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A new ion pair receptor fulfilling a dual function as a chromogenic molecular switch for F^- and ratiometric selective recognition of HSO_4^-

Xiu-Ming Liu, Ya-Ping Li, Wei-Chao Song *,[1], Qiang Zhao, Xian-He Bu *

Department of Chemistry and TKL of Metal- and Molecule-Based Material Chemistry, Nankai University, Tianjin 300071, China

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ABSTRACT

A new ditopic ion pair receptor **1** containing two biindole moieties and a bis-benzocrown ether unit shows a remarkable color switching (ON- and -OFF) function induced by anion (F^-) and cation (K^+) recognition. The ditopic receptor **1** binds in a cooperative fashion to HSO_4^- in the presence of $\mathbf{1}\cdot K^+$ and acts as a selective ditopic receptor to recognize ion pairs with a wavelength-ratiometric manner.

1. Introduction

The design and synthesis of functional molecules [1–5] serving as molecular devices for sensing [6–8], switching [9–12], and signal transduction [13], particularly from optical inputs, have been very actively pursued over the recent years. Compared with simple ion receptors, ion pair receptors are capable of forming simultaneous complexation with cations and anions, and have the potential to act as new selective extraction and membrane transport agents [14–18]. In fact, the related ditopic receptors might offer considerable advantages in terms of affinity or selectivity over monotopic hosts, because the bind guests in a cooperative manner are especially sought for the selective recognition of a specific guest [19–24]. Furthermore, recent studies on anion and ion-pair binding suggest that an anion and counter cation have a strong effect on the binding affinity [25–27]. Thus, the development of this area is stimulated by considerable benefits gained from binding an ion pair. However, the number of pyrrole [28–31] or indole-based [32–34] ion pair receptors remains limited. Therefore, we hope to design an indole-based ion pair receptor that could bind a specific cation–anion pair with high affinity in the form of an ion pair complex.

Herein, we describe the design, synthesis and binding properties of a novel heteroditopic molecular receptor **1**, which contains both biindole and bis-benzocrown moiety (Scheme 1). Biindole moiety was chosen as the anion binding site, since indole-based receptor is better hydrogen bond donor than pyrrole and more prone to deprotonation [35–39]. A bis-benzocrown ether was chosen as the second binding site of the receptor due to its well-known cation binding properties. **1** can function as a chromogenic molecular switch by the adding sequence of F^- and K^+ in DMSO solution to control its color. In addition, when co-bounding cation complex $\mathbf{1}\cdot K^+$, it shows high selectivity for detecting HSO_4^- by the naked eye, and it also demonstrates the obvious fluorescence characteristics change in a wavelength-ratiometric manner in the presence of the HSO_4^-.

2. Experimental

2.1. Apparatus and reagents

All the materials for synthesis were purchased from Alfa Aesar and other companies. DMSO was dried with CaH_2 and then distilled in reduced pressure [40]. 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 fully dried before using. NMR spectra were recorded in $[D_6]$DMSO at 25 °C with a Varian Unity Plus 400 MHz NMR spectrometer (Varian, USA). High resolution mass spectra (HRMS) were determined on an IonSpec 7.0 T

* Corresponding authors. Fax: +86 22 23502458.
E-mail addresses: songweichao@sina.com (W.-C. Song), buxh@nankai.edu.cn (X.-H. Bu).
[1] Present address: Nankai University, Tianjin 300071, China.

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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).

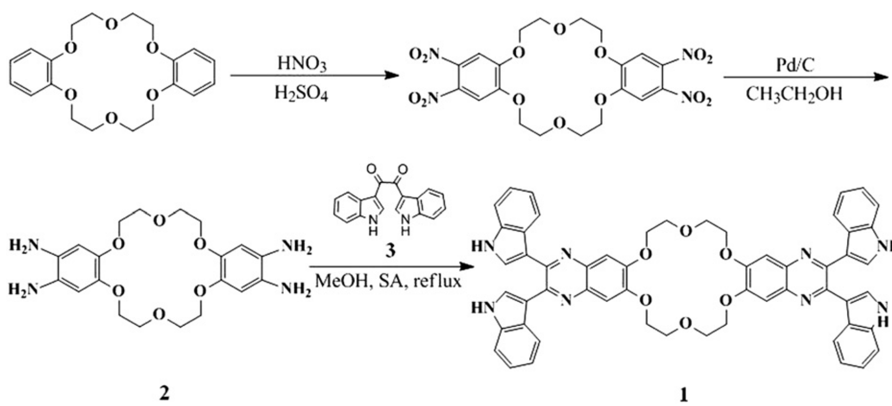
2.2. Synthesis of ion pair receptor 1

The ditopic receptor, **1,** was prepared by condensation of 6,7,9,10,17,18,20,21-octahydrodi-zo[*b*,*k*] [1,4,7,10,13,16] hexaoxa-cyclooctadecine-2,3,13,14-tetraamine (**2**) and 2,3-diindol-3-yl diketone (**3**). **2** and **3** were prepared by previously reported procedures [41–42]. 2,3-Diindol-3-yl diketone (263 mg, 0.91 mmol) and amidosulfonic acid (SA) (670 mg, 5.49 mmol) were dissolved in methanol (30 mL) under N_2 atmosphere, then 6,7,9,10,17,18,20, 21-octahydrodi-zo[*b*,*k*] [1,4,7,10,13,16] hexaoxa-cyclooctadecine-2,3,13, 14-tetraamine (167 mg, 0.40 mmol) was added, and the mixture was heated under reflux (at about 65 °C) for 10 h. The formed precipitate was collected by filtration, washed with methanol for several times and dried in vacuo to afford **1** as red-brown solid in about 60% yield. ^{1}H NMR (400 MHz, [D_6]DMSO, TMS) (ppm) 3.99 (s, 8 H), 4.32 (d, 8 H, J=29.2 Hz), 6.90 (s, 4 H), 7.01 (s, 4 H), 7.14 (s, 4 H), 7.31 (s, 4 H), 7.42 (d, 4 H, J=5.6 Hz), 7.93 (d, 4 H, J=7.4 Hz), 11.30 (s, 4 H); ESI-MS, *m*/*z*: 925.4 $[M+H]^+$, 947.4 $[M+Na]^+$; HRMS (ESI), *m*/*z*: 947.3276 $[M+Na]^+$, calcd for $C_{56}H_{44}N_8O_6$: 924.3384.

3. Results and discussion

3.1. Anion sensing

The sensing ability of **1** was first examined by interacting with some anions (F^-, $H_2PO_4^-$, AcO^-, ClO_4^-, NO_3^-, Cl^-, Br^-, I^- and



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

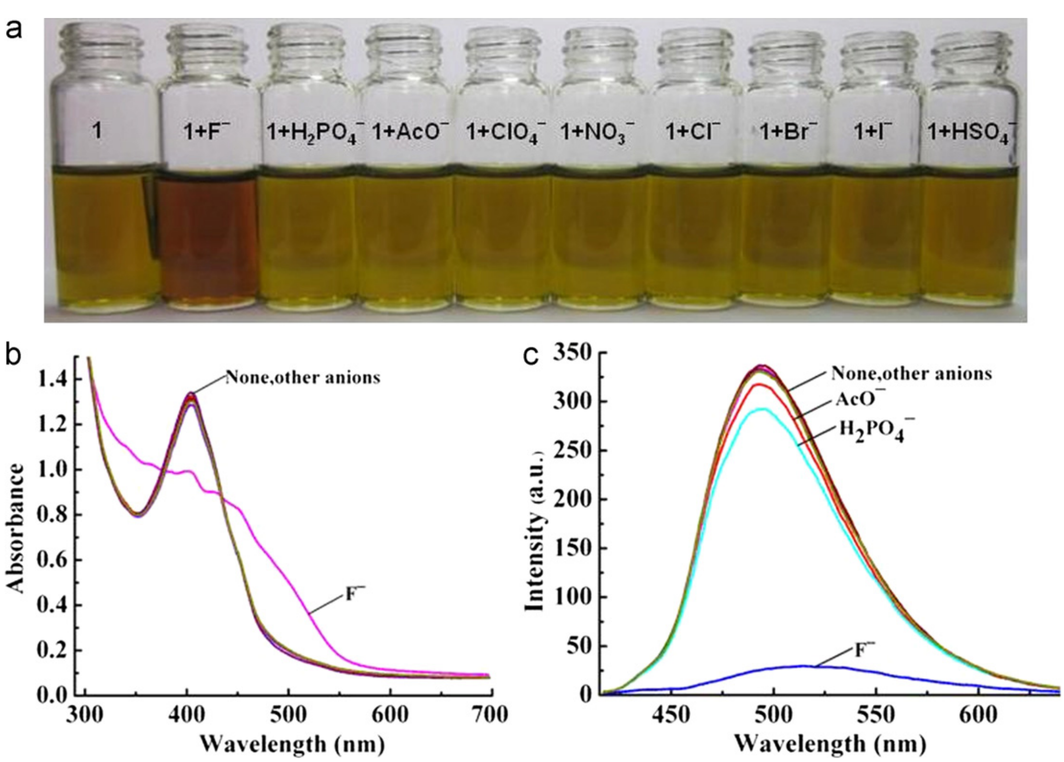


Fig. 1. (a) Color changes induced by the addition of anions (75 equiv.) to a DMSO solution of **1**. [1]=4×10^{-4} M. (b) The UV–vis spectra changes of receptor **1** in DMSO measured in DMSO upon addition of 75 equiv of respective anions (as *n*-bu_4N^+ salt). Other anions are $H_2PO_4^-$, AcO^-, ClO_4^-, NO_3^-, Cl^-, Br^-, I^- and HSO_4^-. (c) Fluorescence (λ_{ex}=390 nm) spectra changes of **1** measured in DMSO upon addition of 75 equiv of respective anions (as *n*-bu_4N^+ salt). Other anions are ClO_4^-, NO_3^-, Cl^-, Br^-, I^- and HSO_4^-. [1]=5×10^{-5} M.