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RESEARCH ARTICLE

Synthesis and crystal structure of a highly selective colorimetric and fluorometric sensor for hydrogen sulfide

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Abstract

A novel Cu(II) complex chemosensor for hydrogen sulfide with azo as the colorimetric group has been synthesized. The complex and ligand crystals were obtained and the molecular structures were characterized by X-ray diffraction and Electrospray ionization High resolution mass spectrometer (ESI-HRMS). The photophysical and recognition properties were examined. The complex can recognize S^{2-}, with an obvious color change from yellow to red based on a copper ion complex displacement mechanism. By contrast, no obvious changes were observed in the presence of other anions (AcO^-, $H_2PO_4^-$, F^-, Cl^-, Br^- and I^-). We present a simple, easily prepared, yet efficient, inorganic reaction-based sensor for the detection of S^{2-}. The complex should have many chemical and analytical applications in the sensing of hydrogen sulfide.

KEYWORDS

colorimetric chemosensor, copper complex crystal, hydrogen sulfide

1 | INTRODUCTION

Traditionally considered a toxic gas with an unpleasant smell, hydrogen sulfide (H_2S), has been identified as the third member of the gasotransmitter family, after carbon monoxide (CO) and nitric oxide (NO).[1,2] It is reported that the typical concentration of H_2S in blood is in the range of 10–600 μM.[3–5] Several studies have shown that H_2S is involved in various physiological processes, including the relaxation of vascular smooth muscles, mediation of neurotransmission, regulation of inflammation and O_2 sensing; it can also protect against ischemia/reperfusion injury.[6–10] By contrast, its deregulation is correlated with Down syndrome and such diseases as Alzheimer's, diabetes and liver cirrhosis.[11–15] Despite the potential therapeutic implications, our understanding of the biological and pathological roles of this intriguing gas remains in its infancy.[16] Tracking and quantifying H_2S inside living cells are crucial to understanding the biological and pathological roles of this gas. To date, a variety of detection methods including colorimetric, electrochemical, chemiluminescence, chromatography and methylene blue assay have been developed for the detection of H_2S.[17–20] However, use of these methods in living organisms is generally limited by their invasive and destructive nature. By contrast, small fluorescent probes confer the advantages of high sensitivity and good cell permeability, and have attracted much attention for use in sensing and visualizing analytes in living cells.[21–28] Reduction-, nucleophilic- and metal sulfide-based strategies are the most frequently employed.[29] This technology provides real-time, easy-to-use, non-destructive detection methods for use in live cells or tissues.

Using this information, we introduced azo as a colorimetric group and synthesized a Cu(II) complex to research its anion binding ability, particularly for Na_2S (a commonly employed H_2S donor). Fortunately, crystals of the Cu(II) complex and ligand were also obtained. As expected, the complex could be used as a candidate colorimetric chemosensor for S^{2-} among the tested anions (S^{2-}, AcO^-, $H_2PO_4^-$, F^-, Cl^-, Br^- and I^-).

Abbreviations used: DMSO, Dimethyl sulfoxide; ESI, Electrospray ionization; HRMS, High resolution mass spectrometer; ESI-HRMS, Electrospray ionization High resolution mass spectrometer; MS, Mass spectrometry; NMR, Nuclear mass resonance; PBS, Phosphate-buffered saline; TMS, Tetramethylsilane; UV, Ultraviolet; Vis, Visible.

2 | EXPERIMENTAL

All reagents and solvents used were of analytical grade. Sodium sulfide hydrate and anions in the form of tetrabutylammonium salts,

e.g. $(n\text{-}C_4H_9)_4NCl$, $(n\text{-}C_4H_9)_4NBr$, $(n\text{-}C_4H_9)_4NI$, $(n\text{-}C_4H_9)_4NAcO$ and $(n\text{-}C_4H_9)_4NH_2PO_4$, were purchased from Aladdin Chemistry Co. Ltd (Shanghai, China). The anions were stored in a desiccator under vacuum and used without further purification. Dimethyl sulfoxide (DMSO) was distilled under vacuum after being dried with CaH_2. ^1H NMR spectra were measured on a Bruker Ascend™ 400 spectrometer, with chemical shifts reported in p.p.m. and using Tetramethylsilane (TMS) as the internal standard. High resolution mass spectrometer (HRMS) was performed with a Bruker Microtof-QIII spectrophotometer. Ultraviolet–visible (UV–vis) titration experiments were made on a Shimadzu UV2550 spectrophotometer at 298 K. The binding constant, K_s, was obtained using a non-linear least squares calculation method for data fitting.

The compound was synthesized according to the route shown in Scheme 1.

2.1 | Synthesis of 5-(azo-benzene)-salicylidene

5-(Azo-benzene)-salicylidene was synthesized in accordance with the literature.[30] HCl (37%, 10 ml) was added slowly to phenylamine (5 mmol, 465 mg) in 2 ml of water at 0–5°C. Then, $NaNO_2$ (20%, 20 ml) was added to the above-mentioned mixture and the solution was stirred for 1 h to give a bright yellow solution. Salicylaldehyde (5 mmol) dissolved in 150 ml of a saturated aqueous solution of Na_2CO_3 was added dropwise to the bright yellow solution for 1 h. After stirring for 4 h, the reaction mixture was neutralized with HCl. The deep-red crude solid was filtered and recrystallized from ethanol to afford a pure product. Yield: 75%. m.p. 124–126°C. ^1H NMR, δ 11.53 (s, 1H, −OH), 10.38 (s, 1H, −CH), 8.19 (d, J = 2.4 Hz, 1H, ph-H), 8.12 (d, J = 2.4 Hz, 1H, ph-H), 8.09 (d, J = 2.4 Hz, 2H, ph-H), 7.87 (d, 2H, J = 6.6 Hz, ph-H), 7.57 (t, 1H, J = 7.8 Hz, ph-H), 7.21 (d, J = 8.7 Hz, 1H, ph-H).

2.2 | Synthesis of ligand (5-(azo-benzene)-salicylidene-aniline)

5-(Azo-benzene)-salicylidene-aniline was synthesized in accordance with the literature.[31] It was obtained by refluxing an ethanol solution (40 ml) of 5-(azo-benzene)-salicylidene (10 mmol) and phenylamine (10 mmol) for 4 h and the red precipitate was recrystallized by ethanol, washed with water and dried under vacuum. A suitable single red crystal for X-ray crystal structural analysis was obtained. Yield: 73%. m.p. 126–128°C. ^1H NMR (400 MHz, $CDCl_3$) δ 13.90 (s, 1H, −OH), 8.79 (s, 1H, −CH=N-), 8.13–8.02 (m, 2H, ph-H), 7.92 (d, J = 7.3 Hz, 2H, ph-H), 7.55 (t, J = 7.4 Hz, 2H, ph-H), 7.51–7.45 (m, 3H, ph-H), 7.38–7.32 (m, 3H, ph-H), 7.18 (d, J = 8.5 Hz, 1H, ph-H) (Figure S1). ESI-MS (m/z): calc. for 302.1293 $(M+H)^+$, 324.1113 $(M+Na)^+$; found: 302.1293 $(M+H)^+$, 324.1087 $(M+Na)^+$ (Figure S2).

2.3 | Synthesis of bis(5-(azo-benzene)-salicylidene-aniline) Cu(II)

In accordance with the literature,[31] copper acetate hydrate (110 mg, 0.5 mmol) was added to a stirred solution of 5-(azo-benzene)-salicylidene-aniline (301 mg, 1 mmol) in 40 ml of ethanol. The mixture was stirred for 6 h at 78°C, and then left to stand for 2 days at room temperature. A suitable single brown crystal for X-ray crystal structural analysis was obtained, separated by filtration, washed with cyclohexane and water. Yield: 71%. ESI-HRMS (m/z): calc. for 686.1467 $(M+Na)^+$; found: 686.1433 $(M+Na)^+$ (Figure S3).

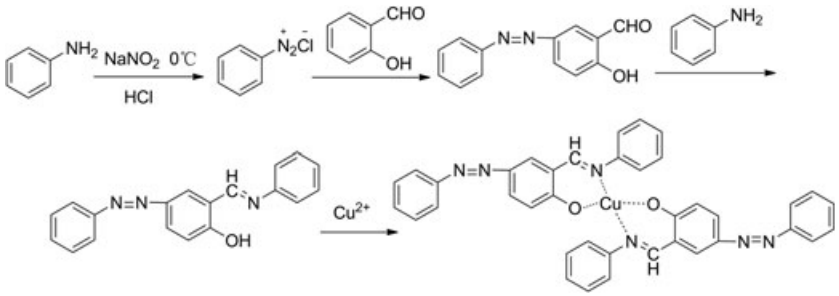
3 | RESULTS AND DISCUSSION

3.1 | X-Ray crystal structure

A brown single crystal of complex was obtained at room temperature from the solvent of CH_3CH_2OH solution by slow evaporation. To confirm the chemical structure of the complex, single crystal X-ray analysis was used to determine the structure of the copper complexes. An ORTEP view of the copper Schiff base complex with its atom numbering scheme is given in Figure 1. A summary of the crystal data, data collection and refinement details are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The bond angles all fit with the ideal value of 180°. The crystallographic data revealed that the metal center was four-coordinated by two phenolate oxygen and two imine nitrogen atoms of two Schiff base ligands. The Cu–O bonds are in the *trans* configuration and Cu–O distances are shorter than Cu–N distances. The Schiff base loses a proton from the hydroxyl group and acts as a single charged bidentate ligand coordinating to Cu(II). The ligands coordinate to the Cu(II) center in the *trans* orientation with respect to each other. The geometry around the metal center was a distorted square-planar, with a P21/c space group. These parameters are in close agreement with those reported for square-planar Cu (II) compounds.[32–35]

3.2 | UV–vis titration

The binding ability of the copper complex with anions was investigated using UV–vis absorption spectra in DMSO and DMSO–H_2O



SCHEME 1 Synthesis route for ligand and copper complex

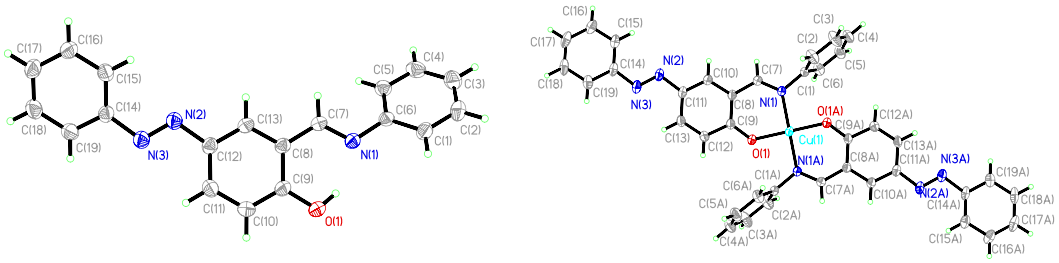


FIGURE 1 Molecular structure of ligand (left) and copper complex (right)

TABLE 1 Crystal Data and Structure Refinement for Complexes

Empirical formula	$C_{19}H_{15}N_3O$	$C_{38}H_{28}CuN_6O_{22}$
Formula weight	301.34	664.20
T (K)	296 (2)	293 (2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/c
Crystal color	Colorless	Brown
Crystal size (mm × mm × mm)	0.325 × 0.219 × 0.098	0.750 × 0.400 × 0.080
a (Å)	10.3339 (4)	10.0455 (10)
b (Å)	12.5776 (5)	19.644 (2)
c (Å)	12.3764 (6)	8.2552 (7)
α (°)	90	90
β (°)	100.3830 (10)	100.667 (3)
γ (°)	90	90
V ($Å^3$)	1582.29 (12)	1600.9 (3)
μ (mm^{-1})	0.081	0.727
Dcalc ($g{\cdot}ml^{-1}$)	1.265	1.378
Z	4	2
F (0 0 0)	632	686
θ range for data collection (°)	3.24 to 25.00	2.926 to 27.102
Index ranges	−11 · h · 12 −14 · k · 14 −14 · l · 14	−12 · h · 12 −25 · k · 25 −10 · l · 10
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F2	1.052	1.076
R1 and wR2 indices [I > 2σ(I)]	R1 = 0.0485, wR2 = 0.1209	R1 = 0.0424, wR2 = 0.0981
R1 and wR2 indices (all data)	R1 = 0.0595, wR2 =0.1341	R1 = 0.0602, wR2 = 0.01054
Largest difference in peak and hole (e $Å^{-3}$)	0.150 and −0.230	0.297 and −0.255

TABLE 2 Selected Bond Lengths (Å) and Angles (°) for the Complex

Cu(1)-O(1)	1.8739 (16)
Cu(1)-O(1)#1	1.8739 (16)
Cu(1)-N(1)	1.9934 (17)
Cu(1)-N(1)#1	1.9934 (17)
O(1)#1-Cu(1)-O(1)	180.0
N(1)-Cu(1)-N(1)#1	180.00 (11)
O(1)-Cu(1)-N(1)	91.83 (7)
O(1)#1-Cu(1)-N(1)#1	91.83 (7)
O(1)#1-Cu(1)-N(1)	88.17 (7)
O(1)-Cu(1)-N(1)#1	88.17 (7)

Symmetry transformations used to generate equivalent atoms: #1 −x + 1, −y + 1, −z + 2.

(4 : 1, v/v) at 298 K. UV–vis spectral changes in the copper complex (4.0×10^{-5} $mol{\cdot}L^{-1}$ in DMSO) are shown in Figure 2. It was clear that the maximal absorption band of the complex at 391 nm red-shifted gradually with increasing amounts of S^{2-}. Two processes were shown in the titration with S^{2-}. The valley at 328 nm changed to a peak when 1.2 equiv. of S^{2-} was added, and two clear isosbestic points at 363 and 462 nm suggested a strong interaction between the complex and S^{2-}. When 20 equiv. of S^{2-} was added, the maximal absorption band red-shifted to 430 nm with one clear isosbestic point at 392 nm. A new shoulder peak appeared at ~ 525 nm with 16 times enhanced absorbance. For an excellent chemosensor, high selectivity is very important. Analogous investigations were carried out on other normal anions. Addition of $H_2PO_4^-$ and F^- to the complex induced a blue shift from 392 to

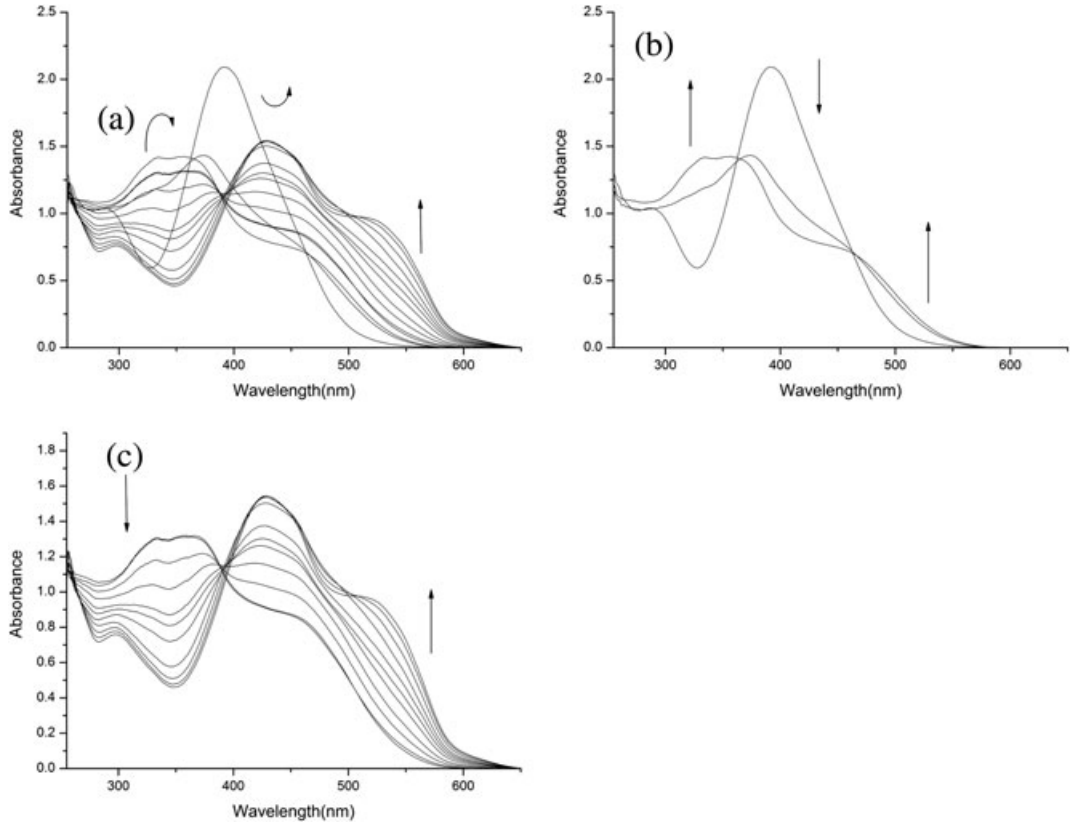


FIGURE 2 UV–vis spectral changes of Cu(II) complex upon the addition of S^{2-}. [complex] = 4.0×10^{-5} mol·L^{-1} in DMSO: (a) [S^{2-}] = 0–5.4×10^{-4} mol·L^{-1}; (b) [S^{2-}] = 0–3.2×10^{-5} mol·L^{-1}; (c) [S^{2-}] = $3.2–54 \times 10^{-5}$ mol·L^{-1}. Arrows indicate the direction of increasing anion concentration

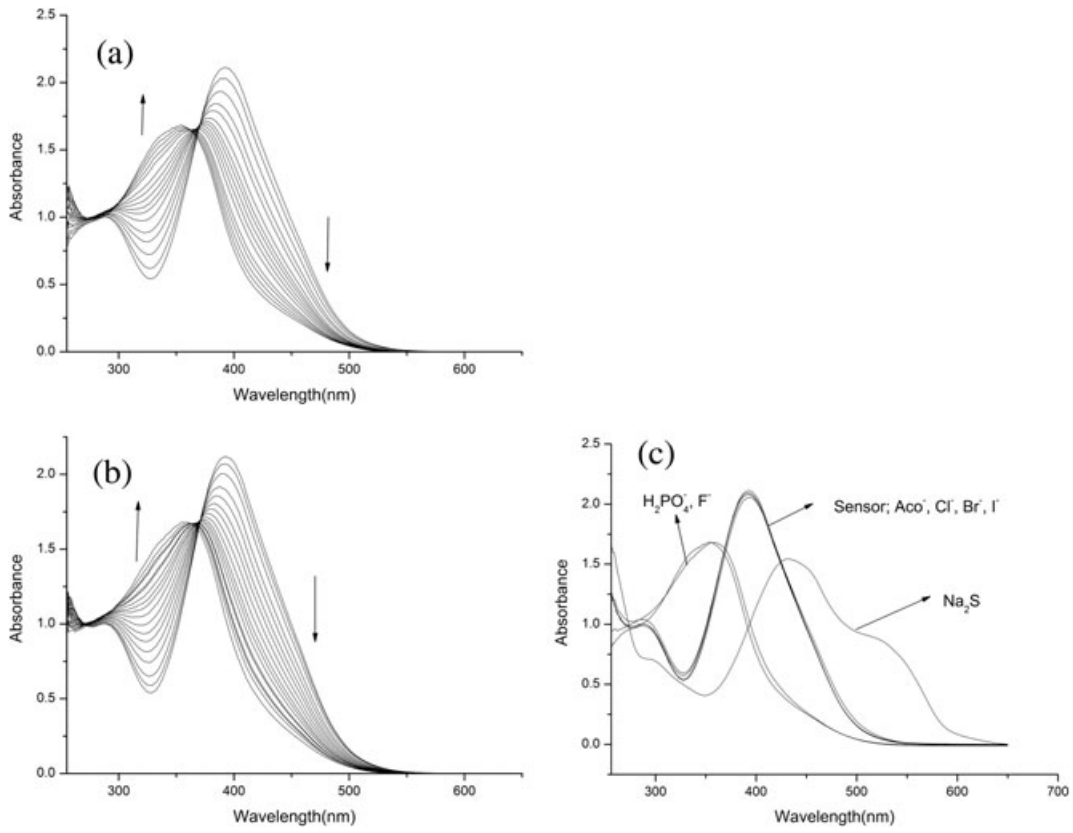


FIGURE 3 UV–vis spectral changes of Cu(II) complex (1) upon the addition of various anions. [complex] = 4.0×10^{-5} mol·L^{-1} in DMSO: (a) $H_2PO_4^-$ 0–6.2×10^{-4} mol·L^{-1}; (b) F^- 0–6.2×10^{-4} mol·L^{-1}. Arrows indicate the direction of increasing anions concentration

356 nm (Figure 3), indicating that the Cu(II) complex also interacted with the above anions. By contrast, the addition of AcO^-, Cl^-, Br^- and I^- did not induce any spectral responses. The above results indicated that Cu (II) complex showed almost no binding ability toward these anions. It was found that S^{2-} could lead to a color change in the complex from yellow to red, whereas other tetrabutylammonium salts did not induce any obvious color change (Figure 4) or spectral changes in the complex at 525 nm (Figure S6). Thus, the complex can be used to detect S^{2-} selectively using the naked eye.

3.3 | Fluorescent response

The fluorescence spectrum of the ligand in DMSO was characterized by strong emission at 341 nm (λ_{ex} = 296 nm). Upon interaction with Cu^{2+}, the system exhibited significant quenching in the fluorescence intensity (Figure S8). The fluorescence properties of the Cu(II) complex were investigated in DMSO–H_2O (4 : 1, v/v). The free probe displayed weak fluorescence upon excitation at 296 nm. As shown in Figure 5, on increasing the concentration of S^{2-}, the fluorescence emission intensity gradually strengthened at ~ 340 nm, because added S^{2-} could coordinate with Cu^{2+} and release the free ligand. Fluorescence titration of the chemosensor with various anions was conducted to examine the selectivity of the sensor. As shown in Figure 5(b), addition of AcO^-, $H_2PO_4^-$, F^-, Cl^-, Br^- and I^- (4.0×10^{-4} mol·L^{-1}) produced a nominal change in the fluorescence spectra of the probe. These results suggest that the complex is a practical probe for the detection of S^{2-} with high selectivity. In order to test the real-world applicability of the probe, we studied the S^{2-} recovery rate of the sensor in tap water. A ninefold enhancement in the fluorescence suggested that the probe would be a good candidate for the detection of S^{2-} in tap water (Figure 5d). In order to exclude the effect of pH, we then evaluated the fluorescence of the sensor in DMSO–phosphate-buffered saline (PBS) (4 : 1, v/v, pH 7.4). The fluorescence intensity of the emission band centered at 340 nm increased significantly. These results suggested that the complex was a practical candidate sensor for the detection of S^{2-} with high selectivity.

FIGURE 4 Photographic images of the complex sensor solution and the sensor solution upon the addition of different anions (20 equiv.). Left to right: free complex, S^{2-}, $H_2PO_4^-$, AcO^-, F^-, Cl^-, Br^- and I^-). The concentration of the sensor is 4.0×10^{-5} mol·L^{-1}

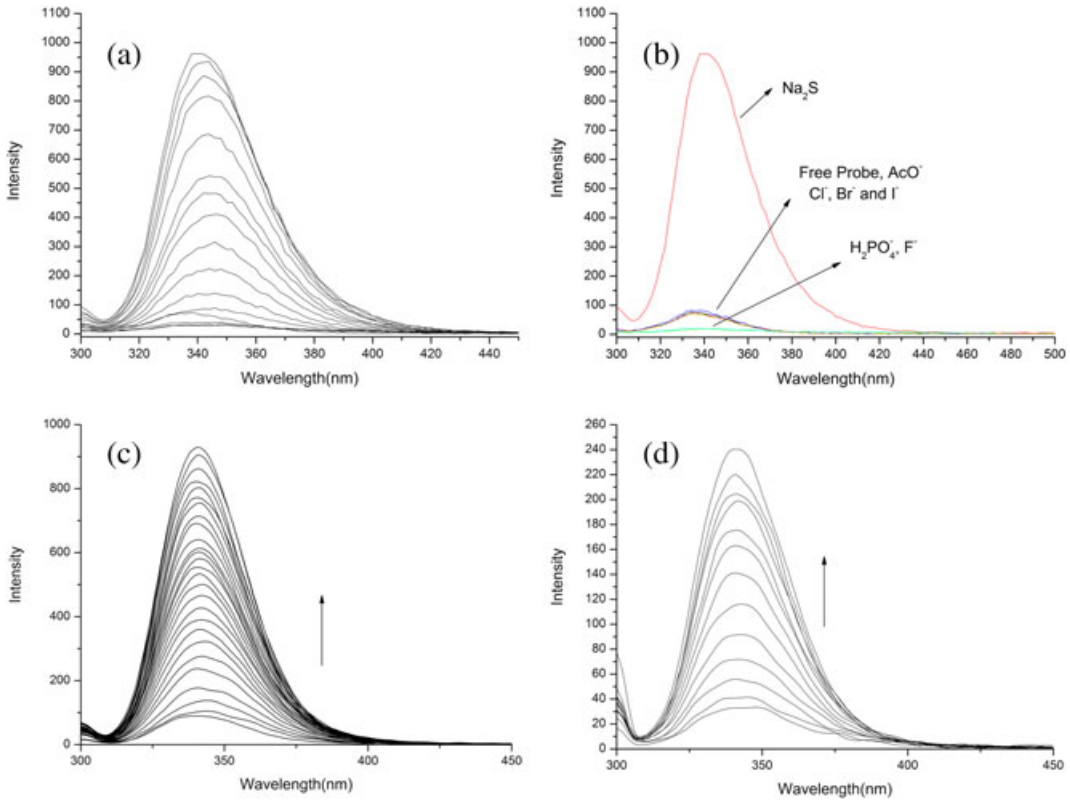


FIGURE 5 (a) Fluorescence response (λ_{ex} = 296 nm; slit widths = 5/5 nm) of copper probe (4.0×10^{-5} mol·L^{-1}) upon the addition of S^{2-} (0–1.4×10^{-3} mol·L^{-1}). Spectra were acquired in DMSO–H_2O (4 : 1, v/v). (b) Fluorescence spectra (λ_{ex} = 296 nm; slit widths = 5/5 nm) of probe (4.0×10^{-5} mol·L^{-1}) upon the addition of anions (8.0×10^{-4} mol·L^{-1}) in DMSO–H_2O (4 : 1, v/v). (c) Na_2S (0–7.2×10^{-4} mol·L^{-1}), in DMSO–tap water (4 : 1, v/v). (d) Na_2S (0–3.2×10^{-4} mol·L^{-1}), in DMSO–PBS (4 : 1, v/v) at pH 7.4

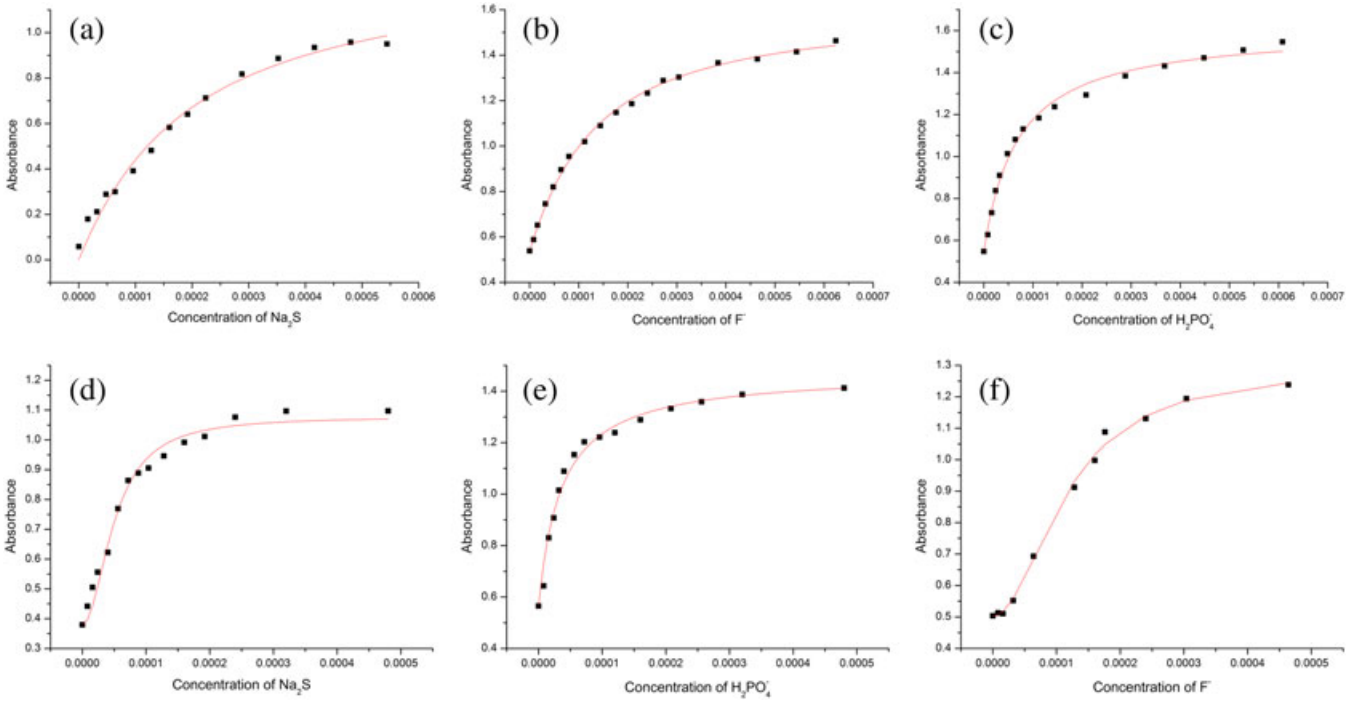


FIGURE 6 Non-linear fitting curves of Cu(II) complex in DMSO (a, b, c) or DMSO–H_2O(d, e, f, 4 : 1) upon the addition of anions

3.4 | Binding constant

The binding constant (*K*) of the complex derived from the fluorescence titration data was found to be 1.07 × 10^2 using a Bensi–Hildebrand plot (Figure S9), suggesting that the ligand showed greater binding capacity than sulfide with Cu^{2+}. Cu(II) complex interacted with S^{2-} at a ratio of 1 : 2 according to the non-linear fitting curves and Job's plot (Figure S10 and Figure 6). However, the complex interacted with other anions at a ratio of 1 : 1. The corresponding coefficients were all > 0.99. The binding constants were obtained and are listed in Table 3 based on the UV–vis data.[36,37] The anion binding constants (K_s) of the Cu(II) complex were in the order: $H_2PO_4^-$ > F^- > S^{2-} >> AcO^- ~ Cl^- ~ Br^- ~ I^-. From Table 3, it can be seen that the Cu(II) complex highlighted the different binding ratio between S^{2-} and other anions tested. This is probably due to the displacement reaction, in which the Cu^{2+} was captured by S^{2-} and free ligand was released from the complex; the other anions could only be coordinated with the complex. The above results indicate that the synthesized copper complex could be used as a chemosensor for the detection of S^{2-} in environmental or pharmaceutical samples.

3.5 | Mechanism

A full understanding of the principles that govern anion recognition has not yet been achieved. Similar to previously reported metal-based H_2S probes,[38–40] the red shift in the absorbance was most likely due to the much higher binding constant between sulfide and copper ions which

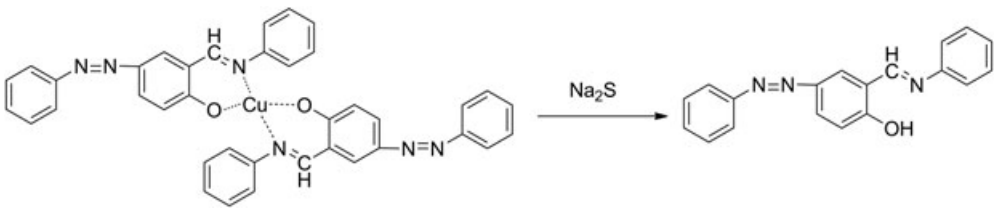
TABLE 3 Binding Constants of Cu(II) Complex with Various Anions

Anions	S^{2-}	$H_2PO_4^-$	F^-	AcO^-, Br^-, Cl^- or I^-
K_s	(2.36 ± 0.04) × 10^{4a}	(2.92 ± 0.09) × 10^{4b}	(2.77 ± 0.08) × 10^{4b}	ND[c]
K_s DMSO–H_2O (4:1, v/v)	(1.74 ± 0.04) × 10^{4a}	(2.27 ± 0.09) × 10^{4b}	(2.12 ± 0.08) × 10^{4b}	ND[c]

[a]The binding ratio of host–guest is 1 : 2.

[b]The binding ratio of host–guest is 1 : 1.

[c]The binding constant could not be determined.



SCHEME 2 Possible binding mode for the sensing of anions

enabled the added S^{2-} to snatch copper ions from the complex (Scheme 2). Direct evidence of the displacement mechanism came from ESI-MS. The copper complex itself exhibited a dominant peak at m/z = 686.1433 (Figure S3), however, after the addition of 0.5 equiv. of S^{2-}, this peak decreased and a new peak was seen at m/z = 302.1282 (Figure S4), corresponding to the developed ligand. By contrast, comprehensive UV–vis analysis shows that the other anions could only coordinate with the complex to form five-coordinated complexes. The binding ratio and binding constants also illustrate this. As shown in Table 3, the copper complex interacted with S^{2-} at the ratio of 1 : 2 in DMSO solution, which indicates that copper atoms were released from the complex.

4 | CONCLUSION

In summary, we designed and synthesized a novel, effectively selective and sensitive colorimetric and fluorometric chemosensor for Na_2S based on a Schiff base copper complex. The complex acts as a colorimetric chemosensor for S^{2-} in DMSO solution and allows the naked-eye detection of S^{2-} at room temperature. These properties make the complex suitable for the direct and rapid detection of biologically important S^{2-}. The advantages of the above method are the simplicity of the analysis and the low cost of the starting material. The complex has great potential in the environmental analysis of HS^-, S^{2-} and H_2S, although its use in bioanalysis remains a challenge. The preparation of a highly fluorescent copper complex is currently under investigation.

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