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Original article

Two new indole derivatives as anion receptors for detecting fluoride ion

Xiu-Ming Liu, Qiang Zhao, Yue Li, Wei-Chao Song, Ya-Ping Li, Ze Chang*, Xian-He Bu

Department of Chemistry, Tianjin Key Lab of Metal and Molecule-based Material Chemistry, Synergetic Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin 300071, China

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ABSTRACT

Two new compounds (**1** and **2**) based on indole were successfully synthesized and characterized. They display highly selective response to F^- in aqueous DMSO medium and pure DMSO with remarkable color and fluorescent changes. Therefore, both receptors may serve as colorimetric sensors for F^- by visual detection.

1. Introduction

In recent years, the sensing of anions has emerged as a vigorous research field of supramolecular chemistry [1–4]. In particular, great effort has been devoted to the recognition of the fluoride ion, because it is highly relevant to environmental and health issues [5–14]. Several successful examples have been reported [15–20], *e.g.*, the receptors based on the chemical affinity between fluoride and silicon can exhibit high selectivity for F^- [21–23], but the rational design of F^- receptors with remarkable fluorescent or colorimetric response is still a great challenge. One of the design strategies of fluoride receptors is based on the formation of a hydrogen bond between the fluoride ion and the active N-H group of an organic chromophore, which will result in a detectable change of spectral characteristicsof the chromophore upon the recognition of fluoride ion. Among the various organic chromophores investigated as fluoride receptors, indole- and carbazole-based chromogenic-sensing molecules are superior hydrogen bond donors than pyrrole and more prone to deprotonation which has been well documented [24,25]. In our earlier works, we have designed and synthesized several colorimetric F^- receptors with bi-indole and indolocarbazole as the recognition sites [26,27]. However, these receptors can only work well in pure organic solvents, since their performances would be decreased in the presence of small amounts of water, because water as a protic solvent can compete for the formation of a hydrogen bond with F^-. Therefore, the development of water tolerant F^- receptors is highly desirable for their practical application.

Herein, we report the design and synthesis of two receptors containing bi-indole (**1**) and indolocarbazole-NH (**2**) moieties as the recognition sites for fluoride sensing (Scheme 1). Compounds **1** and **2** exhibit remarkable color changes in the presence of F^- both in aqueous DMSO medium and pure DMSO. In addition, **2** as an efficient colorimetric sensor, can also distinguish AcO^- and F^- in DMSO.

2. Experimental

All the starting materials for synthesis were commercially available and used as received. All 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 or Aladdin, stored in a vacuum desiccator containing self-indicating silica and fully dried before used. DMSO was dried with CaH_2 and then distilled under reduced pressure. Structural characterizations were carried out in DMSO-d_6 at 25 °C with Varian Unity Plus 400 MHz NMR spectrometer (Varian, USA). High resolution mass spectra (HRMS) were recorded 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).

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* Corresponding author.
E-mail address: changze@nankai.edu.cn (Z. Chang).

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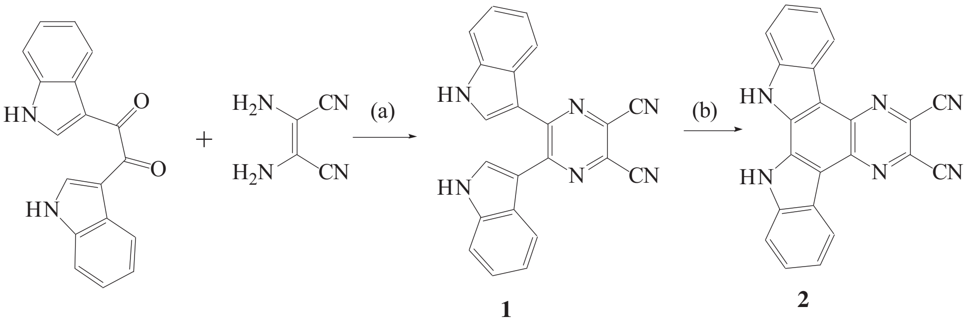

Scheme 1. The procedure for the synthesis of **1** and **2**. (a) Methanol, sulfamic acid and (b) CF_3COOH, DDQ.

Synthesis of **1**: Under N_2 atmosphere, bi-indole (420 mg, 1.4 mmol), diaminomaleonitrile (240 mg, 2.2 mmol) and sulfamic acid (1200 mg, 12.0 mmol) were refluxed in 30 mL of methanol for 3 h. The residual methanol was removed by vacuum distillation, then the resulting precipitate was washed by saturated aq. $NaHCO_3$ and dried in vacuo to afford a yellow solid. The solid was subjected to chromatography over silica gel (ethyl acetate:petroleum ether, 1:1) to give **1** as yellow powder in about 80% yield. ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 7.10 (t, 2H, J = 7.3 Hz), 7.20 (t, 2H, J = 7.5 Hz), 7.48 (d, 2H, J = 8.0 Hz), 7.75 (d, 2H, J = 8.2 Hz), 7.81 (d, 2H, J = 2.4 Hz), 11.85 (s, 2H); ESI-MS (m/z): 359.2 $[M-H]^-$, 394.6 $[M+Cl]^-$, 754.5 $[2M+Cl]^-$; HRMS (ESI) (m/z): 359.1047 $[M-H]^-$, calcd. for $C_{22}H_{12}N_6$ 360.3709.

Synthesis of **2**: Compound **1** (100 mg, 0.28 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (75 mg, 0.33 mmol) were dissolved in neat trifluoroacetic acid (10 mL) and heated at reflux for 4 h. Then trifluroacetic acid was removed by vacuum distillation, and the solid was washed repeatedly with saturated aq. $NaHCO_3$ and dried in vacuo to afford **2** as brown-red solid (95 mg, about 95%). ^1H NMR (400 MHz, DMSO-d_6, TMS): δ 7.50 (t, 2H, J = 7.5 Hz) 7.58 (t, 2H, J = 7.5 Hz), 7.94 (d, 2H, J = 8.1 Hz), 8.73 (d, 2H, J = 7.9 Hz), 12.40 (s, 2H); ESI-MS (m/z): 357.5 $[M-H]^-$, 392.9 $[M+Cl]^-$, 750.9 $[2M+Cl]^-$; HRMS (ESI) (m/z) for: 357.0896 $[M-H]^-$, calcd. for $C_{22}H_{10}N_6$ 358.3550.

3. Results and discussion

Since compounds **1** and **2** were designed and synthesized as potential receptors of fluoride, their UV–vis spectra were investigated to confirm the specific interactions toward fluoride anions. The UV–vis spectra of **1** and **2** upon the addition of F^-, $H_2PO_4^-$, AcO^-, ClO_4^-, NO_3^-, Cl^-, Br^-, I^- and HSO_4^- as tetrabutylammonium salts (n-Bu_4N^+) are shown in Fig. 1. As 6 equiv. of F^- was added to the solution of **1** (DMSO:H_2O, 95:5), the absorption at 505 and 403 nm progressively increased, while the response at 350 nm obviously reduced. Upon the addition of 6 equiv. of $H_2PO_4^-$ or AcO^-, the UV/vis spectra exhibited little change, whereas other anions (ClO_4^-, NO_3^-, Cl^-, Br^-, I^- and HSO_4^-) had almost no effect on the absorption spectra of **1**.

Compound **2**, which has a more rigid skeleton than **1**, showed a different sensing behavior. Upon the addition of 9 equiv. of F^- to **2** (DMSO:H_2O = 90:10), the absorption at 303 nm and 355 nm reduced accompanied with the obvious enhancement at 321 nm and 391 nm, and a new band appeared at 505 nm. The spectra of **2** changed little with the addition of AcO^-, and no detectable changes were observed upon the addition of other anions ($H_2PO_4^-$, ClO_4^-, NO_3^-, Cl^-, Br^-, I^- and HSO_4^-).

In accordance with the investigational results in UV–vis spectra, a remarkable color change could be observed when 5 equiv. of F^- was added to the aqueous DMSO solution of **1** and **2** (from yellow to orange for **1** and from orange to reddish orange for **2**, Fig. 2), while the addition of other anions cause negligible color change. These results indicate that **1** and **2** can serve as colorimetric receptors for the visual detection of F^-.

The fluorescence spectra of **1** and **2** with different amounts of F^- are displayed in Fig. 3. Significant fluorescence quenching was observed with the addition of F^- from 0 to 20 equiv. in aqueous DMSO medium, and the fluorescence quenching effect of F^- could be explained with a photoinduced electron transfer (PET) mechanism. The fitting of the fluorescence titration data shows

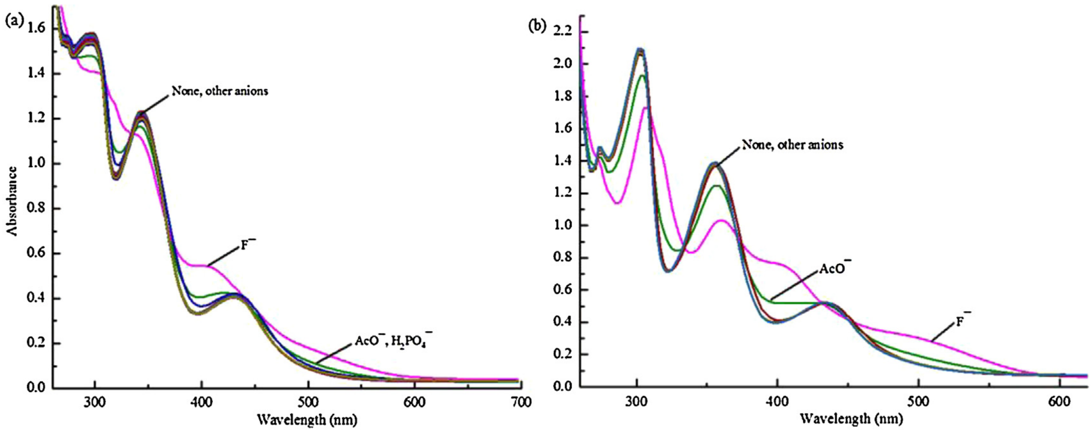

Fig. 1. (a) The changes in UV/vis spectra of **1** in DMSO:H_2O = 95:5 (v/v) upon addition of 6 equiv. of respective anions (as a n-Bu_4N^+ salt). Other anions are ClO_4^-, NO_3^-, Cl^-, Br^-, I^- and HSO_4^-. **1** = 5×10^{-5} mol/L. (b) The changes in UV/vis spectra of **2** in DMSO:H_2O = 90:10 (v/v) upon addition of 6 equiv. of respective anions (as a n-bu_4N^+ salt). Other anions are $H_2PO_4^-$, ClO_4^-, NO_3^-, Cl^-, Br^-, I^- and HSO_4^-. **2** = 2.5×10^{-5} mol/L.