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Novel Fluorescent Chemosensor for Detection of F^- Anions Based on a Single Functionalized Pillar[5]arene Iron(III) Complex

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Novel fluorescent chemosensor with good selectivity for F^- anion was designed and synthesized. The sensor has a bearing on a single functionalized pillar[5]arene and Fe^{3+} metal complex (PN-Fe), which showed prominent fluorescent response for F^- anion over other common anions (Cl^-, Br^-, I^-, AcO^-, $HSO4^-$, $H_2PO_4^-$, ClO_4^-, CN^- and SCN^-). These results were evaluated by fluorescent method. The detection limit of PN-Fe to F^- was calculated to be 2.50×10^{-7} mol/L. Moreover, the sensor PN-Fe^{3+} might serve as a recyclable component in sensing materials.

Keywords pillararene, ferric(III) complex, chemosensor, fluoride

Introduction

Pillar[*n*]arenes as a new class of compounds were first reported in 2008,[1] and known as a novel macrocyclic compounds after crown ethers, cyclodextrins, calixarenes, cucurbiturils and so forth.[2] They were a type of macrocyles consisting of hydroquinone or hydroquinone ether units linked by methylene (CH_2) bridges at *para*-positions of 2,5-dialkoxybenzene rings with unique pillar-like architectures and electrondonating cavities.[3] Because pillar[*n*]arenes have the symmetrical structure and easy functionalization compared with other macrocyclic hosts, their host-guest complexation, self-assembly properties, and applications have been widely researched in supramolecular chemistry field.[4] Pillar[*n*]arene-based organic functional materials have been successfully applied to many different areas, including self-assembly, pesticide adsorption, bacteria and virus inhibition, drug delivery and controlled release, fluorescent sensor, stabilization of nanoparticle, catalysis[5] and so on.

Ions exist in the living processes and in nature, and most of ions are toxic, which is also threatening biotic health and environment safe, so ions recognition plays a significant role in science and technology fields.[6] For fluoride, it is an essential element of the human body, and conducive to treating osteoporosis and protecting dental health.[7] Nevertheless, ingesting excessive fluoride may cause kidney disorders as well as fluorosis and urolithiasis in humans, and very high levels of fluoride can even cause death. Therefore, as the World Health Organization limit is being followed in most of the nations, fluoride is considered beneficial in drinking water at levels of about 5.3×10^{-3} mol/L.[8] Because fluoride is associated with nerve gases, drinking water and the refinement of uranium, the recognition and detection of fluoride ion have aroused more and more interest. Meanwhile, the recognition and detection of fluoride ion also provide significant information for fluoride hazard assessment and fluoride pollution management.[9]

Because of the high sensitivity, simplicity, and real time monitoring without complicated pretreatment, fluorescence spectrometry has become one of the most popular methods for specific measurement.[10] Our research group has a longstanding interest in molecular recognition and also made remarkable achievements.[11] As a novel macrocyclic hosts, pillar[*n*]arenes also could be a type of recognition hosts, however, there were few reports of pillar[*n*]arene-based ion recognition, so our research group combined pillar[5]arenes with recognition for expanding the application of pillar[*n*]arenes and their derivatives. In this study, we designed and synthesized a fluorescent chemosensor based on a single functionalized pillar[5]arene to detect Fe^{3+} ion in DMSO solution. As a simple and effective way of testing, fluorescent detection method was mainly used to prove the complexation between host and guest in this paper. The results showed that the main reason for sensor fluores-

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cence changes was the competition coordination between different ions and the nitrogen atom of sensor.

Experimental

General information and materials

All reagents for synthesis were of analytical grade from commercial sources and were used without further purification. All of the cations were added in the form of perchlorate salt. Anions were added in the form of tetra-*n*-butylammonium (TBA) salts, which were purchased from Sigma-Aldrich Chemical and stored in a vacuum desiccator. UV/Vis spectra were recorded on a Shimadzu UV-2550 spectrometer. Fluorescence spectra were recorded on a Shimadzu RF-5310. The infrared spectra were performed on a Digilab FTS-3000 FTIR spectrophotometer. Mass spectra were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. Melting points were measured on an X-4 digital melting-point apparatus (uncorrected). ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 MHz and Plus 600 MHz spectrometer with CD_3CN and $CDCl_3$ as solvent and TMS as an internal reference.

Synthesis and characterization of receptor PN

Compound **1a** was prepared following a reported procedure,[12] yield 18.26%. ^{1}H NMR (Figure S1, 400 MHz, $CDCl_3$, 298 K) δ: 6.96—6.82 (m, 10H), 3.94 (d, J=5.6 Hz, 4H), 3.76—3.72 (m, 37H), 1.84 (s, 2H), 1.59—1.47 (m, 4H), 1.37—1.28 (m, 2H), 1.10 (s, 2H), 0.86 (s, 1H), 0.68 (s, 1H); ^{13}C NMR (Figure S2, 150 MHz, $CDCl_3$, 298 K) δ: 150.42, 150.32, 150.27, 150,19, 150.15, 149.57,128.27, 128.22, 128.13, 128.08, 128.02, 127.96, 127.91, 114.39, 113.62, 113.35,113.22, 113.14, 113.07, 68.09, 55.55, 55.42, 55.33, 55.28, 55.24, 39.81, 33.00, 30.08, 29.27, 29.12, 27.76; ESI-MS (Figure S3) *m/z*: $[M+NH_4]^+$ calcd for $C_{54}H_{67}Br_1O_{10}NH_4$: 974.41; found 974.4244; [M] calcd for $C_{54}H_{67}Br_1O_{10}$: 956.41; found 956.3892, error 1.2.

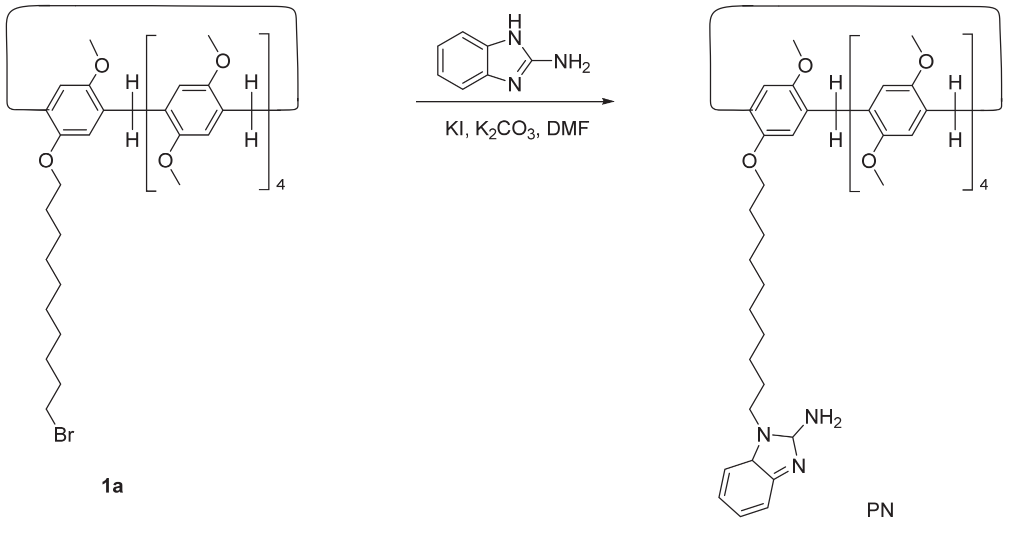
Synthesis of PN: The synthesis of chemosensor PN is outlined in Scheme 1, yield 73.46%. ^{1}H NMR (Figure S4, 400 MHz, CD_3CN, 298 K) δ: 7.23—7.20 (m, 2H), 7.15—7.13 (m, 1H), 6.99 (s, 3H), 6.91—6.87 (m, 10H), 3.91—3.86 (m, 4H), 3.73—3.70 (m, 37H), 1.74 (d, J= 23.9 Hz, 4H), 1.32 (s, 12H); ^{13}C NMR (Figure S5, 150 MHz, $CDCl_3$, 298 K) δ: 150.17, 150.14, 150.12, 150.09, 150.08, 149.47, 142.62, 128.63, 128.60, 128.46, 128.43, 128.41, 128.36, 120.63, 118.78, 117.28, 115.39, 113.95, 113.06, 112.97, 107.81, 68.27, 55.27, 55.22, 55.19, 55.14, 44.14, 42.14, 29,47, 29.16, 29.12, 28.88, 28.98, 28.92, 28.76, 28.57, 26.61, 26.45, 25.96. ESI-MS (Figure S6) *m/z*: $[M+H]^+$ calcd for $C_{61}H_{73}N_3O_{10}H^+$ 1008.55; found 1008.53, error 2.4.

The solution of sensor PN (2.0×10^{-4} mol/L) in DMSO was prepared and stored in dry atmosphere. The solution was used for all spectroscopic studies after appropriate dilution. The DMSO solutions of each anion (4.0×10^{-3} mol/L) were prepared, respectively, via perchlorate salts for F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, ClO_4^-, CN^- and SCN^-. The fluorescence spectra were obtained by excitation at 285 nm. The excitation slit width was 10 nm and emission slit width was 5 nm, respectively. Any changes in the fluorescence spectra of sensor PN were recorded upon the addition of salts while keeping the concentration of sensor PN (2.0×10^{-5} mol/L) in all experiments.

Results and Discussion

The structures of sensors **1a** and PN are shown in Scheme 1. First, we researched the fluorescent response of sensor PN to various ions, and found that both Fe^{3+} and Cu^{2+} ions could coordinate PN and form metal complex (Figure S7). To investigate the complexation between PN and Fe^{3+} ions, the fluorescence titration experiments for PN (2.0×10^{-5} mol/L) were con-

Scheme 1 Synthetic procedures of sensor PN



ducted. As shown in Figure 1, when different amounts of Fe^{3+} ion were added to the solution of PN, the fluorescence of PN gradually decreased, and approached to quenching when 7.4 equivalents Fe^{3+} were added. The job plot showed a 1∶1 complexation stoichiometry between PN and Fe^{3+} (Figure S9 in the SI). Furthermore, the detection limit of the fluorescent spectrum changes calculated on the basis of $3s_B/S$[13] was 1.41×10^{-7} mol/L for Fe^{3+} ion (Figure S11 in the SI).

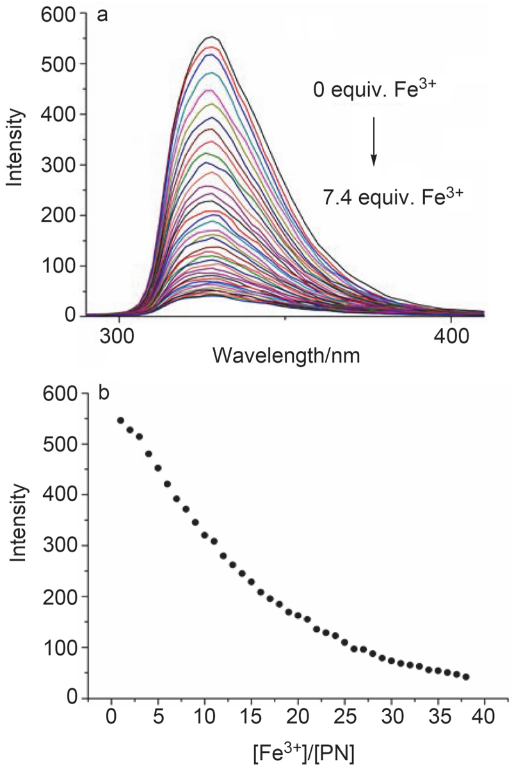


Figure 1 (a) Fluorescence spectra (λ_{ex}=285 nm) of PN in the presence of different concentrations of Fe^{3+} (c=0.1 mol/L). (b) Plot of fluorescence intensity depending on the concentration of Fe^{3+} in the range from 0 to 7.4 equiv.

Secondly, in order to identify the selectivity of metal complex, we carefully investigated the anions response capability of the metal complex of sensor PN by adding various anions (Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, ClO_4^-, CN^- and SCN^-) to the metal complex, respectively. Nearly no clear fluorescence changes were observed in the spectra of these anions, under the identical conditions, while fluorescence enhanced significantly in the presence of F^- anion. It turned out that the different metal complexes have different response to anions and solely the PN and Fe^{3+} metal complex had response to F^- anion (Figure S10 in the SI). As shown in Figure 2, the recognition profiles of PN-Fe toward various anions, including F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, ClO_4^-, CN^- and SCN^-, were studied by fluorescence spectroscopy in DMSO solution. The significant fluorescence enhancement was observed when 50 equiv. of F^- anions were added to the solution of PN-Fe.

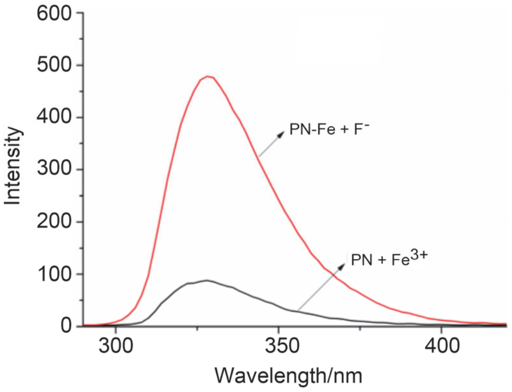


Figure 2 Fluorescence spectra of PN-Fe upon an excitation at 285 nm in DMSO in the presence of F^- anion (λ_{ex}=285 nm).

The fluorescence responses between PN-Fe and F^- at 285 nm were investigated to acquire complex ability of PN-Fe toward F^- anions in detail. As shown in Figure 3, we added fluoride anion into the DMSO solution of PN-Fe, with the increasing of F^- anions, the fluorescence gradually enhanced, the fluorescence intensity of the solution after introducing fluoride at 328 nm was enhanced 6 times while the amount of F^- anions in the solution reached 35.8 equiv. The detection limit of fluoride with PN-Fe under these conditions was estimated to be 2.50×10^{-7} mol/L (Figure S12 in the SI), which is lower than the concentration of fluoride in drinking water (5.3×10^{-3} mol/L).

The competition experiments were executed for PN-Fe to demonstrate the selectivity in detecting F^- anions in the presence of other competing anions (Figure 4).

When 50 equiv. of anions were added to the solution of PN-Fe, except $H_2PO_4^-$ and CN^- anions which caused ignorable fluorescence enhance, and Cl^- and I^- anions which made slight fluorescence decrease, no other anions induced significant fluorescence changes.

The reversibility of the chemosensor was tested by alterning addition of Fe^{3+} ions and F^- anions. Addition of F^- anions to the solution of PN-Fe complex induced the opposite trend in the fluorescent spectra to that observed on titration with Fe^{3+} ions. Upon addition of F^- anions, the optical fluorescence intensity approached to the levels observed for the free PN. The addition of F^- anions to the PN-Fe metal complex showed that the process of titrating sensor PN with Fe^{3+} ions was reversible, and the reversible process could be repeated several times with little fluorescence efficiency loss (Figure 5). Therefore, sensor PN might be considered as a good ON-OFF-ON fluorescent switch.

FTIR spectra were used to better investigate the complex between PN and ions, as showed in Figure 6. The absorption peaks at 3445 and 2934 cm^{-1} were assigned to the stretching vibrations of aromatic amine and the stretching vibrations of C—H bond, respectively. Moreover, at 1674 cm^{-1}, the bending vibrations of N—H bond in the primary amine was observed.

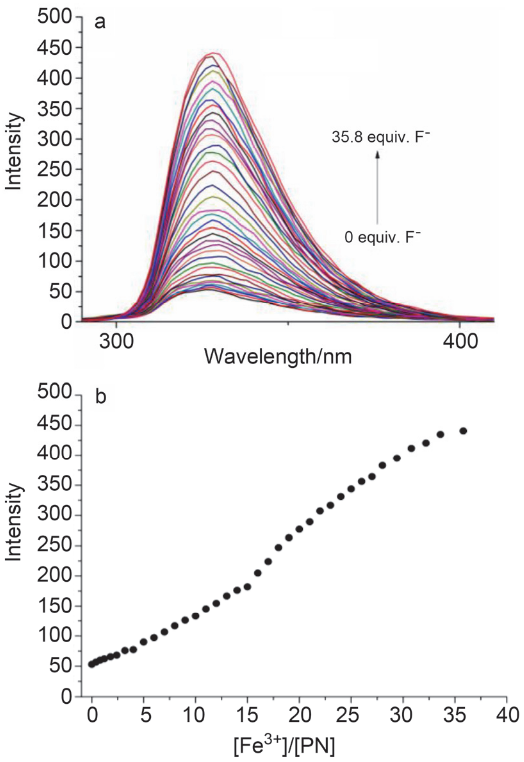


Figure 3 (a) Fluorescence spectra ($\lambda_{ex}=285$ nm) of PN-Fe upon addition of F^- (from 0 to 35.8 equiv., $c=0.1$ mol/L). (b) The plot of emission intensity at 328 nm vs. concentrations.

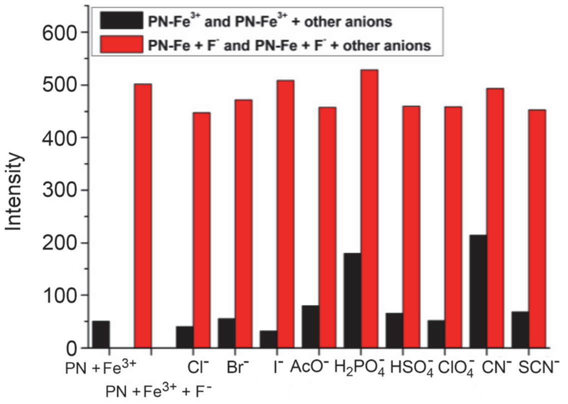


Figure 4 Fluorescence intensity changes of the PN-Fe to F^- (1×10^{-2} mol/L) in the presence of various test anions (1×10^{-2} mol/L) in solution (left to right is F^-, Cl^-, Br^-, I^-, AcO^-, HSO_4^-, $H_2PO_4^-$, ClO_4^-, CN^- and SCN^-).

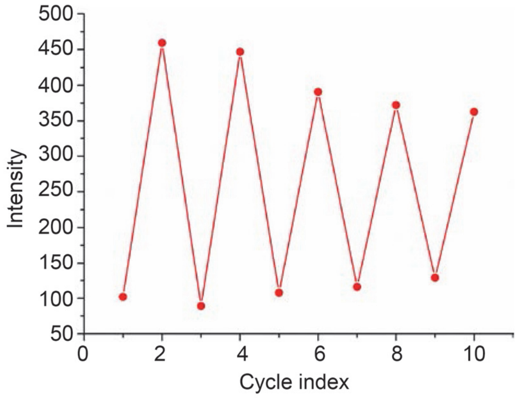


Figure 5 Emission spectrum showing the reversible complexation between PN and Fe^{3+} by introduction of F^- anions ($\lambda_{ex}=285$ nm).

Through the comparison among PN, PN+Fe^{3+}, and PN-Fe+F^-, we could conclude that Fe^{3+} ions coordinated with two nitrogen atoms of PN, indicated by the decrease of primary amine band and appearing of weak tertiary amine band. The primary amine band regained when F^- anions were added to the solution of PN-Fe metal complex, so, we considered that F^- anions coordinated with Fe^{3+} of PN-Fe metal complex. In addition to this, compared to PN and PN-Fe+F^-, the absorption bands of PN-Fe^{3+} at 2934 and 1647 cm^{-1} slightly shifted to the high wave-number, also demonstrating the complex among PN, Fe^{3+} ions and F^- anions.

In addition, we designed a series of contrast experiments to explain the function of pillar[5]arene (Figure S13 in the SI). To gain the fluorescent properties of intermediate **1** toward different metal ions, the emission changes were measured with various metal ions in DMSO [Figure S13 (a)]. When excited at 285 nm, the fluorescence intensity of host **1** showed 208 (a.u.) at 326 nm; the added ions, including Ag^+, Ca^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Cr^{3+} and Mg^{2+}, enhanced the fluorescence intensity; and host **1** exhibited a weak fluorescence in the presence of Fe^{3+}, Hg^{2+}, Cu^{2+} and Co^{2+} ions. As showed in Figure S13(b), obviously, the fluorescence of host **1a** is stronger than that of host **1**. Fe^{3+}, Cu^{2+} and Co^{2+} ions decreased the fluorescence of host **1a**. The host of Figure S13(c) is 2-aminobenzimidazole, it exhibited a weak fluorescence in the presence of Fe^{3+}, Hg^{2+}, Ag^+, Cu^{2+}, Co^{2+} and Cd^{2+} ions, and each of the ions led to different degree of red shift or blue shift. So we summarized that the cyclic conjugated system of pillar[5]arene might enhance the selectivity to ions. Based on the above findings, we proposed that the possible complex process between PN-Fe and fluoride in this system might through the route depicted in Scheme 2.

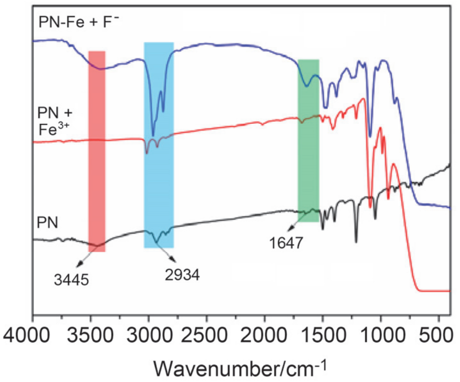
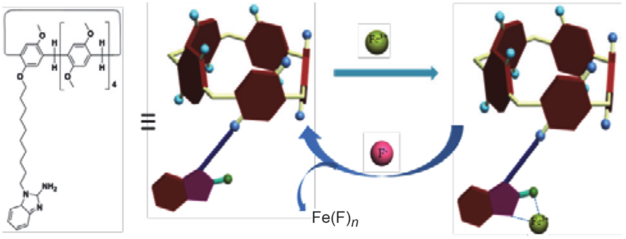


Figure 6 IR spectra of compound PN, PN+Fe^{3+} and PN-Fe+F^- in KBr disk.

Scheme 2 The proposed structures of PN-Fe for F^- ion



Conclusions

In conclusion, we synthesized a new class of supermolecule recognition host based on a single functionalized pillar[5]arene. It was utilized to monitor Fe^{3+} ions. All of experiments indicated metal ions complexation with the nitrogen atoms of PN, leading to its fluorescence decrease. The fluorescence of PN increased when anions coordinated to metal ions from nitrogen atoms of sensor PN. The detection limit of the F^- anion was 2.50×10^{-7} mol/L. It was lower than the WHO permissible limit of fluoride in India which has been reduced from 1.5 to 1.0 ppm in 1998.[8a] Considering the difficulty in acquiring the fluoride anion chemsensor, we expect that the PN-Fe chemsensor might be a latent sensor material for F^- detection.

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