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PAPER

A Novel Functionalized Pillar[5]arene: Synthesis, Assembly and Application in Sequential Fluorescent Sensing for Fe^{3+} and F^- in Aqueous Media

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We designed and synthesised a novel copillar[5]arene PF5, which can be self–inclusion produce a strong blue fluorescence. Pillar[5]arene–based chemosensor PF5 could 10 be a sequential fluorescence sensor for ferric ions ( ) followed by fluoride ions with high sensitivity and selectivity in aqueous solution. When Fe^{3+} was added to the solution of sensor PF5, the blue fluorescence emission will be quenched. While after the addition of F^-, the blue 15 fluorescence emission of the PF5–Fe^{3+} system will be back to the original level. The PF5 has specific selectivity to Fe^{3+} and common cations (Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+}, Mg^{2+}, Fe^{2+}, Al^{3+}) couldn't interfere in the detection process. In addition, PF5–Fe^{3+} has specific 20 selectivity to F^- and common anions (Cl^-, Br^-, I^-, AcO^-, NO_3^-, HSO_4^-, ClO_4^-, SCN^-, CN^-) also have no obvious interfere in the detection process. The detection limit of the sensor PF5 for Fe^{3+} is 9.0×10^{-7} mol/L, and the detection limit of F^- is 2.59×10^{-8} mol/L. Moreover, test 25 strips based on the sensor were fabricated, which could be very good sequential test kits for ferric ions ( ) and fluoride ions. Moreover, the sensor PF5 could also sequential detect Fe^{3+} in tap water and F^- in toothpastes.

Introduction

Among different kinds biologically important metals and nonmetal, iron and fluorine are both the most plentiful necessary elements found in the human body and are critical 35 to maintain significant physiological processes. Given the physiological implications of ferric and fluoride, their detection are very important. The detection of Fe(III) at minute quantity is very meaningful, because iron, with its chemical diversity, is critical for the appropriate functioning 40 of most organisms in the whole spectrum of the biological system.[1] In the human body, iron is one of the most necessary trace elements; poverty of ferric ion (Fe(III)) in the body causes anemia, liver damage, hemochromatosis, Parkinson's disease, and cancer.[2] Ferric ions also play critical roles in the 45 metabolism and growth of living cells and catalytic many physiological processes.[3] A sanitary security limit for the Fe^{3+} ion was restricted to 2 mg L^{-1} by the World Health Organization. Therefore, it is important to exploit simple, rapid, and efficient methods for the prosecutions of Fe^{3+} at a 50 trace level in the circumstance, biological and food specimen.[4] Up to now, several fluorescent receptors for iron and fluoride ions have been reported, however, the realization of both Fe^{3+} and F^- for fluorescence measurements is still a challenge. Fluoride ions are one of the most attractive targets because of 55 their significant meaning for environmental and health concerns. The fluoride ion has unique chemical properties and widespread the existence of in pharmacy and toothpaste and used to prevent tooth decay, enamel demineralization while wearing orthotic devices, and treatment for osteoporosis. 60 However, a high intake of fluoride can result in serious side effect of fluoride, namely fluorosis, which may cause jeopardize the kidneys in both humans and animals and result urinary stones. The United States Environmental Protection Agency (EPA) gives an executable drinking water standard 65 for fluoride of 4 mg L^{-1} to prevent skeletal fluorosis to prevent fluorosis.[5] Accordingly, the design of new chemosensor for the simple and easy detection of Fe^{3+} and F^- of operation is subject to more and more attention.

Pillararenes, a new macrocyclic subject, have a stiffness 70 architecture with an overall cylindrical or pillarlike shape.[6] They have two openings of the tubular structures, and have exhibited distinguished recognition capabilities towards a variety of guests.[7] Functional groups introduced on pillararenes often bring about unique properties that greatly 75 stimulates the interest of chemists of various fields.[8] Due to the hydrophobic nature of these macrocycles, host–guest complexation and self–assembly of pillararenes derivatives have been widely investigated in organic media. However, as many recognition events in nature occur in aqueous media, 80 effort has also been directed towards the development of pillararene based receptors capable of recognizing guests in aqueous phase.[9] Bearing this in mind, we imagine that by proper functionalization, pillararenes can serve as platforms for self–assembly and preorganizing chelating groups for ion 85 sensor to which so far has not been widespread concen.[10]

Pillar[5]arene–based recognition receptors that continuous recognition system in Fe^{3+} and F^- ion has not been reported.

In view of this, and as a part of our research interest in pillararenes chemistry and molecular recognition,[11] we 5 designed and synthesised a novel pillar[5]arene–based ions receptor **PF5** linked 2–aminobenzothiazole at one sites which further self–organize into annularity supramolecular polymers at state of solution utilizing pillar[5]arene–based self–assembly interactions. Furthermore the chemosensor **PF5** 10 could be a sequential fluorescence sensor for ferric ions followed by fluoride ions with high sensitivity and selectivity in aqueous solution.

Results and discussion

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The synthesis of sensor **PF5** is shown in scheme 1 and the synthesis details in scheme S1. Sensor **PF5** and intermediate have been characterized by ^{1}H NMR, ^{13}C NMR, and ESI mass spectrometry (Fig. S1–S6). The monomeric pattern DMP5 and G 20 were also prepared as a control for comparison (Scheme S2). The target molecules and intermediates were characterized by ^{1}H NMR spectrum (Fig. S7–S8).
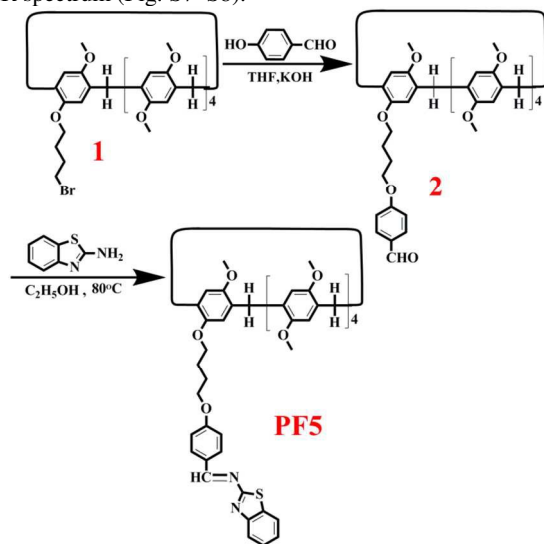
Scheme 1. Synthesis of the functionalized pillar[5]arene **PF5**.

25 To investigate whether the inclusion behavior was produced, the host–guest interaction between DMP5 and G was firstly studied. As shown in Fig. S9, the ^{1}H NMR spectra of DMP5 with the addition of different equivalents of G showed that the chemical shifts of H_{G2-G8} on G gradually shifted upfield, and H_{G1} 30 slightly moving downfield, suggesting that the G deeply threaded into the cavity of the DMP5. Subsequently, variable concentration ^{1}H NMR spectroscopy of **PF5** in $CDCl_3$ was carried out (Fig. 1). It was found that the aggregates formed by self–inclusion were very stable in $CDCl_3$ solution (5 mL). As the 35 concentration increased, the proton resonances did not exhibit obvious changes even at a high concentration of 50 mM, suggesting that **PF5** did not form intermolecular complexes in $CDCl_3$, but as the concentration increased, the subtle signals of protons H_a shifted downfield. Furthermore, all the signals such as 40 the aromatic protons H_{b-f} became broad and the alkyl chain

protons H_j appear peak splitting, which indicated that the self–inclusion function of **PF5** was very weak. This is similar to the previous report by Wang's group.[12]
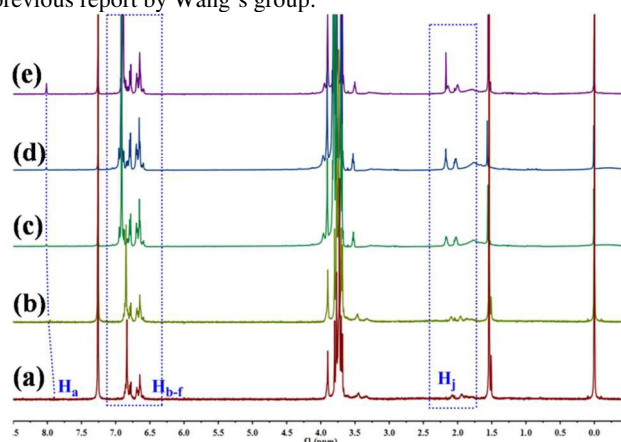
45 **Fig. 1** ^{1}H NMR spectra (600 MHz, $CDCl_3$, 298 K) of **PF5** at various concentrations in $CDCl_3$: (a) 0.5 mM, (b) 1.0 mM, (c) 5 mM, (d) 20 mM, (e) 50 mM.

Furthermore, the correlation of the protons were further validated by a NOESY NMR spectrum of **PF5**, the aromatic 50 protons H_{b-c} have strong correlations with methyl protons (H_h) and methylene protons (H_g) on the pillar as well as alkyl chain protons (H_i), indicating that the monomers self–organization into strong fluorescence aggregates driven by the self–assembled between the pillar[5]arene units and benzothiazole 55 units (Fig. S10). After adding iron, the cavity of pillar[5]arene units was occupied by Fe^{3+}, which with oxygen atoms of pillar[5]arene units undergoing complexation, making benzothiazole units free from the cavity of pillar[5]arene units. The self–inclusion of **PF5** was collapsed, so that fluorescence 60 quenching. Further added F^-, which combined the Fe^{3+}, the **PF5** was self re–inclusion, bring about fluorescence recovery (Scheme 2). Therefore, it can be achieved assembly and application in sequential fluorescent sensing for Fe^{3+} and F^-.
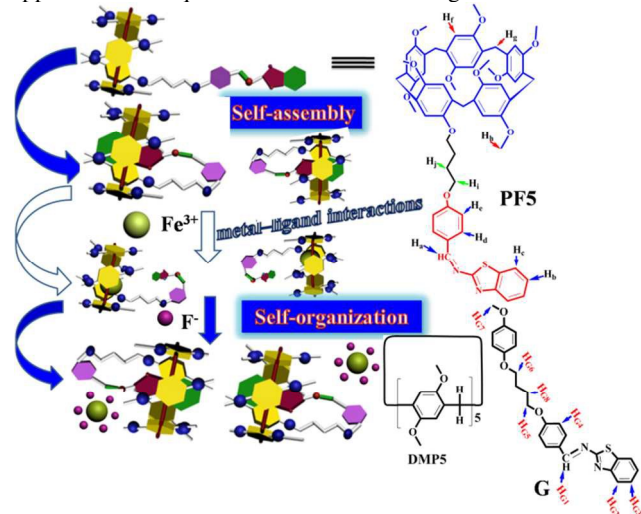
65 **Scheme 2.** Cartoon representation of the self–assembly process of monomer **PF5** and the production of supramolecular polymer fluorescence, metal–ligand interactions cause fluorescence quenching and the fluorine ions complexed fluorescence recovery.

To evaluate the binding ability of compound **PF5** toward Fe^{3+} ions, we carried out UV–vis and fluorescence experiments in DMSO/H_2O (8:2, v/v) by adding divisible of Fe^{3+} as its perchlorate salt. The absorption spectrum of compound **PF5** (1.0 mM) exhibited a maximum absorption band at 360 nm. However, an obvious intensity increase took place upon treatment with 10 equiv. of Fe^{3+} (Fig. S11). Conversely, The fluorescence emission band of compound **PF5** (1.0 mM) in the 380–540 nm range showed an obvious decrease when increase took place upon treatment with 10 equiv. of Fe^{3+} (Fig. S12). These phenomena confirmed the binding behaviour of Fe^{3+} by **PF5**. In order to investigate the Fe^{3+} recognition abilities of the sensor **PF5** in DMSO/H_2O (8:2, v/v) solution, a series of host−guest recognition experiments were carried out. The recognition profiles of the sensor **PF5** toward various cations (including Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+}, Mg^{2+}, Fe^{2+} and Al^{3+}) were primarily investigated using fluorescence spectroscopy. In the fluorescence spectrum, the maximum emission of **PF5** appeared at 432 nm in DMSO/H_2O (8:2, v/v) while excited at λ_{ex} = 360 nm. When 10.0 equivalents of various anions was added to the solution of sensor **PF5**, the fluorescence emission band in the 380–540 nm range only Fe^{3+} showed one of the most obvious decrease. And when sensor **PF5** was treated with selected cations, such as Hg^{2+}, Fe^{2+}, Ag^+ (10 equiv.) in DMSO/H_2O (8:2, v/v) showed little change, which singularity not be affected to identifying Fe^{3+} (Fig. 2). Therefore, in DMSO/H_2O (8:2, v/v), **PF5** showed specific fluorescence selectivity to Fe^{3+}. Furthermore, sensor **PF5** could be considered as a good ON–OFF Fe^{3+} fluorescent switch.
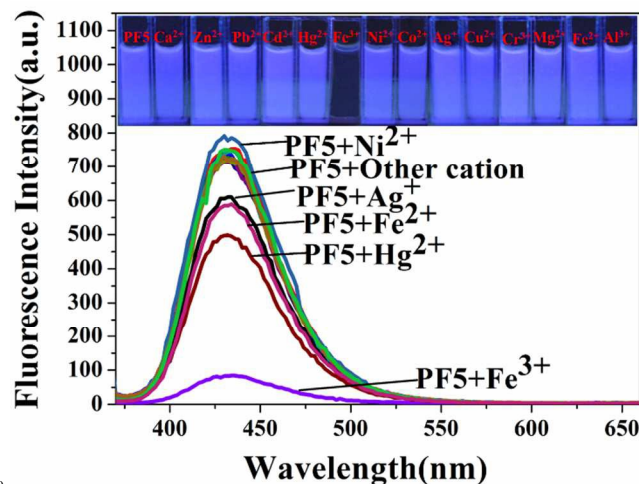

Fig. 2 Fluorescence spectra responses of **PF5** (1.0 mM) in DMSO/H_2O (8:2, v/v) upon addition of 10.0 equiv. of Fe^{3+}, Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+}, Mg^{2+}, Fe^{2+} and Al^{3+} ions (λ_{ex} = 360 nm). Inset: Photograph of **PF5** (1.0 mM) upon adding 10.0 equiv. of various ions, which was observed under a UV–lamp (365 nm).

To further investigate the interaction between sensor **PF5** and Fe^{3+}, fluorescence spectrum variation of sensor **PF5** was monitored during titration with different concentrations of Fe^{3+} (Fig. 3). It turned out that, in DMSO/H_2O (8:2, v/v) solution of **PF5**, with an increasing amount of Fe^{3+}, the fluorescence emission bands at 432nm decreased by an extent of ∼88.4%. The fluorescent titration curve of the **PF5** toward

the Fe^{3+} offers a good linear correlation at the concentration range 0–40.0 equivalents, from which the detection limit for Fe^{3+} is estimated to be 9.0×10^{-7} M (Fig. S13). And the stability constant K_a between **PF5** and Fe^{3+} is $1.02 \times 10^6 M^{-1}$.
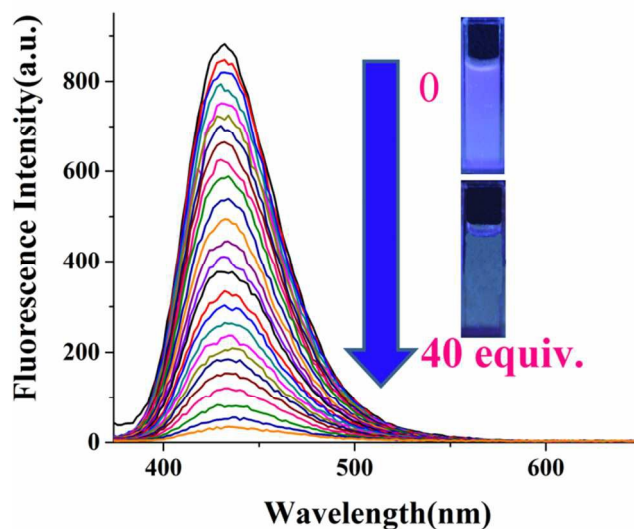

Fig. 3 Fluorescence spectra of **PF5** (0.4 μM) in the presence of different concentrations of Fe^{3+} in DMSO/H_2O (8:2, v/v) (excitation wavelength = 360 nm). Inset: Photograph of **PF5** (1.0 mM) upon adding 10.0 equiv. of Fe^{3+}, which was observed under a UV–lamp (365 nm).

The selectivity of **PF5** to Fe^{3+} was also examined over a wide range of pH values (Fig. S14). The detection of Fe^{3+} can work well in the pH range of 1.0–14.0 in DMSO/H_2O (8:2, v/v). In addition, the changes in the fluorescence intensity depending on the reaction time were recorded from 0 to 40 seconds, for a 1:10 mixture of **PF5** and $Fe(ClO_4)_3$ in DMSO/H_2O (8:2, v/v) at room temperature (Fig. 4). It clearly shows that the reaction completed within 30s after addition of Fe^{3+}.
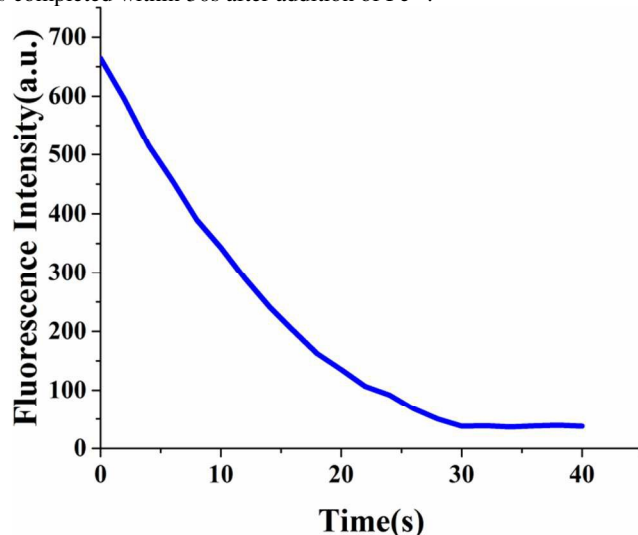

Fig. 4 Time–dependent of **PF5** (1.0×10^{-3} M) upon addition of Fe^{3+} (10.0×10^{-3} M) in DMSO/H_2O (8:2, v/v) with a plot of fluorescence intensity that is estimated as the peak height at 432 nm.

To explore the utility of sensor **PF5** as an ion–selective chemosensor for Fe^{3+}, competitive experiments were carried out in the presence of 10 equiv. of Fe^{3+} and 10 equiv. of various other

ions (Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+} Mg^{2+}, Fe^{2+} and Al^{3+}) in DMSO/H_2O (8:2, v/v). The results of these studies have revealed that these competing ions exerted no or little influence on the fluorescence emission spectra of sensor
5 **PF5** with Fe^{3+}, which further indicated that **PF5** has specific selectivity to Fe^{3+} (Fig. 5). To further verify the resistance to interference of **PF5** with Fe^{3+}, we have to perform metal ion competitive experiments by applying higher concentrations of competitive metal ions compare to the analyze, competitive
10 experiments were carried out in the presence of 20 equiv. of Fe^{3+} and 20 equiv. of various other ions (Hg^{2+}, Ag^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+}, Co^{2+}, Cr^{3+}, Mg^{2+}, Fe^{2+} and Al^{3+}) in DMSO/H_2O (8:2, v/v). The results also showed that that these competing ions exhibited no or little influence on the fluorescence emission
15 spectra of sensor **PF5** with Fe^{3+} (Fig. S15). Additionally, the fluorescence of Job's plot indicates that **PF5** and Fe^{3+} were formed a 1 : 1 complex (Fig. S16).
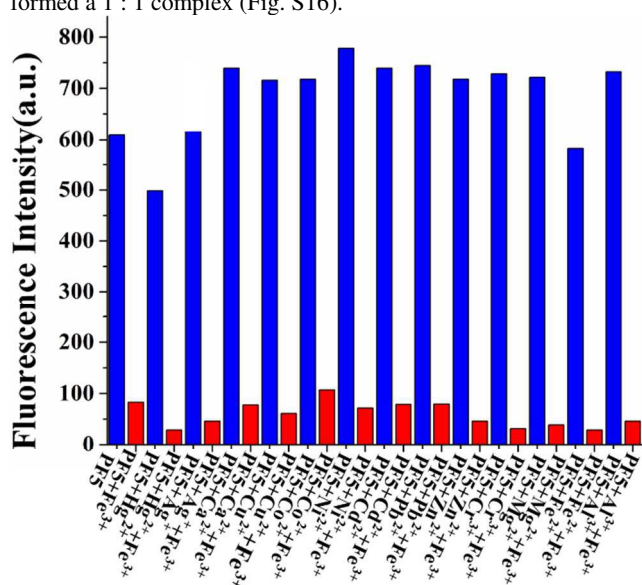

Fig. 5 Fluorescence intensities of **PF5** (1.0 mM) in the presence of
20 10.0 equiv. of various ions containing 10.0 equiv. of Fe^{3+} in DMSO/H_2O (8:2, v/v) (λ_{ex} = 360 nm).

Since the in situ generated **PF5**–Fe^{3+} complex exhibited almost complete fluorescence quenching and F^- is well–known to bind strongly to Fe^{3+} ions, we wonder if we can
25 exploit this ensemble system as a turn–on fluorescent sensor for F^- anions which is known to play important roles in a wide range of chemical and biological processes. Thus, the **PF5**–Fe^{3+} complex prepared by mixing an equal amount of **PF5** and $Fe(ClO_4)_3$ (10.0 mM) in the same mixed aqueous solution,
30 was treated separately with 1.5 equiv. of different anions (F^-, Cl^-, Br^-, I^-, AcO^-, NO_3^-, HSO_4^-, ClO_4^-, CN^- and SCN^-). When a fluoride ion is added to the **PF5**–Fe^{3+} system, the fluorescence intensity is completely regenerated (Fig. 6), as also indicated visually by the fluorescent color change (Fig. 6,
35 inset). However, a series of host–guest recognition experiments were carried out, we found that other anions (Cl^-, Br^-, I^-, AcO^-, NO_3^-, HSO_4^-, ClO_4^-, CN^- and SCN^-) show very little response (Fig. S17). The observed fluorescence and color regeneration can be ascribed to the snatching of Fe^{3+} from its

40 chelated complexes by F^-, resulting in the formation of more stable species $[FeF_6]^{3-}$ and the release of free ligand **PF5**, **PF5** was re–assembled into annulus fluorescent polymer.
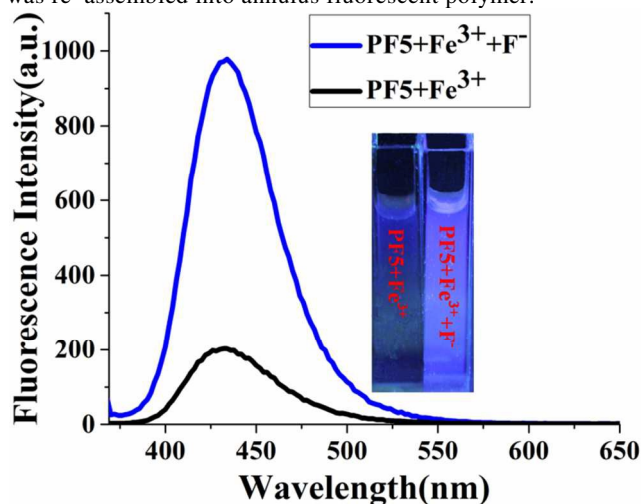

Fig. 6 Fluorescence emission spectra of **PF5**–Fe^{3+} (10 mM) in the
45 presence of 1.5 equiv. F^- in a mixed aqueous medium (DMSO/H_2O, 8:2, v/v); (λ_{ex} = 360 nm). Inset: Photograph of **PF5**–Fe^{3+} (10 mM) upon adding 1.5 equiv. F^-, which was observed under a UV–lamp (365 nm).

The selectivity of **PF5**–Fe^{3+} ensemble as a fluorescent sensor for F^-, It was also examined over a wide range of pH
50 values as shown in Fig. 7. The detection of F^- can work well in the pH range of 1.0–12.0 in DMSO/H_2O (8:2, v/v).
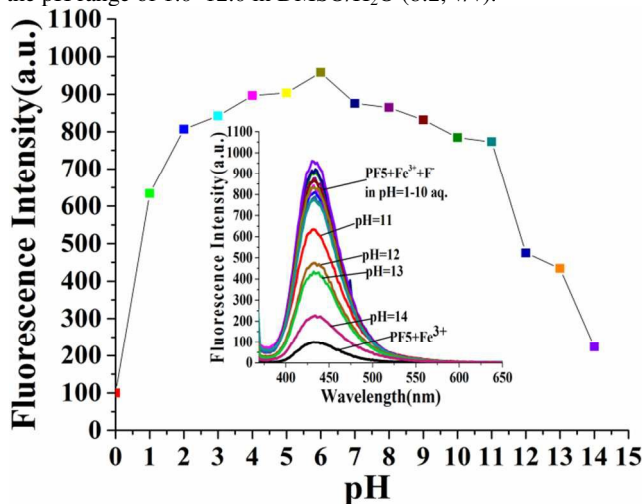

Fig. 7 Influence of pH on the fluorescence of **PF5**–Fe^{3+} complex (10 mM) with fluoride ion (1.5 equiv.) in DMSO/H_2O (v/v = 8:2). Inset: pH
55 fluorescence of a full scan.

To further investigate the interaction between sensor **PF5**–Fe^{3+} and F^-, fluorescence spectrum variation of sensor **PF5**–Fe^{3+} was monitored during titration with different concentrations of F^- (Fig. 8). The fluorescent titration curve of the **PF5**–Fe^{3+} complex
60 toward the fluoride ion offers a good linear correlation at the concentration range 0–1.5 equivalents, from which the detection limit for fluoride is estimated to be 2.59×10^{-8} M (Fig. S18). This value is much lower than the limit concentration level (4.00 mg L^{-1}) in drinking water set by USEPA.[13]
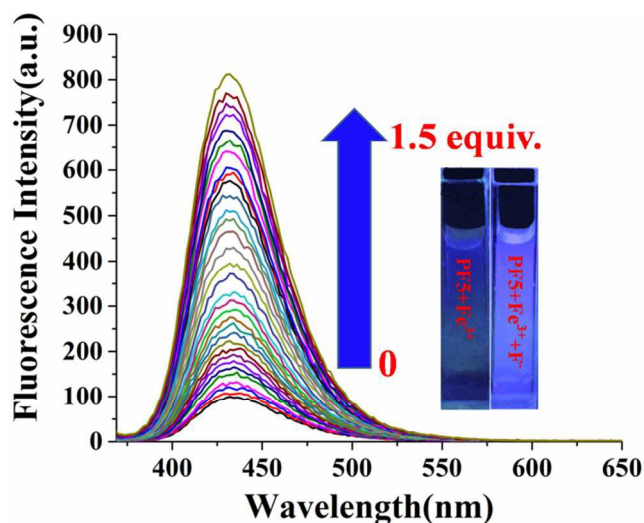
Fig. 8 Fluorescence titration of the **PF5**–Fe^{3+} complex (10 mM) with fluoride ion in a mixed aqueous medium (DMSO/H_2O (8:2, v/v); λ_{ex} = 360 nm). Inset: Photograph of **PF5**–Fe^{3+} (10 mM) upon adding 1.5 equiv. of F^-, which was observed under a UV–lamp (365 nm).

Control experiments of **PF5**–Fe^{3+} even in the presence of 1.5 equiv. of each of the anions indicated the absence of interaction between **PF5**–Fe^{3+} and anions in same solvent system. Competition experiments were conducted by adding fluoride (1.5 equiv.) to the solution of **PF5**–Fe^{3+} in the presence of 2.0 equiv. of other anions (Fig. 9). The fluorescence emission spectra display nearly an identical pattern to that with F^- alone, suggesting that all of the tested anions do not interfere in the sensing of F^-. In addition, the fluorescent intensity could be turned off and on repeatedly with the alternate addition of Fe^{3+} and F^- ions at least in six cycles (Fig. S19). All the above results indicate that the **PF5**–Fe^{3+} ensemble could serve as an outstanding sensitive and selective fluorescent OFF–ON sensor for F^-.
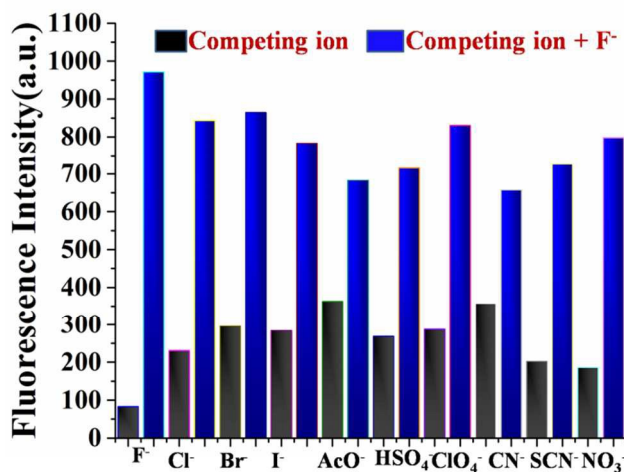

Fig. 9 Fluorescence intensity changes of **PF5**–Fe^{3+} ensemble (10 mM) in the presence of other anions (1.5 equiv.) followed by addition of F^- (1.5 equiv.) in a mixed aqueous medium (DMSO/H_2O (8:2, v/v), λ_{ex} = 360 nm).

To further investigate the practical application of chemosensor **PF5**, test strips were fabricated by immersing filter papers into DMSO/H_2O (v/v = 8:2) solution of **PF5** (2×10^{-3} M) and then drying them in air. The test strips containing **PF5** were utilized to sequential sense Fe^{3+} and F^-. As shown in Fig. 10, when first added Fe^{3+} on the test strips, an obvious color change and subsequently joined F^- the color of test strips once again changes which served as convenient and efficient sequential Fe^{3+} and F^- test kits.
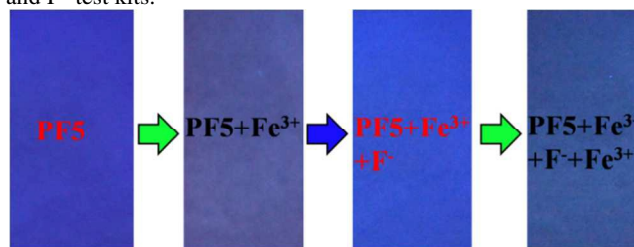

Fig. 10 Photographs of **PF5** on test strips only **PF5** and alternately added Fe^{3+} and F^-.

We also investigated the practical utilities of the probe in daily life sample, we have chosen to detect Fe^{3+} in tap water and F^- in toothpastes to implement the following experiment. Fluorescence emission spectra of **PF5** (1.0mM in 5 mL DMSO) is just like 1 line shown in Fig. 11. Followed: (a) upon titration of concentrated tap water (1.0 mL) to get 2 line; (b) soluble components of Colgate toothpaste sample (10 equiv.) added to solution of (2) to obtain 3 line; (c) soluble components of Colgate toothpaste sample (10 equiv.) added to solution of (3) to obtain 4 line; (d) soluble components of Colgate toothpaste sample (10 equiv.) added to solution of (4) to obtain 5 line. Significant color change can be directly seen the sensor **PF5** is also could sequential detect Fe^{3+} in tap water and F^- in real samples like toothpastes (Fig. 11), confirming that **PF5** is a promising Fe^{3+} and F^- probe for practical applications. Therefore, this novel functionalized pillar[5]arene **PF5** can be used as an original fluorescent sensor for sequential detecting Fe^{3+} and F^- ions, which showed excellent stability, reversibility, as well as repeatability. (Fig. S20).
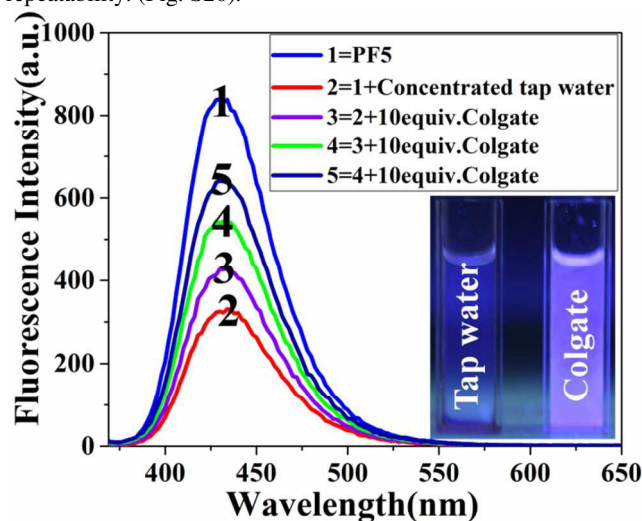

Fig. 11 Fluorescence emission spectra of **PF5** (1.0mM in DMSO) sequential detect Fe^{3+} in tap water and F^- in real samples like toothpastes. Insets: photographs illustrating of optical changes upon addition of analyte. Excitation wavelength is 360 nm.

Conclusions

In summary, a novel functionalized pillar[5]arene was synthesized, which can be self–inclusion produce a strong blue fluorescence. Followed by **PF5** could act as a chemosensor for ferric (□) and fluoride ions through a competitive complexation reaction. For the first time, the recognition ability of specifically binding to Fe^{3+} from among 14 metal ions arises from the formation of a weak fluorescent **PF5**–Fe^{3+}. The resulting **PF5**–Fe^{3+} ensemble can also act as a turn–on fluorescent sensor for fluoride ions over other anions in the same media without interference. Moreover, test strips based on the sensor were fabricated, which served as convenient and efficient sequential Fe^{3+} and F^- test kits, it could be further used for practical applications to sequential detecting Fe^{3+} in tap water and F^- in real samples like toothpastes. The work shown here not only presents the fact of using pillararenes for selective fluorescent recognition towards both ferric ions (□) and fluoride in a sequential fashion, but more importantly, it implicates the potential of pillararene macrocycles for the design of fluorescent sensors towards other metal cations with tailored properties.

Notes and references

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A Novel Functionalized Pillar[5]arene: Synthesis, Assembly and Application in Sequential Fluorescent Sensing for Fe^{3+} and F^- in Aqueous Media

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