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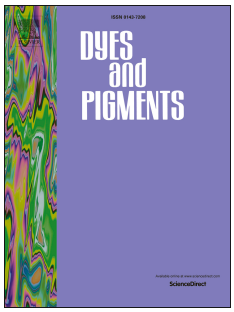

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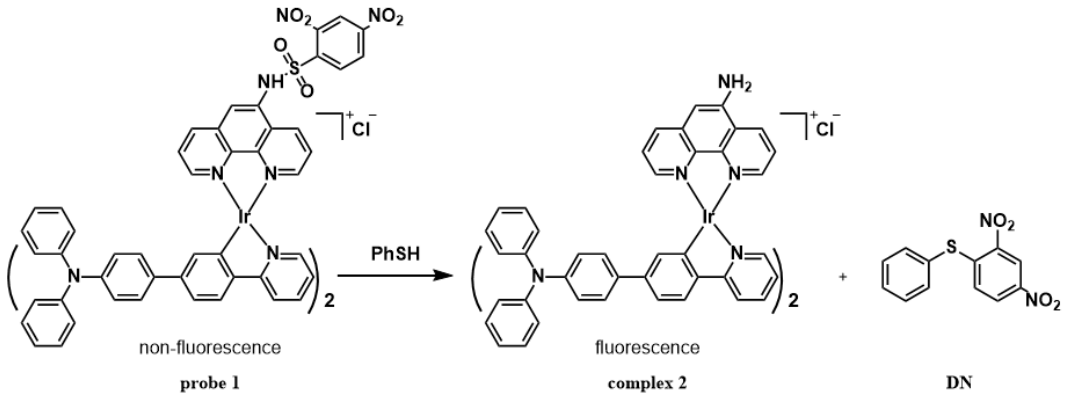

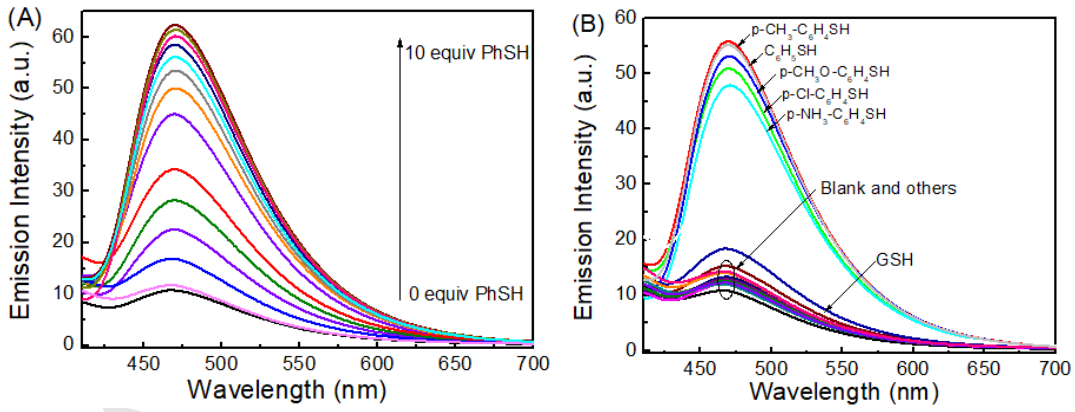

A cyclometalated iridium(III) complex comprised 2,4-dinitrobenzenesulfonamide (DNBS) as the recognition unit (probe **1**) was synthesized and its fluorescent behaviors toward thiophenols in 20% DMSO/PBS solution and water samples were investigated systematically. The results demonstrated that probe **1** could serve as a sensitive and selective fluorescent probe to detect thiophenols and could not be disturbed by aliphatic thiols.

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Abstract

In consideration of the nucleophilic capacity of thiophenols, which could cleave sulfonamide under neutral conditions, a cyclometalated iridium(III) complex (probe **1**) comprised 2,4-dinitrobenzenesulfonamide (DNBS) as the recognition unit was designed and synthesized to high selectivity and sensitivity detect thiophenols successfully based on internal charge transfer (ICT) mechanism. Upon addition with thiophenols to 20% DMSO/PBS solution of nearly non-fluorescent probe **1** (10 μM, pH = 7.4), fluorescent product (complex **2**) was formed after cleavage of DNBS group and a significant emission enhancement at 470 nm was observed. In addition, it could be successfully applied to detect thiophenol in water samples with a high recovery, confirming its practical value in environment science.

Keywords: Thiophenol; Fluorescent probe; Iridium(III) complex; 2,4-dinitrobenzenesulfonamide.

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1. Introduction

Thiophenols are important raw materials for medicine [1], pesticide [2], polymer [3] and additives on organic synthesis [4]. However, their potential hazards, such as volatility, foulsmell and high toxicity to biological and ecological environment, also can not to be ignored. For instance, thiophenols possess very low median lethal concentration (LC_{50}) and dose (LD_{50}) for fish (0.01-0.04 mM) [5] and mouse (2.15-46.2 mg kg^{-1}) [6]. Long term exposure of either liquid or vapor of thiophenols to human beings may cause several symptoms, such as central nervous system lesion, difficulty breathing, muscle weakness, paralysis, coma and even death [7-9]. Therefore, development of a highly sensitive and selective detection method for thiophenols in environmental and even in biological samples is highly demanding. At present, high performance liquid chromatography [10], gas chromatography [11], nonlinear spectroscopy [12] and nanophase material sensor based methods [13-14] have been used to detect the concentration of thiophenols, but complicated sample preparation, low sensitivity, easy interference and expensive instruments, and non-real-time online monitoring limit their further applications. Meanwhile, fluorescent analysis has attracted wide attention due to its advantages of simple operation, rapid response, high sensitivity and selectivity, and even direct detection in living cells or tissues [15-18]. Among the researches on detection of thiophenols, it is noteworthy that aliphatic thiols maybe become a potential interference factor because of their similar chemical structure, the same activity function thiol group (-SH). Fortunately, the different pK_a value between thiophenols (pK_a = 6.5) and aliphatic thiols (pK_a =8.5) (Scheme 1) under neutral conditions provide an approach to discriminate thiophenols from thiols [19]. Thiophenols can produce more nucleophilic thiolate species in the neutral reaction medium to achieve S_NAr process and cleave sulfonamide, but under

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the same reaction conditions, aliphatic thiols are difficult to hydrolyze, thus realizing the purpose of distinguishing aliphatic thiols from aromatic thiols.

<Scheme 1>

Since Jiang [19] synthesized the first fluorescence probe for specifically recognition thiophenol without alkyl mercaptan interference, many similar probes have been synthesized in the last decade, but most of them are small organic molecule probes [20-30]. The studies of fluorescent probes containing metal complex structures have been not much reported [31-32]. Usually, transition organometallic probes possess the following characteristics: (1) highly luminous efficiency, long life and high stability; (2) large stokes shift of excitation and emission, and easy regulation of excitation and emission wavelength; (3) low cell imaging incubation concentration, and less interference of cell normal activity [33]. Meanwhile, because of easy functionalized modification and synthesis, photochemical stability, and desirable photophysical properties [34-43], cyclometalated Ir(III) complexes are widely used as excellent luminescent materials for various applications, such as sensing and bioimaging [33,44], organic light-emitting devices [45], and sensitized photon upconversion [46].

It is well known that a responsive fluorescence probe usually include a fluorescent unit and a switch moiety sensitively regulating to various substrates, such as metal ions, anions and amino acids, and so on. Generally, these fluorescence switches strategy is proposed to induce efficient transfer processes, such as internal charge transfer (ICT), photoinduced electron transfer (PET), electronic energy transfer (EET), and monomer-excimer formation (MEF) [31]. Herein, we introduced cyclometalated iridium(III) complex as fluorophore and electron-withdrawing 2,4-dinitrobenzenesulfonyl (DNBS) group as recognition unit, then successfully synthesized a

probe **1** in order to detect thiophenols. Due to the influence of internal charge transfer (ICT) from cyclometaled iridium moiety to strongly electron-withdrawing DNBS moiety, probe **1** exhibits nearly non-fluorescence. When the cleavage of DNBS group occur through reaction between complex **1** and thiophenols, the luminescence of Ir(□) complex **2** could be recovered. Probe **1** was found to high selectivity and sensitivity response to thiophenols accompanied with obvious fluorescent turn-on around 470 nm. In addition, this probe was also successfully applied to quantitative detection of thiophenols in water samples.

2. Experimental Section

2.1 General procedures and materials

All chemical materials were purchased through commercial channels and were not further purified, except those with further notice. All solvents were purified by standard methods prior to use. All the synthetic operations were performed under a dry argon atmosphere using Schlenk techniques and a vacuum-line system. The solution of probe **1** (1 mM) was prepared in chromatographic grade THF. Standard solution of various analytic samples (10 mM) were prepared after dissolution of C_6H_5SH, *p*-Cl-C_6H_5SH, *p*-CH_3-C_6H_5SH, *p*-CH_3O-C_6H_5SH, *p*-NH_3-C_6H_5SH, $HOCH_2CH_2SH$, PhOH, $(CH_3)_3SH$ and $PhNH_2$ into DMSO. Solutions of glutathione (GSH), cysteine (Cys), homocysteine (Hcy), alanine (Ala), glycine (Gly), NaSH and KI were prepared in distilled water (10 mM, respectively).

*2.1.1 N,N-diphenyl-4'-(pyridin-2-yl)-[1,1'-biphenyl]-4-amine (**4**)*

In a 250 mL round-bottom flask, 2-(4-bromophenyl)pyridine (2.671 g, 11.41 mmol), $Pd(PPh_3)_4$ (250 mg) and (4-(diphenylamino)phenyl)boronic acid (3.00 g, 10.38 mmol) were dissolved in 125 mL of THF, then Na_2CO_3 (12.72 g, 120 mmol) prior dissolved in 60mL water

was added to the mixture solution. After reaction solution was stirred at 80□ for 12 h, solvent THF was evaporated, and the obtained solution was extracted with dichloromethane, which was removed under reduce pressure to get yellow crude product. Crude product was purified by column chromatography on SiO_2 with petroleum ether and ethyl acetate (v/v = 20:1) as eluent to obtained 3.568 g faint yellow solid in 86.2 % yield. ^{1}H NMR (400 MHz, DMSO, ppm) δ: 8.73 (d, *J* = 4.4 Hz, 1H), 8.21 (d, *J* = 8.4 Hz, 2H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.94 (t, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 5H), 7.13 (q, *J* = 7.8 Hz, 8H); HRMS: m/z 399.1839 $[M + H]^+$.

*2.1.2 Chloro-bridged Ir (Ⅲ) complex dimer (**3**)*

In a 100 mL round-bottom flask, compound **4** (0.445g, 1.1176 mmol) and anhydrous $IrCl_3$ (0.152g, 0.508 mmol) were added to 20 mL of 2-ethoxyethanol and water (v/v = 3:1) and the solution was refluxed for 25 h. The solution was filtered after cooling to room temperature, the resulting precipitate was in turn washed with 10 mL 95% ethanol, acetone, to afford crude dimer **3** 0.43g as yellow solid in 82.8 % yield, which was used to next reaction directly without further purification and characterization [47,48].

*2.1.3 Complex **2***

To a mixture of cyclometalated Ir(III) chloro-bridged dimer **3** (0.36 g, 0.176 mmol), 1,10-phenanthrolin-5-amine (0.0687 g, 0.352 mmol) in 50mL of CH_2Cl_2/CH_3OH (v/v = 1:1) were reflux 6 h. After completion of the reaction, solvent was evaporated, crude product was purified by neutral alumina column chromatography using CH_2Cl_2/CH_3OH (v/v = 30:1) as eluent and obtained 0.385 g red solid in 89.8 % yield. ^{1}H NMR (400 MHz, DMSO, ppm) δ: 9.08 (d, *J* = 8.4 Hz, 1H), 8.40 (d, *J* = 8.4 Hz, 1H), 8.25 (t, *J* = 4.2 Hz, 3H), 8.00-7.95 (m, 3H), 7.87 (t, *J* = 7.6 Hz,

3H), 7.73-7.70 (m, 1H), 7.50 (t, *J* = 6.8 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 13H), 7.19 (s, 1H), 7.13 (s, 1H), 7.05 (t, *J* = 7.4 Hz, 5H), 6.99 (d, *J* = 8.0 Hz, 10H), 6.90 (d, *J* = 7.2 Hz, 5H), 6.51 (d, *J* = 12.4 Hz, 2H, $-NH_2$); ^{13}C NMR (100 MHz, DMSO, ppm) δ: 184.03, 167.45, 167.14,167.06, 151.73, 151.30, 150.89, 149.57, 149.32, 147.51, 147.40, 145.97, 145.64, 143.51, 143.46, 141.01, 140.95, 140.33, 139.07, 136.77, 135.51, 134.36, 134.09, 133.70, 132.42, 132.03, 130.06, 192.12, 128.58, 128.45, 128.26, 127.69, 127.10, 126.06, 126.00, 125.93, 124.71, 124.51, 124.10, 124.07, 123.82, 123.45, 121.29, 121.02, 120.97, 120.66, 120.49, 120.43, 109.06, 108.76, 102.22; HRMS: m/z 1182.3739 $[M - Cl]^+$.

*2.1.4 Complex **1***

Under an argon atmosphere, complex **2** (0.10 g, 0.0821 mmol) was dissolved in 10 mL of dry THF and cooled to 0□, followed by addition of NaH (5.00 mg, 60% in purity, 0.125 mmol). Upon stirring for 15 min, 2, 4-dinitrobenzenesulfonyl chloride (0.033 g, 0.125 mmol) in 5 mL dry THF was added dropwise. The resulting reaction mixture was then further stirred at room temperature for another 1 h. After solvent was evaporated, crude product was purified by column chromatography on SiO_2 with CH_2Cl_2/ acetone (v/v = 3:1) as eluent to obtained 0.035 g red solid in 29.6 % yield. ^{1}HNMR (400 MHz, DMSO, ppm) δ: 10.56 (s, 1H, -NH), 8.99 (s, 1H, phenyl-H), 8.89 (d, *J* = 8.4 Hz, 2H), 8.55 (d, *J* = 2.4 Hz, 1H), 8.53 (s,1H), 8.40-8.37 (m, 2H), 8.34-8.29 (m, 3H), 8.10-8.00 (m, 5H), 7.92 (m, 2H), 7.57 (t, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 13H), 7.14 (d, *J* = 9.6 Hz, 1H), 7.07 (t, *J* = 6.8 Hz, 6H), 7.01 (d, *J* = 7.6 Hz, 9H), 6.95-6.92 (m, 4H), 6.54 (s, 2H); ^{13}C NMR (100 MHz, DMSO, ppm) δ: 167.09, 151.88, 151.39, 150.73, 150.55, 149.76, 149.69, 148.02, 147.87, 147.79, 147.57, 147.46, 147.40, 146.92, 146.04, 145.34, 143.47, 141.05, 139.27, 139.09, 139.02, 137.80, 136.77, 135.68, 135.60, 134.00, 133.61, 132.84, 132.44, 132.10, 131.27,

131.13, 130.08, 129.73, 129.13, 128.53, 127.96, 127.72, 126.06, 125.85, 124.75, 124.14, 124.10, 123.87, 123.59, 123.42, 121.53, 121.17, 120.59, 118.75, 118.61, 109.06, 108.76; HRMS: m/z 1348.3910 $[M - Cl - C_6H_3N_2O_4 + Na + K + CH_3CN]^+$; IR (KBr, υ, cm^{-1}): 1335 (−S=O), 1586 ($-NO_2$), 3448 (−N-H).

2.2 Physical measurements

NMR spectra were recorded on a Bruker AV400 (400MHz) spectrometer with $(CD_3)_2SO$ as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra data were obtain with an Agilent 1100 ion trap MSD spectrometer. Absorption spectra were measured on an Agilent 8453 UV–vis spectrometer. Infrared spectra (IR) were collected on a Bruker Vertex-70 spectrometer as KBr pellets and were reported in cm^{-1}. Fluorescence spectra were recorded on a HitachiF-4600 fluorescence spectrophotometer with the excitation and emission slit widths of 5.0 nm and 5.0 nm.

2.3 Measuration of thiophenol in real water samples.

The crude water samples were obtained from Ganjiang River, Kong Mu Lake and Qingshan Lake in Nanchang city, further adapted as through using sodium phosphate buffer (10 mM, pH = 7.4). Aliquots of water sample were then spiked with different concentrations of thiophenol (1, 5, 10, 20 μM) that had been accurately prepared. The sequent samples were further treated with probe **1** in 20% DMSO phosphate buffer (10 mM, pH = 7.4) to obtain final mixtures (2.0 mL) with probe **1** and thiophenol (1, 5, 10, 20 μM). The mixtures were incubated for 40 min at 25 °C, and emission intensity at 470 nm was recorded. The results were reported as the mean ± standard deviation of triplicate experiments.

3. Results and discussion

3.1 Synthesis and Characterization

The synthetic route of probe **1** was displayed in scheme 2. Ligand **4** was obtained through classic Suzuki cross coupling reaction between 2-(4-bromophenyl)pyridine and (4-(diphenylamino)phenyl)boronic acid. Chloried-bridged complex **3** was synthesized from reaction of ligand **4** with anhydrous $IrCl_3$ without further purification, followed by treating with 1,10-phenanthrolin-5-amine in presence of CH_2Cl_2/CH_3OH to afford complex **2**. Probe **1** was prepared through reaction of complex **2** with 2,4-dinitrobenzenesulfonyl chloride in the presence of NaH playing as a deprotonation reagent. Because of the activity of NaH, the deprotonation procedure was carried out at 0 ℃. All compounds were characterized by NMR, ESI-HRMS.

<Scheme 2>

3.2 UV absorption and fluorescence emission studies

The absorption spectra of probe **1** and complex **2** were carried out in DMSO solution (10 μM) at room temperature. Both of them showed two sharp absorption bands around at 289 nm and 380 nm ascribe to intra-ligand-centered $\pi \rightarrow \pi^*$ transitions and metal to ligand charge transfer (MLCT) transitions, respectively (Fig.1A) [49]. The MLCT absorption band displayed properly high molar extinction absorption coefficient (log ε = 4.93) that was much higher than that of MLCT transition of other reported $[Ir(ppy)_2bpy]^+$-form complexed (log ε = ca. 3.0) [50]. This excellent MLCT transitions property of probe **1** would be conducive to improve fluorescence character and increase sensitivity of the probe. The absorption spectra between probe **1** and complex **2** had almost no difference, suggesting that the cyclometalated $[Ir(ppy)_2Phen]^+$ moiety did not participate in recognition process and fluorescence of probe **1** should be probably quenched via ICT mechanism [31]. On the other hand, fluorescence spectra of probe **1** and complex **2** were quite different. As shown in Fig. 1B, when excited at 400 nm, complex **2** exhibited fluorescence emission band at

470 nm (Φ = 0.04). After connecting electron-withdrawing 2,4-dinitrobenzenesulfonyl (DNBS) group, probe **1** showed almost non-fluorescence (Φ = 0.003) because of ICT mechanism.

<Fig. 1>

3.3 Fluorescence response of probe 1 toward thiophenol

Although with non-fluorescence property (Φ of **1** was 0.003), when added 10 equivalents of thiophenol to DMSO/PBS (v/v = 1:4) solution of probe **1** to form corresponding fluorescent complex **2 (**Φ = 0.04**)**, an emission peak at 470 nm was obviously observed and the fluorescence intensity increased significantly and reached maximum after 40 minutes, implying probe **1** could serve as a quite sensitive fluorescent sensor for thiophenol (Fig. 2A). Meanwhile, time response capability of probe **1** for thiophenol was further investigated in 0.01 M 20% DMSO/PBS with fluorescence spectroscopy to evaluated kinetic studies. As depicted in Fig. 2B, upon addition of thiophenol (100 μM), the fluorescence intensity at 470 nm showed a rapid increase initially (0 – 10 min), and reached an equilibrium within 40 minutes with a relatively moderate kinetic constant (*k* = 0.10043 min^{-1}) and half-time ($t_{1/2}$ ≈ 6.90 min, Fig. S5, see SI). Although this value of half-time was only relatively medium, considering the emission intensity at 470 nm enhanced rapidly in the first ten minutes, we still thought that probe **1** could be able to rapidly response to thiophenol.

<Fig. 2>

Moreover, detailed fluorometric titration experiments were carried out in 20% DMSO/PBS (0.01 M, pH = 7.4) to further investigate the responsive fluorescence of probe **1** induced by thiophenol (Fig. 3). As shown as Fig.3 (Inset: its emission intensity curve at 470 nm with addition of various equiv thiophenol), with addition of less than 3 equiv of thiophenol, fluorescence

intensity of probe **1** enhanced significantly initially, as thiophenol was further added gradually, the emission intensity increased slowly and finally reached a plateau when 10 equiv of thiophenol was further titrated. The fluorescence intensity at 470 nm exhibited an excellent linear relationship with the concentration of thiophenol in range of 0 − 30 μM (Fig. 3B), whose slope was calculated to be 1.141×10^{-6} M (R = 0.99942). This indicated that probe **1** could be potentially used for quantitative detection of thiophenol. According to previous method defined by IUPAC [51-54], the limit of detection (LOD) was calculated to be 1.65×10^{-6} mol L^{-1}, demonstrating that our Ir(□) complex-based probe **1** could be sensitive detection of thiophenol (Table S1, see SI).

<Fig. 3>

3.4 Selectivity of probe 1 toward thiophenols

As we known, discrimination thiophenol from aliphatic thiols was a requisite capability for thiophenol probe. In order to explore the specificity of probe **1** toward thiophenols, fluorescence responsive reaction of probe **1** with various analytes, including thiophenol derivatives (C_6H_5SH, *p*-CH_3-C_6H_4SH, *p*-Cl-C_6H_4SH, *p*-NH_2-C_6H_4SH and *p*-CH_3O-C_6H_4SH), aliphatic mercaptan ($HOCH_2CH_2SH$, $(CH_3)_3CSH$, cysteine (Cys), homocysteine (Hcy) and glutathione (GSH)), and other nucleophilic substances ($C_6H_5NH_2$, C_6H_5OH, KI, NaSH, glycine (Gly) and alanine (Ala)), were evaluated under similar conditions. As depicted in Fig. 4, when various analytes were added into probe **1** 20% DMSO/PBS solution, only thiophenol derivatives could induced obvious fluorescence enhancements, indicating that probe **1** was not susceptible influence by these interfering substances. When 10 equivalent thiophenol derivatives were added to the mixture of probe **1** and previous interfering substances, fluorescence enhancements were observed. These results indicated that probe **1** possessed an excellent specificity for thiophenols.

<Fig. 4>

3.5 Probing mechanism of Ir − DNBS toward thiophenols

Similar to the previously reported thiophenol probe with 2,4-dinitrobenzenesulfonyl as recognition group, the sulfonamide bond of probe **1** could also be broke through S_nAr process induced by thiolate. To further elucidate the recognize mode between probe **1** and thiophenol, a series of ^1H NMR experiments were recorded. As shown in Fig. 5, upon addition 10 equiv of thiophenol to probe **1** in DMSO-d_6, the proton signal of H_a at 10.56 ppm corresponding to the 2,4-dinitrobenzenesulfonamide group (−N-H) of probe **1** disappeared due to the cleavage of sulfonamide bond. Meanwhile, H_1 at 8.99 ppm, H_2 at 8.53 ppm and H_3 at 8.15 ppm ascribed to protons on benzene ring of 2,4-dinitrobenzenesulfonamide group showed slight shift to 9.04 ppm, 8.57 ppm and 7.18 ppm, respectively, which was more consistent with the characteristic proton signals of (2,4-dinitrophenyl) (phenyl) thioether (DN). These results confirmed that probe **1** generated complex **2** as the luminescent species and DN as the byproduct through a thiolate triggered S_nAr cleavage process.

<Fig. 5>

3.6 Detection of Thiophenols in Water Samples.

Whereas toxicity of thiophenols and their harms to environment, we employed probe **1** to quantify thiophenol concentrations in water samples to evaluate the practicability of probe **1** in environmental science according to standard addition method [6,27,28]. The crude water samples were obtained from Ganjiang River, Kong Mu Lake and Qingshan Lake in Nanchang city. These water samples were spiked with different concentrations of thiophenol (1, 5, 10, 20 μM), obvious fluorescence was observed and their responsive fluorescence intensity at 470 nm in various water

samples were recorded (Table 1). The thiophenol recovery could be accurately measured and ranged on 90–104%, suggesting that probe **1** had potential application for quantitative detection of thiophenols in water samples.

<Table 1>

4. Conclusions

In summary, an iridium (III) complex (**1**) was successfully designed and synthesized as a probe to highly selective and sensitive detection of thiophenols. Its recognition behaviors and mechanism, in which iridium (III) complex (**2**) as the fluorophore and 2,4-dinitrobenzenesulfonamide as the reaction group through internal charge transfer (ICT), was also confirmed by fluorescence spectroscopy and ^{1}H NMR experiments. The advantages of this probe in detecting thiophenols contained relatively quick ($t_{1/2}$ ≈ 6.90 min) and obvious fluorescence responses (6-fold enhancement), high selectivity and sensitivity. Moreover, probe **1** can be used for the quantitative detection of thiophenols in water samples. Therefore, probe **1** had potential applications for fast detection and quantification of thiophenols in environmental systems.

5. Acknowledgements

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Figures & captions

Scheme 1. Nucleophilicity of thiophenols and aliphatic thios under neutral condition.

Scheme 2. Synthetic routes of complex **1**

Fig. 1. (A) Absorption spectra of probe **1** (10 μM), complex **2** (10 μM) in DMSO at room temperature; (B) Fluorescence sprctra of probe **1** (10 μM), complex **2** (10 μM) in 20% DMSO/PBS at room temperature.

Fig. 2. (A) Changes in fluorescence of probe **1** (10 μM) in 20% DMSO/PBS (0.01 M, pH = 7.4) induced by 100 μM thiophenol at different reaction time, excited at 400 nm (slit: 5/5); (B) Time response curves at 470 nm of probe **1** (10 μM in 0.01 M 20% DMSO/PBS, pH = 7.4) with thiophenol (100 μM).

Fig. 3. (A) Changes in fluorescence of probe **1** (10 μM) in 20% DMSO/PBS (0.01 M, pH = 7.4) induced by different concentrations of thiophenol (0 − 10 equiv), excited at 400 nm (slit: 5/5). Each spectrum was collected 40 minutes after addition of thiophenol; (B) Linear relationship between fluorescence intensity of probe **1** (10 μM) at 470 nm and the concentration of thiophenol from 0 to 30 μM.

Fig. 4. (A) Emission spectral changes in fluorescence of probe **1** (10 μM) induced by various analytes (10 equiv) in 20% DMSP/PBS (0.01 M, pH = 7.4), excited at 400 nm (slit: 5/5). Each spectrum was collected 40 minutes after addition of analyte; (B) Competitive tests on fluorescent responses of probe **1** at 470 nm to various analytes in 20% DMSO/PBS (0.01 M, pH = 7.4). Black bars represent the addition of 10 equiv of various analytes to solution of probe **1**. Red bars represent the addition of thiophenol (10 equiv) to the above solution.

Fig. 5. Partial ^{1}H NMR spectra of probe **1**, probe **1** + thiophenol (10 equiv), complex **2** and DN in

DMSO-d_6.

Table 1. Determination of thiophenol concentrations in water samples

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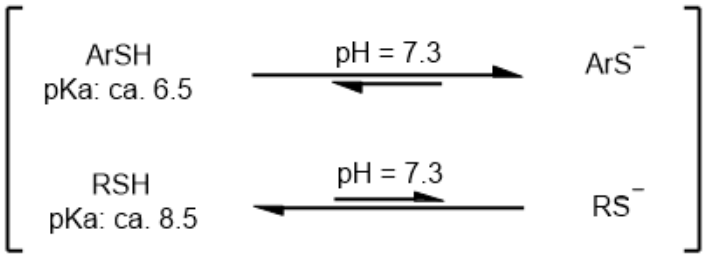

Scheme 1

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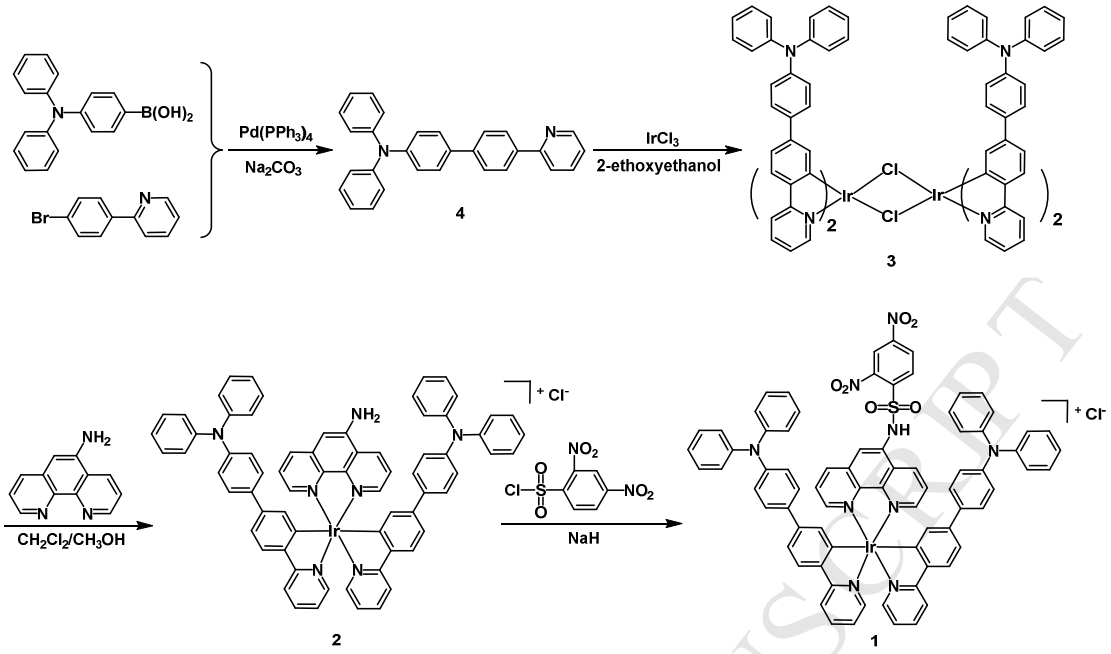

Scheme 2

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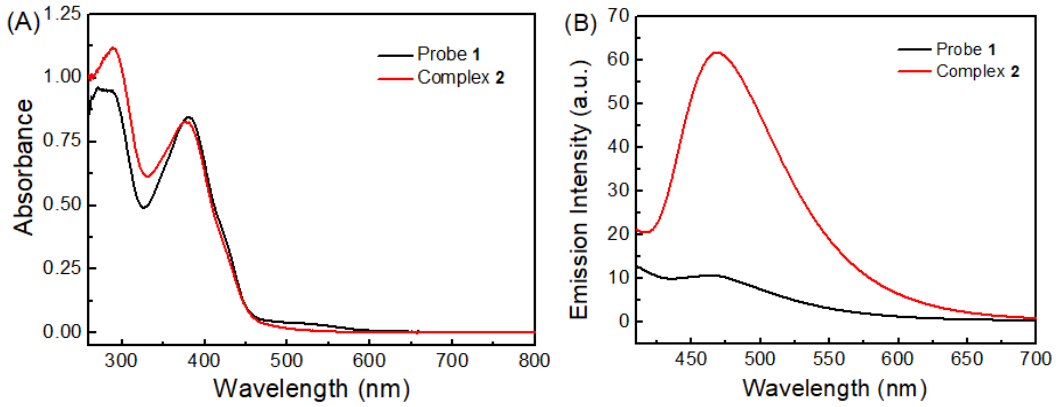

Fig. 1

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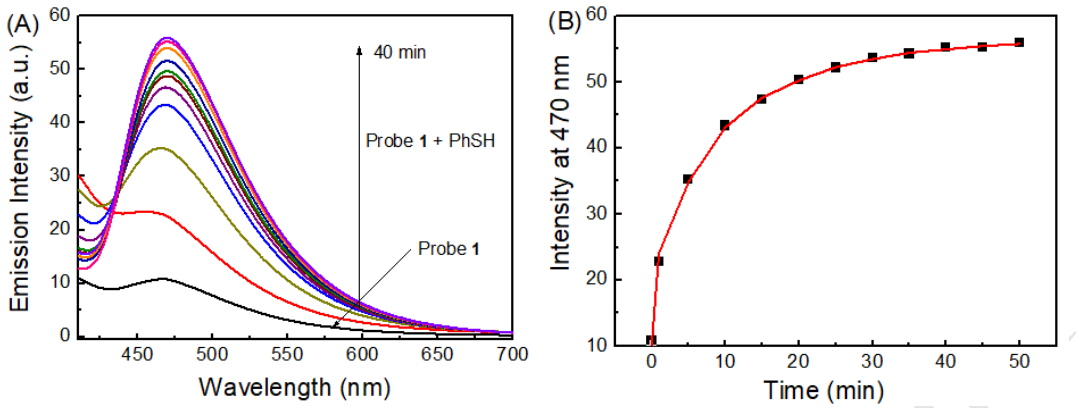

Fig. 2

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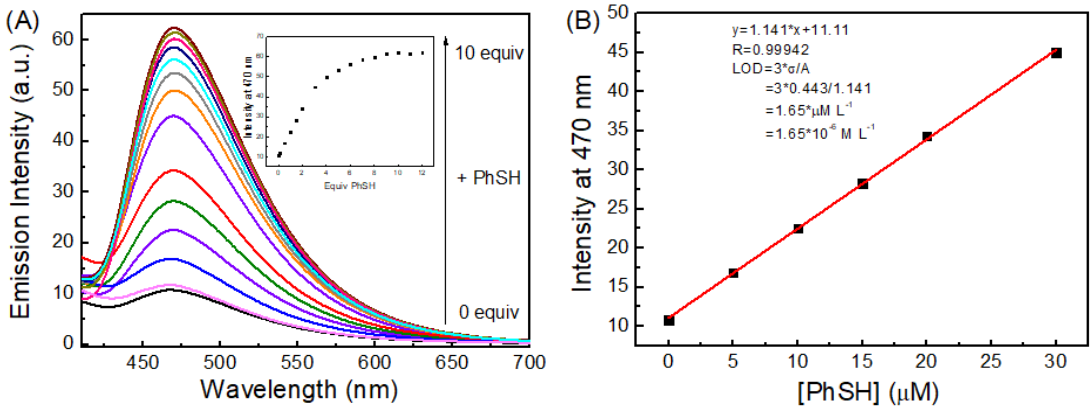

Fig. 3

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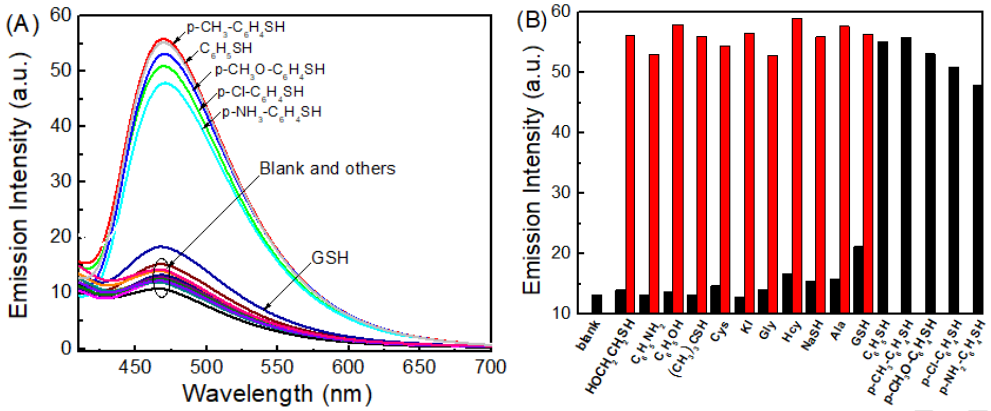

Fig. 4

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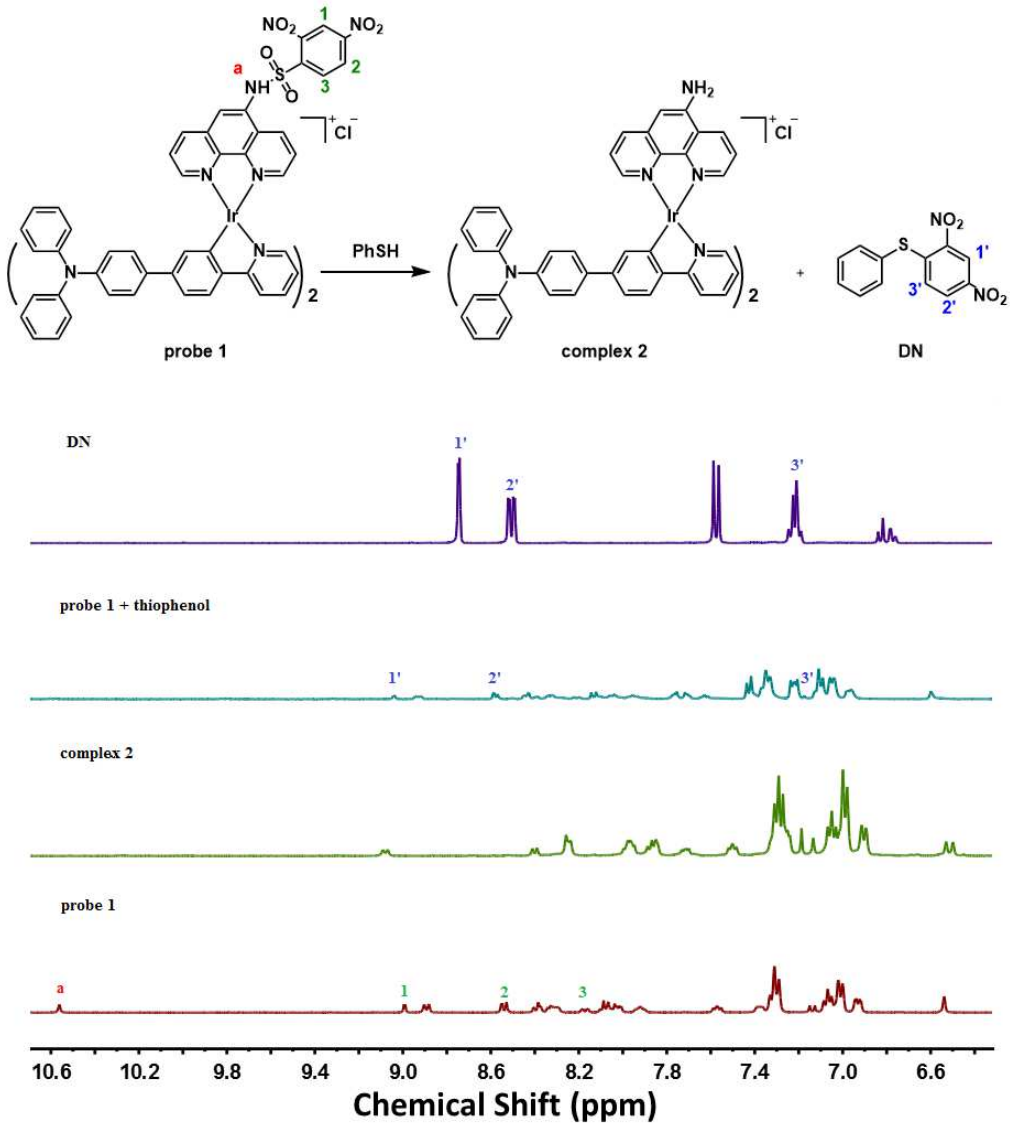

Fig. 5

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Sample	Thiophenol spiked (μM)	Thiophenol recovered (μM)[a]	Recovery (%)[b]
Ganjiang River	0	not detected	
	1	0.90 ± 0.02	90
	5	5.16 ± 0.021	103
	10	10.00 ± 0.02	100
	20	19.95 ± 0.031	99
Kong Mu Lake	0	not detected	
	1	0.91 ± 0.026	91
	5	5.16 ± 0.025	103
	10	9.94 ± 0.079	99
	20	20.87 ± 0.079	104
Qingshan Lake	0	not detected	
	1	0.90 ± 0.055	90
	5	5.15 ± 0.025	103
	10	9.99 ± 0.035	100
	20	19.67 ± 0.061	98

[a] Average values ± standard deviation of actual thiophenol concentrations calculated from the fluorescence intensity corresponding to the standard concentration of Thiophenol in three parallel experiments in each water sample concentration curve. [b] The ratio between average value and standard concentration of thiophenol.

Table 1

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Highlights

- A iridium (□) complex probe **1** comprised 2,4-dinitrobenzenesulfonamide (DNBS) as the recognition unit was designed and synthesized
- Its detection behaviors toward thiophenols in 20% DMSO/PBS and water samples were investigated systematically
- The mechanisms of recognition of thiophenols have been discussed through ^{1}H NMR spectrum

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