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Fluorescence 'on-off-on' chemosensor for sequential recognition of Fe³⁺ and Hg²⁺ in water based on tetraphenylethylene motif

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1. Introduction

Iron(III) ions play an important role in the biological systems, such as cellular metabolisms, and a catalytic site for proteins and enzymes.¹ Meanwhile, mercury ions can be extremely dangerous environmental pollutants because they can bioaccumulate throughout the food chain and are chemically toxic to liver, kidney, and brain function when they are ingested or inhaled by human beings.² Therefore, a lot of excellent sensors have been developed for recognition of Fe^{3+ 3} and Hg²⁺ ions,⁴ respectively. However, a chemosensor for sequential recognition of Fe³⁺ and Hg²⁺ ions in water, to the best of our knowledge, has not been reported.

Recently, many attractive probes for the detection of mercury ions based on the specific mercury-promoted desulfurization reaction have been reported.⁵ More recently, although another series of new sensors based on the mercury-promoted deprotection of the dithioacetal reaction has been explored, those probes for recognition of Hg²⁺ was conducted in organic solutions.⁶ Based upon the Hg²⁺-promoted deprotection reaction of the dithioacetal, we have recently reported a 1,8-naphthalimide-based water-soluble 'turn on' chemosensor for recognition of Hg²⁺ ion over other heavy and transition metal (HTM) ions with high selectivity and sensitivity.⁷ On the other hand, tetraphenylethylene (TPE) motif is usually used as the fluorophore to prepare chemosensors for recognition of different metal cations.⁸ Encouraged by the above-mentioned interesting results, we herein designed a water-soluble chemosensor

ABSTRACT

A novel selective and sensitive fluorescence 'on-off-on' probe based on tetraphenylethylene (TPE) motif for sequential recognition of Fe^{3+} and Hg^{2+} in water has been developed. Especially the complex **6**- Fe^{3+} could behave as a 'turn on' fluorescent sensor over a wide-range pH value for detection of Hg²⁺. The selectivity of this complex for Hg²⁺ over other heavy and transition metal ions is excellent, and its sensitivity for Hg²⁺ is at 2 ppb in water.

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6 (Fig. 1) by incorporating TPE fragment with dithioacetals, which contained four carboxylic groups. Four carboxylic groups would make **6** selectively bind with a metal ion and soluble in aqueous solution, and dithioacetals would let 6 selectively and sequentially recognize Hg^{2+} over other HTM ions. To our delight, the probe **6** exhibited selective and sensitive fluorescence 'on-off-on' for sequential recognition of Fe³⁺ and Hg²⁺ ions in water.

2. Results and discussion

Sensor 6 was efficiently synthesized as shown in Scheme 1. The chemical structures of 2-6 were well characterized by IR spectrometry, ¹H and ¹³C NMR spectroscopy, and high-resolution mass spectrometry (HRMS).

The fluorescent intensity of 6 was almost a constant value when pH value was between 3.65 and 5.71 in water. The fluorscence quantum yield of 6 was 0.06993. First, Figure 2 showed the fluorescent intensity ratio (I_0/I) of **6** in water after adding Ag⁺, Zn²⁺, Fe³⁺, Cd²⁺, Pb²⁺, Ca²⁺, Cu²⁺, Mg²⁺, and Ba²⁺ ions, respectively. The fluorescent behavior of **6** was strong. Interestingly, once Fe³⁺ was added to the water solution of 6, an decreased 8.71-fold of the fluorescent intensity was observed at 465 nm. Because four carboxylic groups of **6** was able to bind with Fe³⁺, accompanied with transforming a high fluorescence (cvan) to a weak fluorescence (colorless, inset of Fig. 2). The fluorscence quantum yield of complex 6-Fe³⁺ was 0.003046. The time of **6** $(1 \times 10^{-5} \text{ M})$ towards Fe^{3+} (1 equiv) in water for the reaction time curve reaching a stable plain was needed for 3 min after Fe³⁺ addition (Fig. S5, see Supplementary data).





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Figure 1. Chemical structure of 6.



Scheme 1. Synthesis of 6.

To obtain more insight into the fluorescent properties, the titration reaction curve of **6** toward Fe³⁺ was investigated (Fig. 3). The fluorescent intensity of **6** decreased in response to the increases in the concentration of the added Fe³⁺ in water, and the titration reaction curve showed a steady increase until a plain was reached when 1 equiv of Fe³⁺ ion was added. Job's plots of fluorescence obtained for **6**-Fe³⁺ system in water obviously demonstrated a formation of 1:1 stoichiometry (Fig. 4). Meanwhile, the dissociation constant (Kd) was calculated to be 1.41×10^{-4} M according to the fluorescence titration profile (Fig. S12). Then fluorescent intensity ratio (I/I_0) of complex **6**-Fe³⁺ in water after adding different metal ions such as Ag⁺, Zn²⁺, Fe³⁺, Cd²⁺, Pb²⁺, Ca²⁺, Cu²⁺, Mg²⁺, Hg²⁺, and Ba²⁺ was examined in Figure 5. The fluorescent intensity of complex **6**-Fe³⁺ was almost a constant minimal value when pH >4.0 in water (Fig. S13). After adding Hg²⁺ to the water solution of complex **6**-Fe³⁺, an increased 5.86-fold of the fluorescent intensity was observed at 474 nm. Because complex **6**-Fe³⁺ was deprotected the dithioacetal by Hg²⁺ to give aldehyde **4**, accompanied with transforming a weak fluorescence (colorless, inset of Fig. 5) to a high fluorescence (cyan). The fluorscence quan-



Figure 2. Fluorescent intensity ratio (I_0/I) of **6** (1×10^{-5} M) in distilled water (pH 5.69) at 298 K upon addition of 10.0 equiv of different metal ions. Inset: photograph of **6** after adding different metal ions. **A: 6** (1.0×10^{-5} M); **B–K: 6**+Fe³⁺, Ca²⁺, Cd²⁺, Mg²⁺, Cu²⁺, Zn²⁺, Ba²⁺, Ag⁺, and Pb²⁺ (1.0×10^{-4} M).



Figure 3. Fluorescence titration of 6 (1×10^{-5} M) with Fe(ClO₄)₃ in distilled water (pH 5.69) at 298 K. [Fe³⁺]: 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 2.5 × 10⁻⁵ M.



Figure 4. Job's plots according to the method for continuous variations, indicating the 1:1 stoichiometry for 6-Fe³⁺ (the total concentration of 6 and Fe³⁺ is 2.446×10^{-5} M).



Figure 5. Fluorescent intensity ratio (l/l_0) of complex **6**-Fe³⁺ (1 × 10⁻⁵ M) in distilled water (pH 5.69) at 298 K in the presence of 10.0 equiv of different metal ions. Inset: Photograph of **6**-Fe³⁺ after adding different metal ions. **A: 6**-Fe³⁺ (1.0 × 10⁻⁵ M); **B–L: 6**-Fe³⁺+Hg²⁺, Mg²⁺, Cu²⁺, Ba²⁺, Ca²⁺, Zn²⁺, Ag⁺, Pb²⁺, Cd²⁺, Fe³⁺(1.0 × 10⁻⁴ M), and **4** (1.0 × 10⁻⁵ M).



Figure 6. Fluorescence titration of compound **6-Fe³⁺** (1 × 10⁻⁵ M) with Hg(ClO₄)₂ in distilled water (pH 5.69) at 298 K. [Hg²⁺]: 0.25, 0. 5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, 3.0, 5.0, 10 × 10⁻⁵ M. The excitation wavelength was 320 nm and the emission intensity was measured at 474 nm.

tum yield of complex **6**-Fe³⁺ with Hg²⁺ (2 equiv) was 0.02718. The time of complex **6**-Fe³⁺ (1 × 10⁻⁵ M) towards Hg²⁺ (2 equiv) in water for the reaction time curve reaching a stable plateau was needed for 5 min (Fig. S17). The titration reaction curve of complex **6**-Fe³⁺ toward Hg²⁺ was investigated as Fig. 6. The fluorescent intensity of complex **6**-Fe³⁺ increased in response to the increases in the concentration of the added Hg²⁺ in water, and the titration reaction curve showed a steady increase until a plateau was reached when 2 equiv of Hg²⁺ ion was added.

To examine the sensitivity of complex **6**-Fe³⁺ towards Hg²⁺, its detection limit was evaluated as Fig. 7. The fluorescence titration profile of complex **6**-Fe³⁺ (5×10^{-7} M) with Hg²⁺ demonstrated that Hg²⁺ could be detected at least down to 2 ppb,⁹ and the fluorescent intensity of complex **6**-Fe³⁺ increased linearly with the concentration of Hg²⁺ ion (0–10) × 10⁻⁹ M (R² = 0.9977). To investigate the utility of complex **6**-Fe³⁺ as an ion-selective fluorescent chemosensor for Hg²⁺ ion, the cross-contamination experiments were conducted in the presence of Hg²⁺ at 2 × 10⁻⁵ M mixed with other metal ions such as Ag⁺, Zn²⁺, Fe³⁺, Ca²⁺, Mg²⁺, Ba²⁺, Pb²⁺, Cd²⁺



Figure 7. Fluorescence titration of complex **6**-Fe³⁺ (5×10^{-7} M) with Hg(ClO₄)₂ in distilled water at 298 K. [Hg²⁺]: 0, 2, 2.5, 4, 5, 6, 7.5, 8, 10, 20, 30, 40, 50, 100 ppb. The excitation wavelength was 320 nm.



Figure 8. Results of the competition experiments between Hg²⁺ and selected metal ions in distilled water at 298 K; the concentration of Hg²⁺ was 2×10^{-5} M and that of each competing metal ions was 1×10^{-4} M.

and Cu²⁺ at 1×10^{-4} M, respectively (Fig. 8). It demonstrated that the selectivity of complex **6**-Fe³⁺ towards Hg²⁺ ion was almost not affected by other competitive ions. As described in the partial ¹H NMR spectra of Fig. 9a, when complex **6**-Fe³⁺ was treated with 2 equiv of Hg²⁺, the resonance of the aldehyde proton appeared with the advance of time as compared with **4**. After 5 min, the whole aldehyde proton appeared at 9.86 ppm. Based on the above ¹H NMR data, the proposed sensing mechanism was described as Fig. 9b.

3. Conclusions

In conclusion, we have developed a new selective and sensitive fluorescence 'on-off-on' probe **6** for sequential recognition of Fe³⁺ and Hg²⁺ in water. Especially the complex **6**-Fe³⁺ could behave as a 'turn on' fluorescent sensor over a wide-range pH value (pH >4.0) for detection of Hg²⁺. The selectivity of this complex for Hg²⁺ over other heavy and transition metal ions is excellent, and its sensitivity for Hg²⁺ is at 2 ppb in water. Therefore, in reality probe **6** would be most useful when pre-equilibrated with Fe³⁺,

which would let it to be a single-use Hg²⁺ sensor for practical applications. More significantly, the strategy described in this paper at least provides a new way for the design of novel fluorescent sensors.

4. Experimental

4.1. General remarks

All solvents and reagents were used as obtained from commercial sources without further purification. Zn(ClO₄)₂·6H₂O, Fe(- $ClO_4)_2 \cdot 6H_2O$, $Ca(ClO_4)_2 \cdot 4H_2O$, $Mg(ClO_4)_2$, $Ba(ClO_4)_2$, $Pb(ClO_4)_2$, $Cd(ClO_4)_2$, $Cu(ClO_4)_2$, $Hg(ClO_4)_2$ and $AgPF_4$ were investigated as sources for metal ions. Analytical thin-layer chromatography (TLC) and preparative thin-layer chromatography (PTLC) were performed with silica gel plates using silica gel 60 GF₂₅₄ (Qingdao Haiyang Chemical Co., Ltd). Melting points are uncorrected. Infrared spectra (IR) were recorded on a Bruker TENSOR 27 spectrometer. Nuclear magnetic resonance spectra (NMR) were recorded on a Bruker Avance III 500 MHz instrument in CDCl₃ or DMSO- d_6 (¹H at 500 MHz and ¹³C at 125 MHz) using TMS (tetramethylsilane) as the internal standard. High-resolution mass spectra (HR-MS) and electron ionization mass spectrometry (EI-MS) were carried out with APEX II Bruker 4.7T AS instrument and HP 5988 mass spectrometry instrument, respectively. Fluorescent spectra were determined on a Hitachi F-4500 spectrophotometer. UV-Visible spectra were determined on a Hitachi U-3310 spectrophotometer.

4.2. Synthesis of 2

A mixture of 4, 4'-dihydroxybenzophenone (4.3 g, 20 mmol), 1, 3-dibromopropane (10.0 g, 50 mmol), and K₂CO₃ (13.8 g, 100 mmol) in DMF (20 mL) under N₂ was stirred at room temperature for 24 h. Then the resulting mixture was extracted with CH₂Cl₂. The CH₂Cl₂ extract was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give a residue, which was purified by column chromatography over silica gel eluting with PE/EtOAc (20:1, v/v) to give **2** (4.06 g, 44% yield) as a white solid: CAS: 288248-49-7; mp 62–63 °C (lit. 62–64 °C) ^{8b}; IR (cm⁻¹): 2931, 2868, 1731, 1637, 1601, 1504, 1416, 1244, 838, 763; ¹H NMR (500 MHz, CDCl₃) δ : 7.77 (d, *J* = 8.5 Hz, 4H), 6.96 (d, *J* = 8.5 Hz, 4H), 4.18 (t, *J* = 5.5 Hz, 4H), 3.61 (t, *J* = 6.0 Hz, 4H), 2.33–2.38 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ : 194.4, 162.0, 132.3, 131.0, 114.0, 65.5, 32.2, 29.8; HRMS (ESI) *m/z* Calcd for C₁₉H₂₁O₃Br₂ [M+H]⁺ 454.9852. Found 454.9844.

4.3. Synthesis of 3

TiCl₄ (2.25 mL, 18.8 mmol) was added dropwise to a stirred suspension of Zn powder (2.6 g, 40.0 mmol) in dry THF (70 mL) under N₂ below –10 °C. After adding, the reaction was allowed to proceed at reflux for 2 h. Then a solution of 2 (2.28 g, 5 mmol) and diphenyl ketone (0.91 g, 5 mmol) in THF (65 mL) was added to the suspension of the titanium reagent. After adding, the reaction was allowed to proceed at reflux for 4 h. The reaction mixture was poured into 10% aq K₂CO₃ (200 mL), and after vigorous stirring for 5 min, the dispersed insoluble material was removed by vacuum filtration. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic fractions were washed with water and dried over anhydrous Na₂SO₄. The mixture was concentrated and purified by column chromatography over silica gel eluting with PE/EtOAc (50:1, v/v) to give 3 (906 mg, 30% yield) as a white solid: CAS: 1067211-23-7; mp 119–121 °C (lit. 123–125 °C) ^{8b}; IR (cm⁻¹): 2936, 2931, 1698, 1607, 1508, 1469, 1243, 756, 698; ¹H NMR (500 MHz, CDCl₃)



Figure 9. Partial spectra of complex (6+1 equiv of Fe^{3+}), and complex (6+1 equiv of $Fe^{3+}+2$ equiv of Hg^{2+} in DMSO- d_6) (a); proposed sensing mechanism for complex (6+1 equiv of Fe^{3+}) with Hg^{2+} (b).

δ: 7.05–7.12 (m, 6H), 7.01 (d, *J* = 7.0 Hz, 4H), 6.92 (d, *J* = 8.5 Hz, 4H), 6.62 (d, *J* = 8.5 Hz, 4H), 4.00 (t, *J* = 6.0 Hz,4H), 3.56 (t, *J* = 6.5 Hz,4H), 2.24–2.29 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ: 157.2, 144.2, 140.0, 136.6, 132.6, 131.4, 127.7, 126.1, 113.6, 65.1, 32.5, 30.1; HRMS (ESI) *m/z* Calcd for C₃₂H₃₀O₂Br₂ [M]⁺ 604.0607. Found 604.0591.

4.4. Synthesis of 4

A mixture of **3** (606 mg, 1 mmol), 4-hydroxybenzaldehyde (366 mg, 3 mmol), K_2CO_3 (414 mg, 3 mmol) and KI (10 mg) in MeCN (20 mL) was refluxed for 8 h under N₂. After cooling, the mixture was filtered, and the filtrate was collected, concentrated and purified by preparative thin-layer chromatography (PTLC) using PE/EtOAc (2:1, v/v) as the eluent to give **4** (461 mg, 67% yield) as a yellow solid: mp 66–68 °C; IR (cm⁻¹): 2927, 2745, 1688, 1599, 1507, 1240, 1057, 832, 700; ¹H NMR (500 MHz, CDCl₃.) δ : 9.88 (s, 2H), 7.81 (d, *J* = 8.0 Hz, 4H), 7.06 (t, *J* = 7.5 Hz, 6H), 6.99 (t, *J* = 8.0 Hz, 8H), 6.91 (d, *J* = 8.5 Hz, 4H), 6.62 (d, *J* = 8.5 Hz, 4H), 4.21 (t, *J* = 6.0 Hz, 4H), 4.06 (t, *J* = 5.5 Hz, 4H), 2.22-2.27 (M, 4H); ¹³C NMR (125 MHz, CDCl₃) δ : 191.1, 164.2, 157.5, 144.5, 140.2, 139.7, 136.9, 132.9, 132.3, 131.6, 130.3, 128.0, 126.4, 115.1, 113.8, 65.2, 64.2, 29.4; HRMS (ESI) *m/z* Calcd for C₄₆H₄₀O₆Na [M+Na]⁺ 711.2717. Found 711.2707.

4.5. Synthesis of 5

A mixture of **4** (344 mg, 0.5 mmol), methyl thioglycolate (0.27 ml, 3 mmol) and BF_3 ·Et₂O (0.38 ml, 3 mmol) in dry CH_2Cl_2

(20 mL) was stirred at 0 °C for 5 h, and then guenched with the addition of water (50 mL). The mixture was extracted with CH₂Cl₂ $(3 \times 80 \text{ mL})$. The combined organic layers were washed with brine and dried over anhydrous Na₂SO₄. The mixture was concentrated and purified by PTLC using PE/EtOAc (2:1, v/v) as the eluent to give **5** (506 mg, 94% yield) as a yellow liquid: IR (cm⁻¹): 2913, 2878, 1735, 1605, 1508, 1471, 1435, 1241, 834, 700; ¹H NMR $(500 \text{ MHz}, \text{ CDCl}_3) \delta$: 7.36 (d, J = 8.5 Hz, 4H), 7.05–7.11 (m, 6H), 7.00 (d, I = 6.5 Hz, 4H), 6.90 (d, I = 9.0 Hz, 4H), 6.85 (d, I = 9.0 Hz, 4H), 6.61 (d, J = 8.5 Hz, 4H), 5.29 (s, 2H), 4.10 (t, J = 6.0 Hz, 4H), 4.05 (t, J = 6.0 Hz, 4H), 3.70 (s, 12H), 3.44 (s, 2H), 3.41 (s, 2H), 3.19 (s, 2H), 3.16 (s, 2H), 2.18-2.23 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) *δ*: 170.5, 158.9, 157.3, 144.3, 136.5, 132.6, 131.4, 130.2, 129.5, 129.2, 127.7, 126.1, 115.5, 114.6, 113.5, 64.5, 64.1, 53.0, 52.5, 33.7, 29.3; HRMS (ESI) *m*/*z* Calcd for C₅₈H₆₀O₁₂S₄Na [M+Na]⁺ 1099.2860. Found 1099.2854.

4.6. Synthesis of 6

A mixture of **5** (366 mg, 0.34 mmol) and aq. NaOH solution (13.6 mL, 0.1 M) in methanol/THF (1:1, v/v, 15 mL) was stirred at rt for 24 h. Then the pH value of the mixture was adjusted to 2–3 by aq HCl solution (0.1 M), and the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under reduced pressure to give a residue, which was recrystallized from methanol/CH₂Cl₂ to afford **6** (152 mg, 44% yield) as a white solid: mp 127–128 °C; IR (cm⁻¹): 3371, 2919, 1703, 1605, 1508, 1243, 1173,837, 651; ¹H

NMR (500 MHz, CDCl₃.) δ : 12.65 (s, 4H), 7.30 (d, *J* = 8.0 Hz, 4H), 7.12 (t, *J* = 7.5 Hz, 4H), 7.07 (t, *J* = 6.5 Hz, 2H), 6.94 (t, *J* = 6.0 Hz, 8H), 6.85 (d, *J* = 8.0 Hz, 4H), 6.70 (d, *J* = 8.0 Hz, 4H), 5.24 (s, 2H), 4.09 (t, *J* = 5.5 Hz, 4H), 4.03 (t, *J* = 5.5 Hz, 4H), 3.39 (s, 4H), 3.22(s, 2H), 3.19 (s, 2H), 2.12–2.14 (m, 4H); ¹³C NMR (125 MHz, DMSO) δ : 171.2, 158.7, 157.5, 144.3, 136.2, 132.5, 131.4, 131.2, 129.3, 128.3, 126.7, 115.0, 114.2, 64.8, 64.5, 52.7, 34.5, 29.1; HRMS (ESI) *m/z* Calcd for C₂₇H₂₅O₆S₂ [(M–2H)/2]⁻ 509.1098. Found 509.1106.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.bmc.2012.11.005.

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