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Zhang and Qi Lin *

A novel sensor (**AHP5**) involving a thioacetohydrazone bridged bispillar[5]arene was developed and demonstrated to fluorescently sense CN⁻. It manifested specificity response for cyanide over other common anions (SCN⁻, AcO⁻, HSO₄⁻, H₂PO₄⁻, I⁻, Br⁻, ClO₄⁻, Cl⁻ and F⁻) in DMSO/H₂O (9 : 1, v/v) solution. Upon treatment with cyanide, **AHP5** exhibited a significant fluorescence response, simultaneously with the remarkable changes in its fluorescence spectra. In addition, competitive anions did not show any obviously influence on the probing behavior. Notably, the investigation of the recognition mechanism indicated that **AHP5** recognized CN⁻ by a deprotonated procedure accompanied with the breakage of intermolecular hydrogen bonds. Furthermore, the sensor was successfully applied to the detection of cyanide in cyanide–containing water samples.

Introduction

As a new kind of emerging macrocyclic compounds next to crown ethers,¹ cyclodextrins,² calixarenes,³ and cucurbiturils,⁴ pillar[n]arenes, which are cyclized by hydroquinone units linked with methylene bridges at 2,5-positions of the benzene moieties, have been studied actively since they were found in 2008.⁵ The highly symmetrical and rigid structures along with easy functionalization of pillar[n]arenes shown fascinating host-guest binding properties with a number of guest molecules, which have captured more and more attention of scientists in recent years. Thus far, the use of host-guest interactions involving pillar[n]arenes and inorganic anions were very limited and only a few publications involve recognition of cyanide by pillar[n]arenes as receptors.⁷ It is noteworthy that bispillar[*n*]arene-based cyanide sensor has been unreported to date.⁸ Therefore, the design and synthesis of novel functionalized bispillar[n]arenes is particularly important.

The recognition of anions has received continuously and significant attention due to their important roles in biological, industrial, clinical, and environmental processes.⁹ As a Janus anion in chemistry, cyanide anion, has been continuously of concern all over the world due to its high toxicity and widespread use in industrial processes, such as paper, textiles, and plastics manufacturing, metallurgy, herbicide production and so forth.¹⁰

Generally cyanide is present in the seeds of apricots, sprouting

pillar[n]arenes chemistry and ions recognition,¹⁵ we designed and synthesized a novel fluorescent sensor AHP5 involving a thioacetohydrazone bridged bispillar[5]arene. The thioacetohydrazone bridged AHP5 was successfully obtained in 31% yield by condensation reaction of benzaldehyde functionalized pillar[5]arene and thioacetohydrazide functionalized pillar[5]arene. In addition, acylhydrazone group is a good ions recognition site.¹⁶ The sensor AHP5 could fluorescently sense CN⁻ anion with high selectivity and sensitivity $(5.14 \times 10^{-8} \text{ mol} \cdot \text{L}^{-1})$. In addition, the competitive anions did not show any obviously influence on the probing behavior. Furthermore, the recognition mechanism was studied by ¹H NMR, Job's plot measurement and electrospray ionization mass spectrometry. Notably, the investigation indicated that AHP5 recognized CN by a deprotonated procedure accompanied with the breakage of intermolecular hydrogen bonds. More importantly, this is the first example that a bispillar[5]arenebased sensor was synthesized for fluorescent recognition of cyanide anion in DMSO/H₂O (9 : 1, v/v) solution.

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potatoes and cigarette smoke etc.¹¹ Cyanide poisoning can lead to vomiting, loss of consciousness, respiratory arrest and eventual death.¹² According to the World Health Organization, the maximum acceptable concentration level of cyanide in drinking water is 1.9 μ M.¹³ Moreover, optical sensors for the detection of cyanide anions, in which a change in color or fluorescence intensity (or emission wavelength) is monitored, have received significant attention due to their simplicity, inexpensive, high selectivity and rapid implementation nature in recent years.¹⁴ Accordingly, the design and synthesis of optical sensors for specific detection of cyanide have been an important task.



Scheme 1 The synthesis of bispillar[5]arene AHP5.

Results and discussion

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In order to investigate the CN⁻ recognition abilities of the sensor AHP5 in DMSO/H₂O (9 : 1, v/v) solution, a series of host-guest recognition experiments were carried out. The sensor AHP5 toward various anions (including SCN, AcO, HSO, CN, H2PO, I, Br, ClO₄, Cl⁻ and F⁻) were primarily investigated using fluorescence spectroscopy. In the fluorescence spectrum, the maximum emission of AHP5 appeared at 504 nm in DMSO/ H₂O (9: 1, v/v) while excited at λ_{ex} = 420 nm. When 5.0 equiv. of CN⁻ was added to the solution of the sensor AHP5, the fluorescence emission band was redshifted to 504 nm, and an approximate 9.0-fold fluorescence enhancement was observed (Fig. S19). In addition, a strong chartreuse fluorescence appeared. In comparison, the same tests were applied using SCN⁻, AcO⁻, HSO₄⁻, CN⁻, H₂PO₄⁻, I⁻, Br⁻, ClO₄⁻, Cl⁻ and F anions, and only CN have significant changes in the fluorescence spectrum of the sensor (Fig. 1), and none of those other anions induced any significant changes in the fluorescent spectrum of the sensor. Upon addition of CN⁻ anion, the band was red-shifted accompanied with its emission intensity significantly enhanced at 504 nm. The apparent color change from colorless to chartreuse could be distinguished under the UV lamp. Therefore, in DMSO/H₂O (9 : 1, v/v) solution, AHP5 showed specific fluorescence selectivity to CN⁻ anion.

To further investigate the efficiency of the sensor **AHP5** toward CN⁻ detection, we carried out fluorescence emission titration experiments. The emission spectral variation of **AHP5** upon gradual addition of CN⁻ anion is shown in Fig. 2. In the fluorescence spectrum, upon addition of increasing amounts of CN⁻ anions (0–1.4 equiv.) to the solution of **AHP5** in DMSO/H₂O (9:1, v/v), the fluorescence emission at 478 nm is gradually red–shifted to 504 nm, directly leading to a strong chartreuse emission. The detection limit of the fluorescent spectrum changes calculated on the basis of 3 σ /S is 5.14×10⁻⁸ M for CN⁻ (Fig. S20), which is far lower than the WHO guideline of 1.9 µmOl L⁻¹ cyanide.



Fig. 1 Fluorescence spectral response of **AHP5** (2.0×10^{-4} M) in DMSO/H₂O (9 : 1, v/v) in the presence of cyanide and other anions (5.0 equiv.). Inset: color changes observed for **AHP5** upon the addition of SCN⁻, AcO⁻, HSO₄⁻, CN⁻, H₂PO₄⁻, I⁻, Br⁻, ClO₄⁻, Cl⁻ and F⁻ in DMSO/H₂O (v/v = 9 : 1) solution on a spot plate.



Fig. 2 Fluorescence spectra of **AHP5** (0.2 mM) in the presence of different concentration of CN^- in DMSO/H₂O (9 : 1, v/v) solution. Inset: a) a plot of fluorescence intensity depending on the concentration of CN^- in the range from 0 to 1.6 equiv. Each measurement was done at room temperature of mixing for **AHP5** and CN^- in DMSO/H₂O (9 : 1, v/v). b) color changes observed for **AHP5** upon the addition of CN^- .

To further explore the utility of sensor **AHP5** as an anion–selective chemosensor for CN⁻, competitive experiments were carried out in the presence of 5.0 equiv. of CN⁻ and 1.0 equiv. of various other anions (including SCN⁻, AcO⁻, HSO₄⁻, CN⁻, H₂PO₄⁻, I⁻, Br⁻, ClO₄⁻, Cl⁻ and F⁻) in DMSO/H₂O (9 : 1, v/v) solution. The fluorescence selectivity was examined at an emission wavelength of 504 nm, all the competing anions did not interfere in the detection of CN⁻ (Fig. 3). This result indicated high selectivity of the sensor **AHP5** toward CN⁻ over other analytes mentioned above.

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Fig. 3 Fluorescence of the sensor AHP5 at 504 nm with addition of 5.0 equiv. of CN^{-} in the presence of 1.0 equiv. of other anions in DMSO/H₂O (v/v = 9 : 1) solution.

The recognition mechanism was investigated by ¹H NMR, Job's plot measurement and ESI–MS. In the concentration dependent ^{1}H NMR of AHP5 (Fig. 4), with the concentration of AHP5 rising, the signals of H₁ and H₂ showed obvious downfield shifts, which indicated that H₁ and H₂ formed stable intermolecular hydrogen bonds with -C=O on adjacent molecule. Besides, ¹H NMR titration displayed the chemical shift changes of AHP5 upon the addition of CN⁻. As shown in Fig. 5, the proton of -NH- showed two peaks at 11.3 and 11.4 ppm in DMSO- d_6 , which were due to the impact of tautomerism. The presence of cyanide anions could taking the proton away via deprotonating during the thioacetohydrazone moieties of AHP5 and cyanide itself. In the corresponding ¹H NMR spectra, upon addition of 1.0 equiv. CN^- by DMSO- d_6 solution, the signal at 11.3 and 11.4 ppm (-NH-) disappeared. Meanwhile, the intermolecular hydrogen bonds among H_1 , H_2 and -C=O were destroyed. This is a novel recognition mechanism of AHP5 encounter CN⁻ occurred deprotonation effect accompanied with the breakage of intermolecular hydrogen bonds. In addition, the fluorescence of Job's plot measurement was conducted by varying the concentration of both AHP5 and CN⁻ (Fig. S21). The inflection point appears at the mole fraction of 0.5, indicated AHP5 and CN were formed a 1:1 stoichiometry. It was further confirmed by the appearance of a peak at m/z 1864.7559 which can be assignable to [AHP5-H+2Na]⁺ in the ESI-MS (Fig. S22). These common phenomenon could be explained from the propose sensing mechanism show in Scheme 2.



Fig. 4 ¹H NMR spectra (600 MHz, 298 K) of **AHP5** in DMSO– d_6 at various concentrations: (a) 2.0 mM; (b) 10.0 mM; (c) 20.0 mM; (d) 50.0 mM; (e) 120.0 mM.







Scheme 2 The proposed sensing mechanism of the sensor AHP5 to CN^{-} .

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Fig. 6 Fluorescence spectral response of the sensor AHP5 to detect cyanide in water sample.

We also investigated the practical utilities of the sensor in our daily life, we selected the water samples containing cyanide whose concentration was unknown to carry out the below experiment. Some distilled water and some cyanide–containing DMSO solution were added in a 10 ml burette. The burette was shaken for 5 minutes, and then this solution was used as water sample. The fluorescence emission spectrum of **AHP5** (0.2 mM in 4.5 mL DMSO) is shown as black line in Fig. 6, then, upon the titration of water sample (0.5 mL) red line is obtained. The cyanide concentration of samples was 5.83×10^{-5} M calculated by the linear equation of minimum detection limit of **AHP5** with CN⁻ (Fig. S20). Therefore, the sensor could conveniently detect CN⁻ in water, confirming that **AHP5** is a promising CN⁻ probe for practical applications.

The detection limit is one of the most important parameters in ion sensing. For many practical purposes, it is very important to detect the analytes at low concentrations. The fluorimetric detection limits of sensor **AHP5** for CN⁻ were also determined. As shown in Fig. S23, the minimum concentration of CN⁻ that could be observed though one order of magnitude lower for fluorescence naked eye detection was 5×10^{-4} M, by using a UV lamp at 365 nm.

Finally, to investigate the practical application of **AHP5**, a thin film was prepared by immersing a glass sheet into a high concentration solution of **AHP5** (0.1 M) and then drying it in air. The thin film was utilized to sense CN⁻. As shown in Fig. 7, when CN⁻ were added onto the thin film, the obvious color change was observed under irradiation at 365 nm using a UV lamp. Therefore, the thin film could be a convenient test kit for detecting CN⁻.



Fig. 7 Photos of the thin film utilized to sense CN^{-} under irradiation at 365 nm using a UV lamp.

Conclusions

In summary, we have developed a thioacetohydrazone functionalized bispillar[5]arene, which could detect CN^- with specific selectivity and high sensitivity $(5.14 \times 10^{-8} \text{ mol} \cdot L^{-1})$. The investigation of the recognition mechanism indicated that the sensor **AHP5** recognized CN^- by a deprotonated procedure accompanied with the breakage of intermolecular hydrogen bonds. More importantly, this is the first example that a bispillar[5]arene-based sensor was synthesized for fluorescent recognition of cyanide anion in DMSO/ H₂O (9 : 1, v/v) solution. Therefore, this novel cyanide triggered hydrogen bonds breakage deprotonation mechanism will extend the application of pillar[*n*]arenes.

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Color Graphic:



Text:

Bispillar[5]arene-based fluorescent sensor was used for fluorescence detection cyanide anion by a deprotonated procedure accompanied with the breakage of intermolecular hydrogen bonds.