



ELSEVIER

Contents lists available at ScienceDirect

Talanta

journal homepage: [www.elsevier.com/locate/talanta](http://www.elsevier.com/locate/talanta)

## Ratiometric fluorescence detection of fluoride ion by indole-based receptor



Xiu-Ming Liu, Ya-Ping Li, Ying-Hui Zhang, Qiang Zhao, Wei-Chao Song, Jian Xu<sup>1,\*</sup>, Xian-He Bu

Department of Chemistry and TKL of Metal- and Molecule-Based Material Chemistry, Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education) and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

### ARTICLE INFO

#### Article history:

Received 17 April 2014

Received in revised form

31 July 2014

Accepted 6 August 2014

Available online 19 August 2014

#### Keywords:

Anions

Cations

Fluoride recognition

Ratiometric fluorescence

Colorimetric sensing

### ABSTRACT

A novel artificial receptor **1** containing the indolocarbazole-NH moieties as the recognition sites exhibited high selectivity and sensitivity toward  $F^-$  over other typical anionic species in DMSO solution. Upon addition of  $F^-$  into the solution, receptor **1** showed a remarkable ratiometric shift of the fluorescence maximum from 535 to 590 nm, and also a prominent color change from light yellow to orange, which was observable by the naked eye. The recognition properties of receptor **1** were investigated by  $^1H$  NMR, UV-vis, and fluorescence titration experiments, with the results suggesting a two-step strategy of binding with  $F^-$ . In addition, the theoretical calculations were carried out to reveal the role of intramolecular charge transfer in the ratiometric fluorescence recognition process.

© 2014 Elsevier B.V. All rights reserved.

### 1. Introduction

Selective recognition and sensing of anionic species via artificial receptors have recently emerged as an important multidisciplinary research field across biology, chemistry, and environment science [1–6], considering the vital roles of anions in our daily life. Among various anions, fluoride ion ( $F^-$ ), one of the most important nucleophilic anions, is of particular interest owing to its extensive application in dental health and clinical treatment for osteoporosis [7–11]. On the other hand, excess intake of  $F^-$  may cause many diseases due to its toxicity, such like gastric and kidney disorders, dental and skeletal fluorosis, urolithiasis, or even death [12–15]. Therefore, there is a significant requirement to develop novel artificial receptors with high selectivity and sensitivity toward fluoride anions.

To date, a diverse array of artificial receptors for detecting  $F^-$  have been reported [16–22], and most of them operate based on the measurement of fluorescence at a single wavelength, which is closely related to the photoinduced electron transfer (PET) in the complexation of receptors with anionic guests [23,24]. With the guest-induced “off-on” or “on-off” fluorescence indicating,

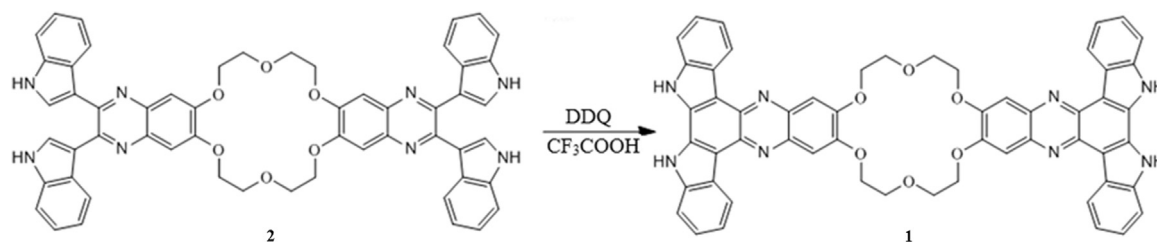
(i.e., the detectable fluorescence enhancement or quenching), such PET signaling systems demonstrate the natural “all or none” switch ability in the recognition of anion guests. However, the PET process can be of either intra- or intermolecular origin and inevitably suffers from the environmental influence, leading to some difficulty in signal rationing. On the other hand, the selective and sensitive sensing of anions could be alternatively achieved in a ratiometric manner by monitoring the changes in the ratio of the fluorescence intensities at two different wavelengths, thus providing a built-in correction for environmental effects and increasing the dynamic range of emission measurements [25–27]. Moreover, the ratiometric fluorescence measurement of analyte concentration can be rationalized by the intramolecular charge transfer (ICT) mechanism [28–30]. In view of aforementioned advantages, the development in the design and synthesis of the ratiometric fluorescent receptors with high affinity and selectivity for  $F^-$  has been actively pursued by chemists in recent years.

Herein, we report a new colorimetric and ratiometric fluorescent receptor **1** containing the indolocarbazole-NH moieties as the recognition sites, in line with our previously reported strategy [31]. Following a two-step anion binding strategy, receptor **1** exhibits a high sensing selectivity and sensitivity for  $F^-$  over other common anions, highlighted by a large ratiometric emission shift by about 55 nm and also a prominent color change visible to the naked eye. To further investigate the recognition properties of receptor **1**, the  $^1H$  NMR, UV-vis, and fluorescence titration studies

\* Corresponding author. Fax: +86 22 23502458.

E-mail address: [jxu@nankai.edu.cn](mailto:jxu@nankai.edu.cn) (J. Xu).

<sup>1</sup> Present address: Nankai University, Tianjin 300071, China.



**Scheme 1.** The procedure for the synthesis of **1**.

are carried out, together with relevant theoretical calculations to reveal the role of ICT in spectroscopic recognition of fluoride anions (Scheme 1).

## 2. Experimental

### 2.1. Apparatus and reagents

All the starting materials for synthesis were purchased from Alfa Aesar and used as received. The solvents used for titration measurements were purified by standard procedures. In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, which were purchased from Alfa Aesar and Aladdin, stored in a vacuum desiccator containing self-indicating silica and dried fully before using. DMSO was dried with CaH<sub>2</sub> and then distilled in reduced pressure. Structural characterizations of [D<sub>6</sub>]DMSO at 25 °C were carried out with Varian Unity Plus 400 MHz NMR spectrometer (Varian, USA). High resolution mass spectra (HRMS) were determined on an IonSpec 7.0T FT-ICR mass spectrometer (IonSpec, USA). UV–vis absorption spectra were measured with a Hitachi U-3010 UV–vis spectrophotometer (Hitachi, Japan). Fluorescence spectra were recorded at room temperature on a Varian Cary Eclipse fluorescence spectrometer (Varian, USA).

### 2.2. Synthesis of receptor **1**

The receptor **1** was prepared by the condensation of 2,3,15,16-tetra(1*H*-indol-3-yl)-7,8,10,11,20,21,23,24 -octahydro-[1,4,7,10,13,16]hexaoxacyclooctadecino[2,3-*g*:11,12-*g'*]diquinoxaline (**2**) [32] (100 mg, 0.11 mmol) and DDQ (96 mg, 0.35 mmol), which were dissolved in neat trifluoroacetic acid (12 mL) and heated under reflux for 4 h. Then, the trifluoroacetic acid was removed by vacuum distillation, followed by repeated wash with saturated aqueous NaHCO<sub>3</sub> and dried in vacuo to afford pure **1** as black solid (91 mg, about 90%) that is air stable and soluble in DMSO.

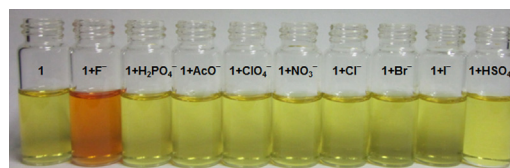
#### Receptor **1**

Black solid (90%). IR (KBr)  $\nu$  3160, 2367, 2171, 1621, 1491, 1470, 1435, 1331, 1281 cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, TMS, 400MHz)  $\delta$  4.10 (s, 4H), 4.52 (s, 4H), 7.54 – 7.37 (m, 4H), 7.74 (s, 4H), 7.88 (d, *J* = 8.2 Hz, 4H), 9.14 (d, *J* = 6.9 Hz, 4H), 11.88 (s, 4H). ESI-MS *m/z*(%): 921.6 [M+H]<sup>+</sup>, 943.7 [M+Na]<sup>+</sup>. HRMS: (ESI) *m/z*(%) for C<sub>56</sub>H<sub>40</sub>N<sub>8</sub>O<sub>6</sub>; calcd 920.3671; found 943.2968 [M+Na]<sup>+</sup>.

## 3. Results and discussion

### 3.1. Anion sensing

The selective recognition properties of receptor **1** were first investigated by monitoring the naked-eye visible color changes, induced by the addition of 20 equiv of different anions



**Fig. 1.** Color changes induced by the addition of respective anions (20 equiv) to a DMSO solution of **1**. [**1**] =  $5 \times 10^{-5}$  M. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(F<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, AcO<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and HSO<sub>4</sub><sup>-</sup>) to the DMSO solution of **1**. As Fig. 1 demonstrates, only the addition of F<sup>-</sup> caused a prominent color change from light yellow to orange, indicating the colorimetric selectivity of receptor **1** toward F<sup>-</sup> over other anions.

Further investigations on the interaction of receptor **1** with anions were performed by using UV–vis absorption and fluorescence emission spectroscopy. As illustrated by Fig. 2a, a considerable UV–vis red shift appeared at 500 nm after addition of 50 equiv of F<sup>-</sup> to the DMSO solution of **1**. For comparison, the addition of either H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or AcO<sup>-</sup> resulted in only a very minor shift toward lower energy in the absorption spectrum, while that of the other anions (i.e., ClO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> and HSO<sub>4</sub><sup>-</sup>) seemed to cause no change at all. A very similar situation also occurred in the emission spectra of receptor **1**. As illustrated by Fig. 2b, the addition of F<sup>-</sup> caused a more significant fluorescence red shift (~55 nm) as compared to that induced by the presence of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> or AcO<sup>-</sup> (~20 nm), while the emission spectrum upon the addition of other anions almost remained unchanged. These results suggest that receptor **1** has an excellent ratiometric sensing selectivity to F<sup>-</sup>, which may arise from the fact that F<sup>-</sup> is of stronger basicity than H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and AcO<sup>-</sup>, and the latter two are insufficient to induce the complete deprotonation of receptor **1**.

#### 3.1.1. UV–vis and fluorescence titration studies of **1** with F<sup>-</sup>

To assess the ratiometric fluorescence sensing ability of receptor **1** toward F<sup>-</sup>, we further studied the spectral changes upon the addition of F<sup>-</sup> with increasing concentrations, ranging from 0 to 68 equiv. As depicted in Fig. 3a, the concentration increase of F<sup>-</sup> led to a dramatic decrease in the intensity of absorption band at 433 nm, while in opposite, the intensity of the band centered at 344 nm moderately increased upon titration of F<sup>-</sup>, along with the appearance of a new band at around 500 nm. The presence of two sharp isosbestic points at 375 and 455 nm implies that only two chemical species coexist at the equilibrium throughout the titration process, in accompany with an obvious color change from light yellow to orange.

Upon excitation at 430 nm, the emission spectrum of receptor **1** exhibited the remarkable changes in response to the variation in the concentration of F<sup>-</sup>, illustrated by a large ratiometric shift of the fluorescence maximum from 535 to 590 nm, as shown in Fig. 3b. While the characteristic fluorescence at 535 nm was significantly

Download English Version:

<https://daneshyari.com/en/article/7679783>

Download Persian Version:

<https://daneshyari.com/article/7679783>

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