A Novel Thiophene Functionalized Silicon-cored compounds:
Aggregation-induced Emission Enhancement and Aqueous Fluorogenic Fe³⁺
Probes in Bovine Serum Albumin

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Abstract

“silicon-cored” compounds are well known for their high value glass transition temperature, high therm stability and excellent optical properties, but the excellent optical properties was not used for fluorogenic probes especially for Fe^{3+} probe. In this paper, a novel Fe^{3+} probe based on thiophene functionalized silane, namely, bis[3,4-diphenyl-2,5-di(2-thienyl)phenyl]methylphenylsilane (MPS) was designed and synthesized. MPS exhibits aggregation-induced emission enhancement (AIEE) property in water/ tetrahydrofuran mixtures because of restricted intramolecular rotation. The abnormal optical properties enable MPS to detect Fe^{3+} in aqueous-based solutions. The binding behavior of MPS aggregates to Fe^{3+} and other transition metal ions were studied through UV-vis, fluorescence spectroscopy, and scanning electron microscopy. Exceptional fluorescence quenching of MPS occurred during Fe^{3+} binding. The calculated detection limit was at ppb level, and the complex ratio of MPS to Fe^{3+} is approximately 1:1. MPS has both exemplary activity and high selectivity toward Fe^{3+} even in the presence of other metal ions. The test conditions were also expanded from water to bovine serum albumin and solid films. This study was an advancement for the application of “silicon-cored” compounds and provides guidance for using simple, low-cost, and high-selectivity Fe^{3+} probes in aqueous solutions and in clinical applications.

Key Words

AIEE, Fluorogenic probe, Silicon-cored effect, Fe^{3+}

1. Introduction

As one of the most essential and abundant transition metal trace elements in the human body, iron is indispensable in metabolism [1-3]. Iron carries oxygen to all tissues in the form of hemoglobin and helps transport electrons as cytochromes. The total content of iron in well-nourished individuals is approximately 4 g [4]. Both deficiency and overloading lead to biological disorders, such as anemia, diseases of the pancreas kidney, and breathing problems [1, 3, 5]; recent research suggests that iron deficiency is related to Parkinson's and Alzheimer's diseases [6-8].

With the close relationship between human health and iron especially its trivalent form (Fe^{3+}), exploring reliable detection methods for iron has become increasingly important. Among the available detection methods, chemosensors are predominately attractive in terms of sensitivity, selectivity, response time, and local observation [9-11]. Thus, efficient chemosensors for Fe^{3+} are in demand, especially fluorescence probes for Fe^{3+} detection in aqueous solutions [12-19]. Moreover, conventional organic fluorescence probes enjoy high fluorescence in dilute solutions. However, this type of fluorescence is quenched in the condensed phase because of the “aggregation-caused quenching” effect. These fluorescence probes work effectively in organic-based or co-organic-based solvents, and lack sufficient selectivity to detect Fe^{3+} ions [20]. The organic-based solvents limit the application environment of biological systems. Significant demand exists for new efficient Fe^{3+} fluorescence probes in

aqueous solutions. Luminogens with aggregates that emit more efficiently than those in solutions have attracted considerable attention.

In 2001, Tang et al. first reported that silole molecules exhibited stronger fluorescence in aggregate than in dispersed state [21]. They coined the novel phenomenon called aggregation-induced emission (AIE). Since then, the synthesis and exploitation of AIE or AIEE (aggregation-induced emission enhancement) luminogens were included in the field, and various types of AIE or AIEE luminogens were synthesized, such as tetraphenylethene [22-24], multiple benzene [24], and heterocyclic derivatives [25]; similarly, mechanisms that include the restriction of intramolecular rotation (RIR), special excimer formation, relatively loose molecular packing, formation of J-aggregates, inhibition of intramolecular photochemical or photophysical process, and intramolecular coplanarization of AIE or AIEE phenomenon have been investigated. Additionally, barring a few scattered reports, the nanoparticles with AIE properties have not been used widely as fluorescent sensors for Fe^{3+} ion. The applications of AIE or AIEE luminogens should undergo continuous development.

Silicon-cored molecules are known for their high-value glass transition temperature, excellent thermal stability, efficient luminescence, and other attractive properties [26-30]. However, the excellent optical silicon-cored molecules can't be used as Fe^{3+} probes for lacking of activity groups and no paper has been report the silicon-cored fluorescence Fe^{3+} probes so far. Thus, we introduced thiophene to silicon-cored molecules, and synthesized thiophene functionalized silane (MPS), as shown in

Scheme 1. In our previous study, MPS exhibited response to explosives[31]. Moreover, the introduction of thiophene enabled silicon-cored molecules to detect Fe^{3+} ions. What's more, MPS could form nano-aggregates in aqueous solutions, and exhibited excellent AIEE properties on account of restricted intramolecular rotation (RIR)[31]. The excellent characteristics of AIEE endow MPS with properties to detect Fe^{3+} ions in aqueous solutions. The detection limit of MPS fluorescent probes for Fe^{3+} was 86.24 ppb (1.54 μM). The detection mechanism was attributed to static quenching. Multianalyte sensors have a promising prospect[32-34] and this work will inspire the development of "silicon-cored" based multianalyte sensors using modifiable thiophene and other lateral groups.

<Inserted Scheme 1>

2. Materials and Methods

All reagents and solvents were purchased from a commercial source and used without further purification, unless otherwise specified. Dichloromethane and tetrahydrofuran were obtained from Tianjin Fuyu Chemical Co. Ltd. Dichloromethane was used after fractionation. 2-Thiopheneacetic acid, dicyclohexylcarbodiimide, dimethylaminopyridine, and ethynyltrimethylsilane were purchased from Aladdin Industrial Company. Benzil was obtained from Sinopharm Chemical Reagent Company. Inorganic salts, including $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, were purchased from Guangfu Chemical Industry Research

Institute. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, PbCl_2 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, ZnCl_2 , and $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ were purchased from Aladdin Industrial Company.

UV/visible and fluorescence spectra were performed on TU-1901 and HITACHI-F-7000. Absorption and emission measurements were conducted on samples in $1\text{ cm} \times 1\text{ cm}$ quartz cuvettes. All detection experiments were conducted at room temperature ($\sim 25^\circ\text{C}$) unless otherwise specified. MPS was dissolved in distilled water and stirred 5 minutes to obtain the MPS aggregates. Different amounts of Fe^{3+} was added to the MPS aggregates and stirred 30 seconds to measure the fluorescence intensity. Compounds 2, 3, and MPS were synthesized based on the previous reports [31]. The detailed contents are presented in the Supporting Information.

3. Results and Discussion

3.1 AIEE properties of MPS

MPS exhibits perfect aggregation induced emission enhancement (AIEE) characteristic. As water is a poor solvent and THF is a good solvent for MPS, thus, the AIEE property of MPS was first experimented in water–THF mixtures. In detailed, MPS was dissolved in water–THF mixtures at 1×10^{-6} mol/L with different water content. When excited at 281 nm, slight fluorescence could be observed at around 390 nm as the water content is 10%, and the emission intensity increased with increasing water content (**Fig. 1a**). Ultimately, the final emission intensity (water content is 99%) is 3 times higher than the initial intensity (water content is 10%). The fluorescence quantum

yield of MPS in water was 44.6% with quinine sulfate as a standard, which is higher than the fluorescence quantum yield value of MPS in THF (15.2%). The fluorescent lifetime of MPS in water and THF were 0.707 ns and 0.620 ns respectively. **Fig. 1c** shows the absorption of MPS in water and THF. The maximum absorption of MPS in THF occurred at near 279 nm, which was due to the π - π^* transition. The absorption wavelength showed red-shifted and a shoulder band peak at around 300nm. The absorption cross section of MPS in THF and water was calculated by (Eq. (1)) to be $1.4 \times 10^{-16} \text{ cm}^2$ and $2.1 \times 10^{-16} \text{ cm}^2$.

$$\sigma = \frac{\varepsilon}{N_A} \ln^{10} \quad (1)$$

Where σ is absorption cross section, ε is molar absorption coefficient, N_A is avogadro's number. Moreover, when MPS was dissolved in THF at different concentrations (1×10^{-6} , 1×10^{-5} , 1×10^{-4} , 1×10^{-3} and 1×10^{-2} mol/L), fluorescence intensity was enhanced as concentration increased. The emission wavelength bathochromic shifted from 389nm to 428nm (**Fig. 1b**). MPS has desirable AIEE properties and the mechanism of AIEE is restricted intramolecular rotation of peripheral groups (phenyl, thienyl and $-\text{SiMe}_3$ groups) [31, 35]. Peripheral groups (benzene, thiophene and $-\text{SiMe}_3$) linked at benzene core and Si atom with single bond. These peripheral groups could rotate freedom. When MPS aggregate with each other, the rotation of peripheral groups are restricted because of space limitation. Molecules at excited states returned to ground state through radiation other than non-radiation channels.

This process caused emission enhancement. The emission enhancement and wavelength red-shifted were attributed to the “Silicon effect”, which was caused by the disorderly arrangement (prevent π - π stacking) and the weak intramolecular interactions and proposed in our previous reports [36-37]. The excellent AIEE fluorescence property makes MPS a good candidate for fluorescent probes. Since various pH environments have identical effect in practical applications, the effect of pH on fluorescence intensity was tested. Slightly influence could be seen on fluorescence intensity when pH range from 2 to 13 (**Fig. S1** in ESI†). This result indicated that MPS possessed extremely high stability in different pH environments. The presence of thiophene moieties and the AIEE properties of MPS prompted the investigation of its response to various metal cation ions in aqueous solutions because sulfur-containing molecules and metal ions can be bound easily to form stable complexes [38-40].

<Inserted Figure 1>

3.2 Fluorescence response in detecting Fe^{3+}

To evaluate the sensing ability of MPS towards various metal ions, fluorescence and UV-vis experiments were conducted in $\text{H}_2\text{O}/\text{THF}$ mixture with 99% water content. The fluorescence spectra of MPS (1 μM) binding to Fe^{3+} in $\text{H}_2\text{O}/\text{THF}$ mixtures is shown in **Fig. 2a**. MPS probe emitted fluorescence at around 390 nm when excited at 281 nm. The addition of Fe^{3+} ions to the solution of MPS (H_2O -THF, 99:1, v/v) quenched fluorescence

emission immediately. Fluorescence intensity decreased with the concentration of Fe^{3+} ions increased in the system. The fluorescence of MPS was quenched to 91% of its initial intensity when 5 μmol Fe^{3+} ions were added to the system and the absorption cross section of MPS increased to $6.45 \times 10^{-16} \text{ cm}^2$ after the addition of Fe^{3+} . The quenching efficiency can be best studied by Stern–Volmer equation (Eq. (2)).

$$\frac{I_0}{I} = 1 + K_{sv} \times [C] \quad (2)$$

Where I_0 is the initial fluorescence intensity of MPS, I is the fluorescence intensity in the presence of Fe^{3+} . K_{sv} and C are the quenching constant and the concentration of Fe^{3+} . **Fig. 2b** shows the linear dependence (the linear correlation coefficient is 0.98) of the fluorescence intensity ratio (I_0/I) to Fe^{3+} concentration when Fe^{3+} ions at lower concentration. The Stern–Volmer quenching constant (K_{sv}) was obtained from Eq. (1) as $5.7 \times 10^4 \text{ M}^{-1}$. The plots swift curves upward as the amounts of ferric ions increase. The bend upward phenomenon shows MPS probe exhibits high efficiency for ferric detection and indicates the detection mechanism is not collisional deactivation [41]. The detection limit of Fe^{3+} ions has been obtained by calculating the signal-to-noise ratio using equation (Eq. (3)) and it was found to be 1.54 μM (86.24 ppb). MPS has reasonable detection limit for Fe^{3+} sensing in water, which was significantly lower than the maximum allowed limit (300ppb) by the U.S. Environmental Protection Agency (EPA).[42]

$$\text{LOD} = 3 \times \frac{s_d}{k} \quad (3)$$

Where LOD is detection limit, S_d is standard deviation of blank fluorescence intensity of MPS, k is the slope of the calibration curve.

<Inserted Figure 2>

3.3 Proposed mechanism

The possible fluorescence quenching mechanism can be interpreted by measuring the fluorescence spectra of MPS- Fe^{3+} system at different temperatures. As **Fig. S5** shows, the Stern-Volmer plots are nearly linear and the quenching constants decrease as the temperature increase, which phenomenon indicates the quenching is static quenching. In good solvent (THF), MPS exist as single molecule state. Due to the hydrophobic effect, monodispersed MPS could aggregate with each other to form nanoparticles in poor solvent (water), the aggregation behavior and nano-structure can be characterized via scanning electron microscopy (SEM) studies (**Fig. 3a**). We suspected the static quenching was probably attributed to the interaction of ferric ions with the MPS nanoparticles to form larger aggregates. The formation of this complex (larger aggregates) facilitates electron transfer from the LUMO of excited MPS to one of the “d” orbitals of the ferric ions. The electron is then transferred to the HOMO of another MPS. This double-electron exchange process restores the fluorophore to its ground state following a non-radiative process and results in emission quenching[43]. A plausible schematic diagram has been depicted in **Fig. 5b**. Larger aggregates formation was further proved

by SEM studies. Spherical nano-aggregates were observed of the MPS in the water solvent, the diameter of the aggregates were less than 100 nm (**Fig. 3a**). Larger aggregates with irregular shape could be observed in the presence of ferric ions (**Fig. 3b**). Furthermore, the energy dispersive X-ray detector (EDX) of aggregates of MPS binding to ferric ions was conducted, the EDX spectra inhibits the existence of sulfur and ferric in the bigger aggregates (**Fig. S7** in ESI†). Further, the lifetime values (Table 2) of MPS and MPS + Fe³⁺ in water were nearly same, indicating the static quenching mechanism[44].

<Inserted Figure 3>

<Inserted Table 2>

To determine the binding stoichiometry for MPS and Fe³⁺, the continuous variation method of analysis is employed. In the solvent of H₂O–THF (99:1, v/v), the concentrations of MPS and Fe³⁺ are change in order, but the total amount of the two analysis is kept constant at 10.0 μM. As shown in **Fig. 4**, fluorescence intensity decreased with the increase of Fe³⁺ concentration. A complex that contains MPS: Fe³⁺ at 5:5 has the weakest intensity, except for the MPS/Fe³⁺ complex with a ratio of 1:9 and 0:10, which two complexes have too little MPS luminescent materials to emit enough strong fluorescence. Thus, the corresponding binding ratio is 1:1 for MPS to Fe³⁺.

The possible Fe³⁺-MPS complex according to the 1:1 binding ratio is shown in **Fig. 5**, where one Fe³⁺ ion can coordinate with four thiophene groups from four MPS molecules to form a complex. Nano-aggregates combine with each

other by the connection of Fe^{3+} ion, then larger aggregates are formed.

<Inserted Figure 4>

<Inserted Figure 5>

3.4 Competitive experiments

In order to proven the high selectivity of MPS fluorogenic probe for Fe^{3+} , fluorescence studies with competitive ions (such as Fe^{2+} , Cu^{2+} , Hg^{2+} , Ag^+ , Zn^{2+} , Co^{2+} , Ni^{2+} , and Cr^{3+}) was also conducted and the experiment was performed under the same conditions with Fe^{3+} . Fluorescence intensity change of MPS caused by other metal ion was very different from the fluorescence change caused by Fe^{3+} (**Fig. 6, S2 and S3** in ESI†). Furthermore, competitive binding studies on MPS with Fe^{3+} (5 μmol) were also conducted in the presence of 5 μmol other metal cations in H_2O -THF (99:1, v/v) mixtures. Whether competitive metal ions were present or absent, no significant variation was observed in fluorescence intensity (**Fig. 6 and S3** in ESI†). The selectivity of Fe^{3+} can be evaluated by the selectivity coefficient ($K_{\text{Fe}^{3+}} = \frac{S_{\text{Fe}^{3+}}}{S_0} \times 100\%$), where $S_{\text{Fe}^{3+}}$ is the response of MPS to Fe^{3+} and S_0 is the response to any other cation. The orbital matching degree of MPS and metal ions determines the value of selectivity coefficient[45-46]. On binding to MPS, ferric ions has larger orbital matching degree with MPS than other metal ions. The selectivity coefficient of Fe^{3+} is 100, which was very larger than the selectivity coefficient of other metal ions (Table S1). Thus, compound MPS can recognize Fe^{3+} even in the presence of other cations. Upon addition of various metal cations (5 μmol)

in H₂O-THF (99:1), the UV-vis spectra of MPS (1 μmol) mixtures also indicate the high selectivity of MPS toward Fe³⁺ (**Fig. S4** in ESI†). The absorbance of ferric ions with MPS in a level-off tail suggests that ferric ions interact with the nano-aggregates of MPS to form larger aggregates [47-49], which leads to scattering [50].

Given that several metal probes are easily affected by the presence of counter anions, we performed the fluorescence titrations of MPS toward Fe³⁺ with different counter-ion salts. Ferric sulfate and ferric nitrate salts were chosen. The amount of ferric sulfate is half that of ferric nitrate and ferric chloride to ensure that the iron has the same content. As shown in **Fig. S6**, similar quenching efficiency was observed from the fluorescence emission spectra. Thus, we conclude that the Fe³⁺ sensor responses of MPS were not affected by different counter anions. As shown in Table 1, the results of MPS sensor for detecting Fe³⁺ are compared with that of other reported fluorescent sensors (Tz-1[51], Thiophene Schiff-base[43], Coumarin derivatives[52], DPTDA[53], Rotaxane-R1[54]), which suggests that MPS demonstrate higher selectivity and efficiency in water solutions.

<Inserted Figure 6>

<Inserted Table 1>

3.5 Applicability experiments

The biological applicability experiment of MPS probe toward ferric ions was performed by testing the fluorescence response of MPS with addition of the same amount of ferric ions in the presence of different concentrations of bovine

serum albumin (BSA). BSA was dissolved in water and buffered with HEPES. MPS (1 μM) and Fe^{3+} (10 μM) were added to a solvent mixture of H_2O -THF (99:1, v/v), the solvent was buffered with HEPES. When different amounts of BSA were added to the system, no change in fluorescence intensity was observed in the spectra (**Fig. 7**). This result would suggest that MPS can be used as fluoreogenic probe to detect Fe^{3+} ions in physiological conditions even in the presence of BSA.

The applicability of MPS chemosensor in real sample was evaluated for detection of Fe^{3+} in tap water (**Fig. S8**). A corrected linear relationship ($R^2=0.9998$) was obtained and the Fe^{3+} concentration in tap water was 2.02 μM , which satisfying the practical Fe^{3+} concentration (2.3 μM) obtained by atomic absorption spectrophotometry (AAS) method[55]. The results indicate MPS probe is likely to be capable of the practical application in biological and environmental for the detection of Fe^{3+} .

<Inserted Figure 7>

3.6 Solid matrix experiments

Fe^{3+} detection at solid films was also conducted (**Fig. 8**). MPS was dissolved in tetrahydrofuran at 10^{-3} M, then the MPS solutions was spread out on the silica gel plate. When the plate was dried, a cotton swab dipped with Fe^{3+} (10^{-3} M) was used to write the letters “SDU”. The plate was then immediately placed under the UV lamp. Fluorescence was obviously quenched at a position when

Fe³⁺ ions were present. The result indicated that MPS can also be used as Fe³⁺ probe when it was fabricated in solid matrices.

<Inserted Figure 8>

4. Conclusions

In this work, a novel Fe³⁺ probe based on thiophene functionalized silane, namely, bis[3,4-diphenyl-2,5-di(2-thienyl)phenyl]methylphenylsilane (MPS), is prepared. The excellent properties of AIEE enable MPS to detect Fe³⁺ in aqueous-based solutions. Exceptional fluorescence quenching of MPS occurred during Fe³⁺ binding, and 5 μmol of Fe³⁺ caused 91% quenching in fluorescence intensity. The calculated detection limit was 1.54 μM, and the detection mechanism was static quenching mechanism. The corresponding binding ratio of MPS to Fe³⁺ was 1:1. MPS exhibits both exemplary activity and high selectivity toward Fe³⁺ even in the presence of other metal ions. The test conditions can expand from water to BSA and solid films. This study will broaden the research area of silicon-cored compounds and provide guidance for using Fe³⁺ probes with high selectivity in aqueous solutions or in clinical applications.

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Figure captions

Fig.1. Fluorescence emission spectra of MPS (a) in water/THF mixtures with different water content (MPS at 1×10^{-6} mol/L; excitation wavelength is 281nm; PMT voltage is 700V), (b) in tetrahydrofuran at different and (c) absorption spectra of MPS in water/THF mixtures with water at 0 and 99%.

Fig.2. (a) Change in fluorescence of MPS (1 μ M) upon addition of different amounts of Fe^{3+} ; **(b)** Stern–Volmer plot in response to Fe^{3+} ions. The inset figure shows the Stern–Volmer plot obtained at a lower concentration of Fe^{3+} (excitation wavelength is 281nm; PMT voltage is 700V).

Fig.3. Scanning electron microscopy images of MPS (a) nano-aggregates in the solvent mixture of H_2O –THF (99:1, v/v), and (b) aggregates of MPS after adding ferric chloride (5 μ M).

Fig.4. Fig. 4 Fluorescence spectra of stoichiometry calculations in the binding process of MPS/ Fe^{3+} at different concentration ratios (excitation wavelength is 281nm; PMT voltage is 700V).

Fig.5. (a) Possible stoichiometry of Fe^{3+} -MPS complex. (b) Structure of Fe^{3+} -MPS complex. (c) Proposed mechanism for detection of MPS upon binding with Fe^{3+} .

Fig.6. Fluorescence response of MPS upon addition of competitive cations (black bars) and MPS upon addition of competitive cations and ferric ions (red bars) in H_2O -THF (99:1, v/v) mixtures.

Fig.7. (a) Fluorescence spectra and (b) Bars represent competitive selectivity of MPS toward Fe^{3+} ions in the presence of different concentrations of BS (1 = MPS + 10 μ M

$\text{Fe}^{3+} + 0 \mu\text{L BSA}$, 2 = MPS + $10\mu\text{M Fe}^{3+} + 25 \mu\text{L BSA}$, 3 = MPS + $10\mu\text{M Fe}^{3+} + 50 \mu\text{L BSA}$, 4 = MPS + $10\mu\text{M Fe}^{3+} + 100 \mu\text{L BSA}$, 5 = MPS + $10\mu\text{M Fe}^{3+} + 200 \mu\text{L BSA}$), buffered with HEPES, $\text{PH} \approx 7.0$ (excitation wavelength is 281nm; PMT voltage is 700V).

Fig.8. Preparation and Photos taken under UV lamp at 365 nm of solid film experiment.

Scheme 1. Synthesis of MPS

Fig.1.

Fig.2.

Fig.3.

Fig.4.

Fig.5.

Fig.6.

Fig.7.

Fig.8.

Scheme 1.

Table 1. Comparison of different fluorescent sensors for Fe^{3+} detection

Table 2. Time-resolved fluorescence decay constant (τ) values of MPS in THF, water and $\text{MPS} + \text{Fe}^{3+}$ in water.

Table 1.

Probe	Linear range	R ²	Solvents	pH	Interferents	DOL (μM)	Ref.
Tz-1	0-100μM	0.998	DMSO:H ₂ O =7:3	/	No	1.37	[32]
Thiophene Schiff-base	0-200μM	0.9947	Ethanol	/	Ag ⁺ , Cu ²⁺	0.0037	[33]
Coumarin derivatives	0-300μM	/	Water	/	Cu ²⁺	51.7, 48.7	[34]
DPTDA	0-200μM	0.9491	Acetonitrile	/	Pb ²⁺	0.38	[35]
Rotaxane-R1	0-16μM	0.946	DMSO	/	No	/	[36]
MPS	0-100μM	0.9998	Water	No	No	1.54	This Work

Table 2.

Sample	τ_1 (ns)	τ_1 %	τ_2 (ns)	τ_2 %	τ (ns)	χ^2
MPS in THF	0.1895	88.44 %	3.9150	11.56 %	0.620	0.993
MPS in water	0.3602	89.98 %	3.8241	10.02 %	0.707	0.953
MPS + Fe ³⁺ in water	0.3584	90.06 %	3.8340	9.94 %	0.704	0.962

Graphical abstract

A novel thiophene functionalized “silicon-cored” material has been developed for detecting ferric ions in multiple context.