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Original article

Turn-on fluorescence sensing of cyanide ions in aqueous solution

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ABSTRACT

A sensitive fluorescent probe, 2,2′-bisbenzimidazole (**L**), for CN^- has been developed. This structurally simple receptor displays great selectivity for the cyanide anion over other common inorganic anions in an aqueous environment. In addition, further study demonstrates the lower detection of the fluorescence response of the sensor to CN^- is in 10^{-9} mol/L range. Thus, the present probe should be applicable as a practical system for the monitoring of cyanide concentrations in aqueous samples.

1. Introduction

Anion recognition is an area of growing interest in supramolecular chemistry due to its important role in a wide range of environmental, clinical, chemical, and biological applications [1–4]. Cyanide detection is particularly important due to its extreme toxicity in physiological systems and the increasing environmental concerns caused by its widespread industrial uses in petrochemical, gold mining, photographic, and steel manufacturing [5–9]. To detect cyanide anions, fluorescence sensing is one of the most powerful methods owing to its simplicity and high sensitivity [10–13].

In recent years, some organic molecules and transition metal complexes capable of signaling the presence of cyanide by pronounced changes in their absorption and emission properties have been already identified [14–16]. Some of these chemosensors can even detect micromolar amounts of cyanide [17–19]. However, most of them suffer the deleterious interference of other anions and in addition, many of them are reported to work only in organic media [20–22]. Consequently, the search for effective sensing systems in aqueous environment is still a great challenge.

With the above-mentioned criteria in mind, herein, we have designed 2,2′-bisbenzimidazole (**L**), which behaves as a highly sensitive fluorescence turn-on sensor for the cyanide anion in aqueous solutions. In this article, we illustrate the logic behind our molecular design and we report the synthesis and characterization of **L** with its fluorescent response to cyanide.

2. Experimental

2.1. Apparatus and instruments

Melting points were measured on X-4 digital melting-point apparatus and were uncorrected. The infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Mass spectra were measured with a Bruker Daltonics Esquire 6000. Fluorescence spectra were recorded on a Shimadzu RF-5301 fluorescence spectrometer. ^{1}H NMR spectra were recorded on a Varian Mercury plus-400 MHz spectrometer with DMSO as solvent and analytical grade TMS as an internal reference.

All reagents were obtained commercially for synthesis and used without further purification. In the titration experiments, stock solutions of the tetrabutyl ammonium salts of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, ClO_4^-, but CN^- was prepared in NaCN. All were purchased from Alfa-Aesar Chemical, stored in a vacuum desiccator containing self-indicating silica and dried fully before using.

The synthesis route of receptor molecule **L** is demonstrated in Scheme 1. Components *O*-phenylenediamine (5 mmol) and oxalic acid (2 mmol) were mixed in glycol (40 mL), with PPA (polyphosphate phosphoric acid) as a catalyst. Then, the resulting solution was stirred under refluxed conditions for 2 h at 160 °C. After cooling to room temperature, the bright green precipitate was filtrated, washed with distilled water three times, then recrystallized with glacial acetic acid to get green crystals of **L** in 96% yield (mp > 300 °C), ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.91 (s, 2H),

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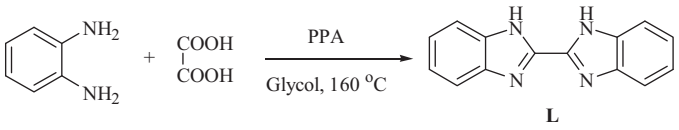

Scheme 1. Synthetic procedures for receptor **L**.

7.77 (s, 1H), 7.57 (s, 1H), 7.30 (s, 2H), 7.07–7.14 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 115.263, 123.127, 143.923, 155.354, 172.210. IR (KBr, cm^{-1}): ν 1620.13 (CH=N), 3250.78 (NH). MS/(EI): m/z 235.2 (**L**+H)$^+$; Anal. Calcd. for $C_{14}H_{10}N_4$: C 71.78, H 4.30, N 23.92; found: C 71.69, H 4.10, N 24.21.

Fluorescence spectroscopy was carried out after the addition of perchlorate metal salts and the tetrabutyl ammonium salts in DMSO, while keeping the ligand concentration constant (2×10^{-5} mol/L) on a Shimadzu RF-5301 fluorescence spectrometer. The excitation wavelength was 352 nm.

3. Results and discussion

To evaluate the selectivity of **L**, we measured the fluorescence intensity of **L** in the presence of various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^- and ClO_4^-) as well as CN^-. Only when 20 equiv. of CN^- were added to the H_2O/DMSO (1/1, v/v) solutions of sensor **L**, the chemosensor responded with a dramatic color change, from colorless to bright blue (Fig. 1). Receptor **L** produced a band at λ_{max} = 365 nm in the absorption spectrum recorded at a 2×10^{-5} mol/L concentration of the receptor in a H_2O system. Using these anions (20 equiv.), compound **L** showed a large fluorescent enhancement only with CN^-. However, under identical conditions, no obvious changes were observed for other tested metal ions (Fig. 2).

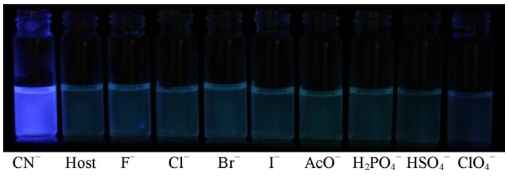

Fig. 1. Visual fluorescence emissions of probe **L** upon the addition of various anions (20 equiv.) in DMSO/H_2O (1/1, v/v) solutions on excitation at 365 nm using UV lamp at r.t.

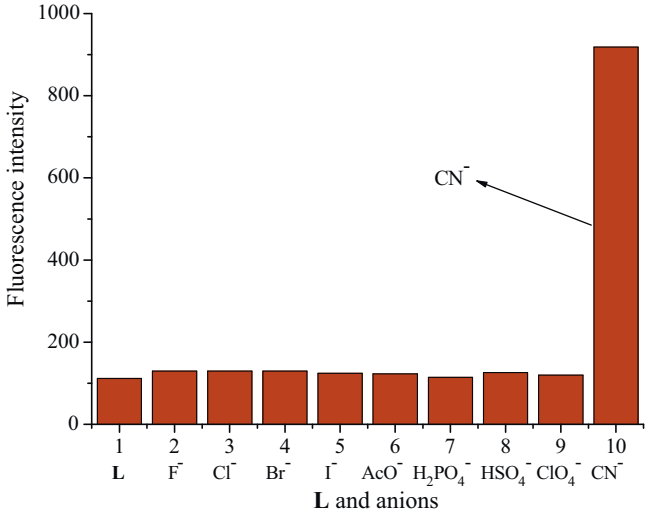

Fig. 2. Fluorescence spectra of **L** and in the presence of 20 equiv. of various anions in H_2O/DMSO (1/1, v/v) binary solution at room temperature.

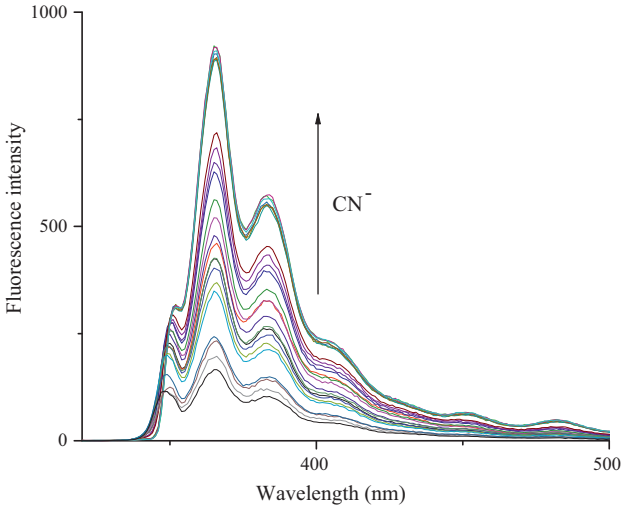

Fig. 3. Fluorescence spectral titration of sensor **L** with CN^- in (H_2O/DMSO, 1/1, v/v) solution.

Fluorescent titration was performed to gain insight into the recognition properties of receptor **L** as a CN^- sensor (Fig. 3). Upon addition of CN^- to receptor **L**, the emission band at 365 nm gradually increased. Furthermore, the detection limit on fluorescence response of the sensor to CN^- is 2.1×10^{-9} mol/L.

To confirm the binding stoichiometry between **L** and CN^- in the aqueous solution, a job plot was performed. The results illustrate that the receptor–guest complex concentration approaches a maximum when the mole fraction of the host is about 0.5, which indicates that the anion forms a 1:1 complex with the receptor (Fig. 4).

Fig. 5 illustrated the fluorescence response of **L** to CN^- in the presence of other anions. From the bar diagram, one could easily understand that the effects on emission intensity of **L** upon the addition of higher concentrations of various anions were almost negligible except for CN^-. Therefore, it was clear that other ions' interference was negligibly small during the detection of CN^-.

Upon mass spectral analysis, an ion peaks was detected at m/z 235.2, which corresponds to [**L**+H]$^+$. The peak at m/z 257.2 also demonstrated the presence of [**L**+Na−H]$^+$ (**L**+Na$^+$ complex). Thus, on the basis of above observations, in accordance with the 1:1

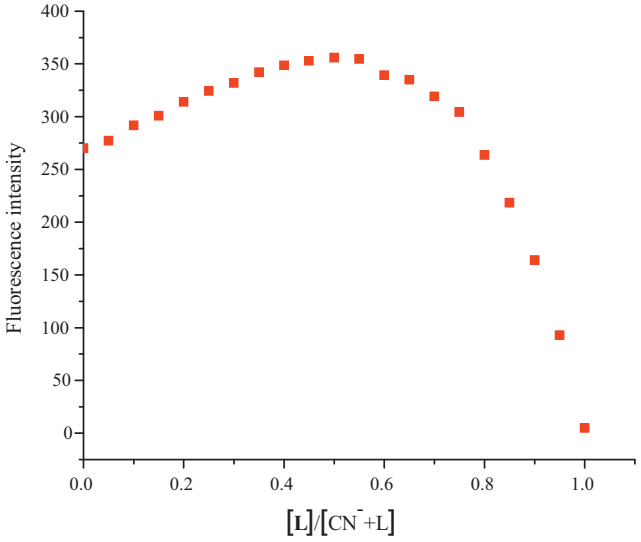

Fig. 4. Job's plot of **L** and CN^-, which indicated the stoichiometry of **L**–CN^- complex is 1:1.