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A copillar[5]arene-based fluorescent "on-off-on" sensor is applied in sequential recognition of iron cation and fluoride anion

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We have synthesized a copillar[5]arene-based fluorescent "on-off-on" sensor (DBP5) and used it for sequential fluorescent sensing for Fe^{3+} and F^- in H₂O/DMSO (1 : 9, v/v) solution. Copillar[5]arene DBP5 can produce blue fluorescence because it easily forms [c2]daisy-chain dimers by the self-assembly behavior in solution. DBP5 exhibits high selectivity and sensitivity (1.65×10^{-8} M) to Fe^{3+} . Moreover, the *in situ* formed DBP5– Fe^{3+} complex further utilized to sense the F^- through complexation reaction with high selectivity and sensitivity (6.44×10^{-8} M) to F^- . Furthermore, we designed the fluorescent switch of DBP5 between Fe^{3+} and F^- . The structure of DBP5 was proved by single crystal XRD.

Introduction

Among the many metals and nonmetals in ecology and the environment, both iron and fluorine are the most plentiful necessary elements found in the human body and are critical for maintaining significant physiological processes. Iron ion (Fe³⁺) plays the crucial roles in oxygen uptake, oxygen metabolism, electron transfer, and transcriptional regulation.¹ Lack of iron ions can lead to the permanent loss of motor skills, and its excess can lead to diseases such as Parkinson's and Alzheimer's.² A safe limit for the Fe³⁺ was restricted to 2 mg L^{-1} by the World Health Organization. Therefore, it is very necessary to find some simple, rapid, and efficient methods for the detection of Fe³⁺ at trace levels in biological and food specimens.³ Generally speaking, the iron complexes may be used to detect $H_2PO_4^$ because $H_2PO_4^-$ has better binding ability with Fe^{3+} to form a complex (Fe(H₂PO₄)₃),⁴ several fluorescent receptors for iron and fluoride ions have been reported, so the realization of both Fe³⁺ and F⁻ for fluorescence measurements is still a challenge. Fluoride anion extremely attracting our attention because they significantly influence our environment and health. A high intake of fluoride can result in dental fluorosis and skeletal fluorosis, but a low intake of fluoride can result in caries.⁵ The United States Environmental Protection Agency (EPA) obtains an executable drinking water standard for fluoride of 4 mg L⁻¹ to prevent skeletal fluorosis. Therefore, the synthesis of new sensors for the

simple, easy and sequential detection of Fe^{3+} and F^- has attracted our attention.

Pillararenes are a newest group of supramolecular macrocycles first developed in 2008.⁶ they have novel host–guest binding properties due to being easier to functionalize by special substituents on the benzene rings,⁷ thus functionalized pillararenes attracted a lot of attention of scientists.⁸ Due to pillararenes have π electronic cavities, they should have corresponding ion responsive fluorescent properties.⁹ However, only a handful of paper reported that pillararenes are used to recognise ions,¹⁰ this may greatly impede the application of pillararenes. Therefore, it is quite necessary to design and synthesize ion responsive fluorescent pillararenes.

In view of this, and as a part of our research interest in pillararenes chemistry and ion recognition,¹¹ we synthesize a fluorescent "on-off-on" sensor DBP5 for Fe^{3+} and F^- . According to a previous report,¹² the sensor DBP5 was synthesized via a 2-step pathway (Scheme 1). The target compound and intermediates were characterized by ¹H NMR spectrum, ¹³C NMR spectrum and ESI-MS (Fig. S1-S4). Fortunately, by slow evaporation of a solution of DBP5 in a dichloromethane/ethanol mixture (1 : 1, v/v) at room temperature, crystals suitable for X-ray analysis were obtained (Fig. 1). The crystal structure gave direct proof copillar[5]arene DBP5 that contained four 1,4-dimethoxybenzene units and one 1,4-bis (4-bromobutoxy)benzene units. The self-assembly behavior of the [c2]daisy chain-forming compound DBP5 was reported.¹³ This report suggested that the aggregates of copillar[5]arene **DBP5** changed from self-encapsulation monomers into [c2]daisy chain dimers in solution. The 2D NOESY spectrum (Fig. S5) also shows that there is a certain self-assembly behavior. Thus, the monomers **DBP5** may forms strong fluorescence dimers by the self-assembled between the pillar[5]arene units and Br(CH₂)₄- units. It is noteworthy that the **DBP5** could be a sequential fluorescent sensor for iron ions followed by fluoride ions with high sensitivity and selectivity in aqueous solutions.



Fig. 1 The crystal structure of **DBP5**: (a) side view and (b) top view. Oxygen atoms are red balls, hydrogen atoms are green balls, carbon atoms are white balls.

Experimental section

Materials and instruments

1, 4–Dimethoxybenzene, boron trifluoride ethyl ether complex and 1,4–dibromobutane were reagent grade and used as received. Solvents were either employed as purchased or dried by CaCl₂. ¹H NMR spectra were recorded on a Mercury–600BB spectrometer at 600 MHz and ¹³C NMR spectra were recorded on a Mercury–600BB spectrometer at 150 MHz. Chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Melting points were measured on an X–4 digital melting–point apparatus (uncorrected). Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker–FranzenAnalytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer.

Synthesis

Synthesis of 1,4-bis(4-bromobutoxy)benzene 1

Hydroquinone (2.3 g, 20.0 mmol), K_2CO_3 (16.6 g, 120 mmol), KI (6.6 g, 40 mmol), 1,4–dibromobutane (34.6 g, 160 mmol) and acetone (400.0 mL) were added in a 500 mL round–bottom flask stirred at room temperature. The reaction mixture was stirred at reflux for 1.5 days. After the solid was filtered off, the solvent was evaporated and the residue was dissolved in CH₂Cl₂. Column chromatography (silica gel; petroleum ether : CH₂Cl₂=10 : 1) afforded a white solid (6.0 g, 80%). Mp 83–85°C. ¹H NMR (600 MHz, CDCl₃) δ 6.83 (d, J = 0.8 Hz, 4H), 3.96 (t, J =6.0 Hz, 4H), 3.52–3.25 (m, 4H), 2.10–1.88 (m, 8H).

Synthesis of a copillar[5]arene DBP5

To a solution of 1,4-bis(4-bromobutoxy) benzene (1.9 g, 5.0 mmol) and 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in 1, 2-dichloroethane (200 mL), paraformaldehyde (0.75 g, 25.0 mmol) was added under nitrogen atmosphere. Then boron trifluoride diethyl etherate (6.75 mL, 25 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h and concentrated by rotary evaporation. The resultant oil was dissolved in CH₂Cl₂ and washed twice with H₂O. The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford the crude product, which was isolated by flash column chromatography using petroleum ether/ethyl acetate (20 : 1, v/v) to give **DBP5** (1.69 g, 34%) as a white solid. Mp 187-189 °C. ¹H NMR (600 MHz, CDCl₃) δ 6.84–6.74 (m, 10H), 3.87 (t, J= 5.9 Hz, 4H), 3.83–3.78 (m, 10H), 3.72 (t, J= 19.9 Hz, 24H), 3.33 (s, 4H), 1.94 (s, 4H), 1.84 (s, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 150.80 (s), 150.75 (s), 150.70 (s), 150.58 (s), 149.84 (s), 128.44 (s), 128.30 (s), 128.08 (s), 114.89 (s), 114.15 (s), 113.92 (s), 113.71 (s), 67.32 (s), 55.95 (d, J= 3.6 Hz), 55.76 (s), 55.70 (s), 33.34 (s), 30.55 (s), 29.75 (s), 29.48 (d, J= 5.2 Hz), 29.19 (s), 28.32 (s). ESI-MS m/z: $(M+NH_4)^+$ Calcd for C₅₁H₆₄O₁₀Br₂N 1010.2871; Found 1010.2878.

Results and discussion

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In order to investigate the influence of metal ions of the sensor **DBP5** in $H_2O/DMSO(1:9, v/v)$ solution, a series of host-guest recognition experiments were carried out. The sensor DBP5 toward various cations (including Fe³⁺, Hg²⁺, Co²⁺, Ca²⁺, Ni²⁺, Pb²⁺, Cd²⁺, Zn²⁺, Cr^{3+} , Mg^{2+} , Fe^{2+} and Ag^{+}) were primarily investigated using fluorescence spectroscopy. The free sensor DBP5 showed an absorption peak at 295 nm (Fig. S6). In the fluorescence spectrum, the maximum emission of DBP5 appeared at 330 nm in H₂O/DMSO (1 :9 , v/v) solution while excited at $\lambda_{ex} = 295$ nm. When 2.0 equiv. of Fe³⁺ was added to the solution of sensor DBP5, the fluorescence emission band was quenched (Fig. S7). The same tests were applied using Fe3+, Hg2+, Co2+, Ca2+, Ni^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} , Cr^{3+} , Mg^{2+} , Fe^{2+} and Ag^+ cations, and only Fe³⁺ have significant changes in the fluorescence spectrum, and none of those other cations induced any significant changes in the fluorescent spectrum (Fig. 2).



Fig. 2 Fluorescence spectra responses for **DBP5** $(2 \times 10^{-4} \text{ M})$ and each of the various cations $(4 \times 10^{-4} \text{ M})$ as the perchlorate, in the H₂O/DMSO (1 : 9 , v/v) solution. Inset: color changes observed for **DBP5** upon the addition of Fe³⁺, Hg²⁺, Co²⁺, Ca²⁺, Ni²⁺, Pb²⁺, Cd²⁺, Zn²⁺, Cr³⁺, Mg²⁺, Fe²⁺ and Ag⁺ cations in H₂O/DMSO (1 : 9 , v/v) solution.

To further investigate the efficiency of the sensor **DBP5** toward Fe³⁺ detection, we carried out fluorescence emission titration experiments. In the fluorescence spectrum, upon addition of increasing amounts of Fe³⁺ ions (0~0.66 equiv.) to the solution of **DBP5**, directly leading to a light purple emission almost completely quenching (Fig. 3). The detection limit of the fluorescent spectrum changes calculated on the basis of $3\delta/S$ is 1.65×10^{-8} mol·L⁻¹ (Fig. S8), indicating the high sensitivity of the sensor to Fe³⁺. Simultaneously, this detection limit is lower than other detection techniques (Table S1). In addition, the fluorescence of the Job's plot suggests that **DBP5** forms a 1:1 complex with Fe³⁺ ion (Fig. S9).

To further exploit the utility of the sensor **DBP5** as cation selective sensor for Fe^{3+} , competitive experiments

were carried out in the presence of 2.0 equiv. of Fe^{3+} and 2.0 equiv. of various cations in H₂O/DMSO (1 : 9 , v/v) solution. The fluorescence selectivity was examined at an emission wavelength of 330 nm, all the competing cations did not interfere in the detection of Fe^{3+} (Fig. 4). This result displayed high selectivity of the sensor **DBP5** toward Fe^{3+} over other analytes mentioned above.



Fig. 3 Fluorescence spectra of **DBP5** (2×10^{-4} M) in the presence of different concentration of Fe³⁺ in H₂O/DMSO (1 : 9, v/v) solution.



Fig. 4 Fluorescence of the sensor DBP5 at 330 nm with addition of 2.0 equiv. of Fe^{3+} in the presence of 2.0 equiv. of other cations in H₂O/DMSO (1 : 9 , v/v) solution.

It is well known that anions has binding ability with cations to form complexes, so we investigated the fluorescence behavior of the sensor **DBP5** between Fe³⁺ and anions. The variations of fluorescent spectrum of the **DBP5**-Fe³⁺ complex ([**DBP5**]/[Fe³⁺]= 1 : 2, [**DBP5**]= 2×10^{-4} M) caused by the anions (1×10^{-3} M), namely, F^{-} , Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, SCN⁻ and CN, are summarized in Fig. 5. We found when a fluoride ion was added to the **DBP5**-Fe³⁺ system, the fluorescence intensity is completely regenerated. The other anions (Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, SCN⁻ and CN⁻) show very little response. The observed fluorescence and color regeneration can be ascribed to the capture of Fe^{3+} from its chelated complexes by F^{-} , resulting in the formation of more stable species $[FeF_6]^{3-1}$ and the release of free compound DBP5.

At the same time, fluorescence emission spectral variation of sensor **DBP5**– Fe^{3+} in H₂O/DMSO (1 : 9 , v/v) solution was monitored during titration with different concentrations of F⁻ from 0 to 7.0 equiv. The addition of increasing concentrations of F⁻, the emission peak at 330 nm gradually enhanced intensity and the fluorescence of DBP5-Fe³⁺ was essentially recovered by 5.6 equiv. of F⁻ ion (Fig. 6). The detection limit of the **DBP5**– Fe^{3+} for the determination of F^- was estimated to be 6.44×10⁻⁸ mol·L⁻ (Fig. S10) pointing to the high detection sensitivity. In addition, the changes in the fluorescence intensity depending on the reaction time were recorded from 0 to 150 seconds, for a 1 : 5 mixture of **DBP5-**Fe³⁺ complex and F⁻ in H₂O/DMSO (1:9, v/v) at room temperature (Fig. S11). This clearly shows that the reaction was complete within 30 s after the addition of F⁻.



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Fig. 5 Fluorescence spectra responses for **DBP5**–Fe³⁺ and each of the various anions $(1 \times 10^{-3} \text{ M})$ as the tetrabutylammonium salts, in the H₂O/DMSO (1 : 9 ,v/v) solution. Inset: color changes observed for **DBP5**–Fe³⁺ upon the addition of F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, ClO₄⁻, SCN⁻ and CN⁻ anions in H₂O/DMSO (1 : 9 , v/v) solution.



Fig. 6 Fluorescence spectra of **DBP5**– Fe^{3+} in the presence of different concentration of F^- in H₂O/DMSO (1 : 9, v/v) solution.

To further explore the utility of **DBP5**– Fe^{3+} as an anion–selective sensor for F^- , competitive experiments were carried out in the presence of 5.0 equiv. of F^- and

5.0 equiv. of various other anions in H₂O/DMSO (1 : 9, v/v) solution of **DBP5**–Fe³⁺ (Fig. 7). The fluorescence emission spectra displayed a similar pattern to that with F^- alone, suggesting that all the tested anions do not interfere in the sensing of F^- .

Due to fluoride anion has binding ability with iron cation to form a complex $[FeF_6]^{3-}$, we investigated the fluorescence "on–off–on" behavior of the sensor **DBP5** between Fe³⁺ and F⁻. Fig. 8 shows the repeated switching behavior when altering adding amounts of F⁻ and Fe³⁺ to **DBP5**, which evidently proved the excellent reusability and stability of **DBP5** toward Fe³⁺ at least for six successive cycles.



Fig. 7 Fluorescence of the sensor **DBP5**–Fe³⁺ at 330 nm with addition of 5.0 equiv. of F^- in the presence of 5.0 equiv. of other anions in H₂O/DMSO (1 : 9 , v/v) solution.



Fig. 8 Emission spectra showing the reversible complexation between **DBP5** and Fe^{3+} (2.6 equiv.) by introduction of $F^{-}(10.0 \text{ equiv.})$.

The possible mechanism was also put forward by emission spectra. As can be seen from the emission spectra, when adding iron ion, acyclic monomeric analog **1** fluorescence is quenched (Fig. S12). This shows that iron ion is coordinated with Br atom. However, fluorescence intensity of **DBP5** was significantly higher than **1** (Fig. S13), because the monomers **DBP5** may forms strong fluorescence dimers by the self-assembled between the pillar[5]arene units and Br(CH₂)₄– units. This shows that the sensor **DBP5** is most likely to band with Fe³⁺ via Br atom on the alkyl chain formed linear supramolecule, thereby forming a 1 : 1 complex (Scheme 2). When F⁻ was added to the Published on 02 February 2017. Downloaded by University of Colorado at Boulder on 02/02/2017 07:37:10

DBP5–Fe³⁺ system, the capture of Fe³⁺ from its more stable complex $[FeF_6]^{3-}$ by F⁻ and the release of free compound **DBP5**. Hereafter, the free **DBP5** forming the [c2]daisy chain by self-assembly behavior.

The recognition possibilities were also investigated by ¹H NMR. Partial proton NMR spectra of **DBP5**, **DBP5**–Fe³⁺ and **DBP5**–Hg³⁺+F⁻ system are shown in Fig. S15. The addition of 2.0 equiv. of Fe³⁺ to **DBP5** solution led to the signals of H₃ of **DBP5** appeared changes. This suggested that the complexation reaction have been taken place. When 5.0 equiv. of F⁻ had been added to **DBP5**–Fe³⁺ system, the signals of H₃ peak restored the original location. This implies that F⁻ dissociated **DBP5**–Fe³⁺ complex.



Scheme 2 The sensing mechanism of the sensor **DBP5** to Fe^{3+} and F^- .

Finally, to investigate the practical application of **DBP5**, a thin film was prepared by immersing a glass sheet into a high concentration solution of **DBP5** (100 mM) and then drying it in air. The thin film was utilized to sense Fe^{3+} . As shown in Fig. 9, when Fe^{3+} 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 Fe^{3+} . Same manner, a glass sheet was immersed into a high concentration solution of **DBP5** + Fe^{3+} (100 mM) and then drying it in air, when F^- were added onto this thin film, the obvious fluorogenic change was observed under irradiation at 365 nm using a UV lamp.



Fig. 9 Photos of (A) the thin film utilized to sense Fe^{3+} cation and F^- anion were added onto the (B) thin film under irradiation at 365 nm using a UV lamp.

The practical utility of the probe in a daily life sample was investigated using Fe^{3+} in tap water and F^{-} in toothpastes. The fluorescence emission spectra of DBP5 (0.2 mM in 4.5 mL DMSO) is just as line 1 shown in Fig. 10, then, upon the titration of concentrated tap water (0.5 mL) to obtain line 2. The fluorescence emission spectra of the **DBP5**– Fe^{3+} complex (0.2 mM **DBP5** and 0.4mM Fe^{3+}) is just as line 3, then, upon the titration of soluble components of Colgate toothpaste sample (0.5 mL DMSO) to obtain line 4. The sensor could detect sequentially Fe³⁺ in tap water and F⁻ in real samples such as toothpastes (Fig. 10), confirming that **DBP5** is a promising Fe^{3+} and F^{-} probe for practical applications. Therefore, this copillar[5]arene DBP5 can be used as an fluorescent sensor for the sequential detection of Fe³⁺ and F⁻ ions, which showed excellent stability, reversibility, and repeatability.



Fig. 10 Fluorescence emission spectra of **DBP5** (0.2 mM in DMSO) sequential detect Fe^{3+} in tap water and F^- in real samples such as toothpastes.

Conclusions

In summary, a fluorescent "on-off-on" sensor (**DBP5**) has been applied in sequential fluorescent sensing for iron cation and fluoride anion in H₂O/DMSO (1 : 9, v/v) solution. **DBP5** shows highly selective and sensitive fluorescence "on-off" behavior toward Fe³⁺ over other cations. The *in situ* prepared **DBP5**–Fe³⁺ complex exhibits high selectivity and sensitivity to F⁻ over other anions through a complexation reaction. Furthermore, we designed the fluorescent switch of **DBP5** between Fe³⁺ and F⁻. This sequential recognition behavior makes sensor **DBP5** as a potential probe to detect Fe³⁺ and F⁻ in the environmental monitoring works.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information of complete experimental procedures, CCDC: 1496652]. See DOI: 10.1039/c0xx00000x/

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A copillar[5]arene-based fluorescent "on-off-on" sensor is applied in sequential recognition of iron cation and fluoride anion

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Text:

A copillar[5]arene-based [c2]daisy-chain dimer is applied in sequential detection of Fe^{3+} and F^- through competitive complexation reaction.