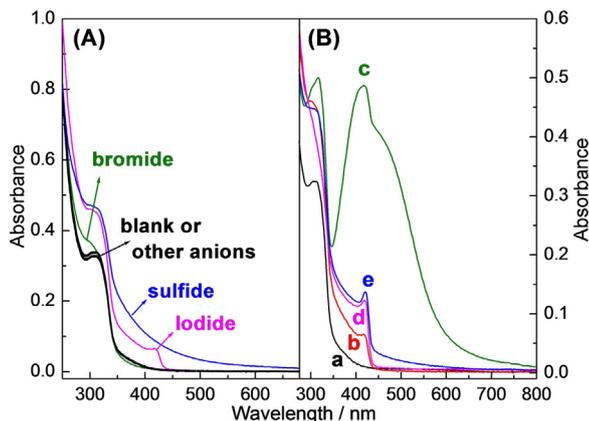
2,2'-Dithiosalicylic acid, taurine and silver nitrate were purchased from Sigma–Aldrich Co., Ltd. They were used without any further purification. All other reagents were of analytical grade or better and used without further purification.

\* Corresponding author.

E-mail address: [lishua@xmu.edu.cn](mailto:lishua@xmu.edu.cn) (S. Li).



**Scheme 1.** Proposed working mechanism for allosteric sensing of iodide by **1**.

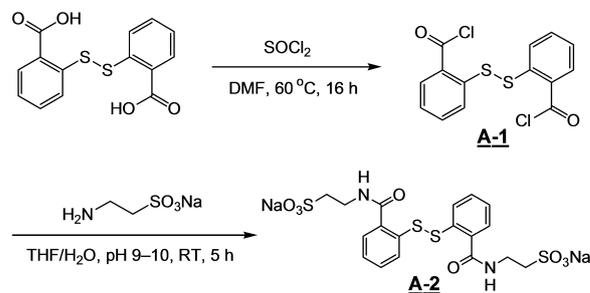


**Fig. 1.** (A) Absorption responses of **1** (50  $\mu\text{M}$ ) upon addition of different species (1.0 equiv.) including NaF, NaCl, NaBr, NaSCN, Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, NaNO<sub>2</sub>, NaNO<sub>3</sub>, NaHCO<sub>3</sub>, NaAcO, and Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in the dark. (B) Absorption responses of **1** (50  $\mu\text{M}$ ) upon addition of different amounts of iodide: a, **1** blank; b, **1** + I<sup>-</sup> (1.0 equiv.), no irradiation; c, **1** + I<sup>-</sup> (1.0 equiv.), IR irradiation; d, **1** + I<sup>-</sup> (2.0 equiv.), no irradiation; e, **1** + I<sup>-</sup> (2.0 equiv.), IR irradiation. The IR irradiation was provided by a common IR lamp (0.76–5.0  $\mu\text{m}$ ,  $\lambda_{\text{max}}$  = 4.0  $\mu\text{m}$ , 275 W).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance II 400 MHz NMR spectrometer. Electrospray ionization (ESI) mass spectra were recorded on a Bruker ESQUIRE-3000<sup>+</sup> mass spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker-Dalton Reflex III mass spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were acquired with a VG ESCA LAB MK-2 instrument. Absorption and fluorescence spectra were recorded on a Hitachi U-3900 ultraviolet–visible spectrophotometer and a Hitachi F-7000 fluorophotometer, respectively.

## 2.2. Preparation of the disulfide ligand

To a solution of 2,2'-dithiosalicylic acid (3.06 g, 10 mmol) in thionyl chloride (10 mL) was added one drop of DMF. The mixture was stirred at 60 °C for 16 h to give a brown solution. The residual thionyl chloride was evaporated under vacuum to produce compound **A-1** as a brown solid. The resulting solid was dissolved in



**Scheme 2.** Synthesis of the disulfide ligand.

THF (15 mL) and the solution was added dropwise into a solution of taurine (3.5 g, 28 mmol) in 40% (v/v) THF/water (25 mL) at 0 °C. The reacting system was kept at pH 9–10 and stirred for 5 h at room temperature. THF was removed under vacuum. The residual solution was poured into ethanol (200 mL) to give a yellow precipitate, which was collected by filtration. The residual taurine was removed by ion exchange chromatography. The yellow effluent was collected and evaporated under vacuum to produce compound **A-2** as yellow powder. Yield: 1.50 g, 26.8%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, ppm):  $\delta$  = 7.65 (d, 2H,  $J$  = 8.4 Hz, ArH), 7.42–7.34 (m, 4H, ArH), 7.27 (t, 2H,  $J$  = 7.9 Hz, ArH), 3.56 (t, 4H,  $J$  = 7.0 Hz, CH<sub>2</sub>), 3.04 (t, 4H,  $J$  = 7.0 Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, ppm):  $\delta$  = 170.54, 135.77, 135.02, 131.73, 131.06, 128.18, 127.76, 49.48, 35.60. ESI-MS  $m/z$  for [M+Na]<sup>+</sup>: calc. 586.96; found 586.97 (Scheme 2).

## 2.3. Preparation of the disulfide-bridged binuclear silver(I) complex **1**

A mixture of **A-2** (56.4 mg, 0.10 mmol) and AgNO<sub>3</sub> (34.0 mg, 0.20 mmol) in water (10 mL) was stirred for 20 h in the dark at room temperature. The resulting solution was poured into ethanol to give a yellow precipitate. The precipitate was collected and dried under vacuum to produce compound **1** as yellow powder. Yield: 8.3 mg, 10.6%. XPS (eV): Na (2s, 63.8; Auger, 497.6; 1s, 1072.0), C (1s, 284.8; C=O, 294.4), O (1s, 532.8), N (1s, 398.4); S (2p, 182.4; loss, 256.0); Ag (3d<sub>5/2</sub>, 369.6; 3d<sub>3/2</sub>, 377.6). <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O, ppm):  $\delta$  = 7.88 (d, 2H,  $J$  = 8.0 Hz, ArH), 7.75–7.61 (m, 4H, ArH), 7.43 (t, 2H,  $J$  = 7.5 Hz, ArH), 4.21 (t, 4H,  $J$  = 6.9 Hz, CH<sub>2</sub>), 3.28 (t, 4H,  $J$  = 6.9 Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O, ppm):  $\delta$  = 166.93, 141.03, 132.66, 125.96, 125.61, 123.39, 120.89, 49.12, 40.20.

## 3. Results and discussion

### 3.1. Spectral responses of **1** to different anions

**1** was a highly water-soluble receptor easily obtained from direct complexation of AgNO<sub>3</sub> with a 2,2'-dithiosalicylic acid derivative. The optical responses of **1** in 1:1 reaction with various inorganic anions were tested in aqueous solutions. In the dark, addition of iodide results in a new edge-shape absorption band at 419 nm which is characteristic of the 1 5p → Ag 5s electronic transition [33–35], while other anions induce no obvious absorption responses except that the sulfide-titrated solution is slightly turbid because of the formation of Ag<sub>2</sub>S (Fig. 1A). Under IR illumination, the iodide-titrated solution changes from yellow to deep brown gradually, while other anions cause no similar absorption responses. As shown in Fig. 1B, besides the Ag–I charge transfer absorption at 419 nm, an intense absorption band centered at 470 nm appears under IR illumination. The formation of I<sub>3</sub><sup>-</sup> ions was precluded from the cause of this distinct response by spectral comparison (Supplementary Fig. S1). Like what is usually observed from J-aggregated dyes [36,37], the new absorption band is broad

Download English Version:

<https://daneshyari.com/en/article/7145261>

Download Persian Version:

<https://daneshyari.com/article/7145261>

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