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Fluorescence Signaling of Hydrogen Sulfide in Broad pH Range Using a Copper Complex Based on BINOL−Benzimidazole Ligands

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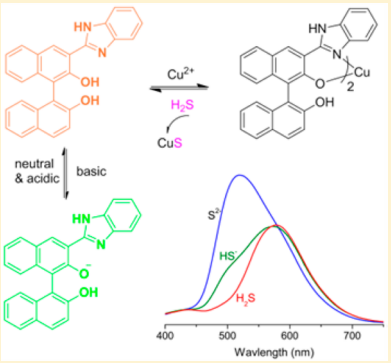
Supporting Information

ABSTRACT: A weakly fluorescent complex derived from a binaphthol−benzimidazole ligand was designed and synthesized for hydrogen sulfide at different pH conditions. It was demonstrated that the probe showed the same reactivity to various hydrogen sulfide species in a broad range of pH values to generate highly fluorescent product through a displacement reaction mechanism, whereas the product's fluorescence spectrum exhibited a hypsochromic shift of ∼73 nm (2393 cm^{-1}) as pH increased from neutral to basic, which can be used for distinguishing the various species of hydrogen sulfide. This turn-on fluorescence probe was highly selective and sensitive to hydrogen sulfide with a detection limit of 0.11 μM. It was then applied for evaluating the total content of sulfide (including hydrogen sulfide, hydrosulfide, and sulfide) as well as for the visual detection of gaseous H_2S in air using a simple test paper strip.



INTRODUCTION

Fluorescence molecular probes have been extensively applied in biological and environmental applications due to their advantages for the real time and space detection.[1−5] The fluorescent probes can provide multiple signaling modes such as quenching, enhancement, excimer/exciplex formation, lifetime, and anisotropy for substrate analysis.[6−8] Therefore, more efforts have been exerted on the synthesis of probes with new fluorescence spectral properties, especially organic molecule/complex-based fluorescent probes,[9−13] since they exhibit exceptional advantages and can be easily functionalized to monitor intra- and extracellular events with high chemoselectivity and biocompatibility.

Hydrogen sulfide, an important pollutant often found in environments, is emitted from industrial processes or microbial reduction of sulfate and sulfur-containing amino acids.[14] The toxic and explosive gas can rapidly deaden the sense of smell, which greatly increases the exposure risk. Hydrogen sulfide has also been found endogenously produced in endothelium cells and played important roles in biological systems.[14] The relevant species of hydrogen sulfide, namely, S^{2-}, HS^-, or H_2S, have been discovered involving many physiological processes, depending on various pH conditions.[15,16] However, many methods including colorimetric analysis,[17] electrochemical analysis,[18] and chemical analysis[19−22] for H_2S are dependent on the pH values of the systems. Thus, the selectivity and sensitivity of these methods greatly varies as different pH conditions. In fact, pH value of a sensing system is one of the main concerns and plays important and broad implications in environmental, industrial, and biomedical fields.[23−27] Therefore, a novel fluorescence probe that can distinguish the various species and evaluate the total content of sulfide is significant for the determination of hydrogen sulfide at different pH conditions.

We therefore designed a new benzimidazole derivative based on binaphthol (BINOL) ligand (Scheme 1) for two aims. First, benzimidazole is a derivative of imidazole with pK_a value of 5.5,[28] and binaphthol usually has a pK_a value of 10.28.[29] By constructing the combination of imidazole and BINOL ligand, more extensive application scopes would be possible using the synthesized molecule. In addition, new conjugated system with new optical properties would be achieved by deprotonation or protonation and thus could form a ratiometric fluorescence system with the change of pH value. Second, benzimidazole compound can coordinate with Cu^{2+} to form a stable copper coordination compound, and the paramagnetic Cu^{2+} center has a pronounced quenching effect on fluorophores.[30,31] As we know, the Cu^{2+} ion can form a very stable species with the targeting sulfide anion with K_{sp} of CuS = 1.27×10^{-36}.[32,33] On the basis of these facts, we expected that H_2S would selectively bind to Cu^{2+} of the complex in the presence of other similar species, resulting in selective fluorescence enhancement. The copper complex fluorescence probe could react to various species of hydrogen sulfide at different pH conditions and produce a strong fluorescent product in high yield as well as

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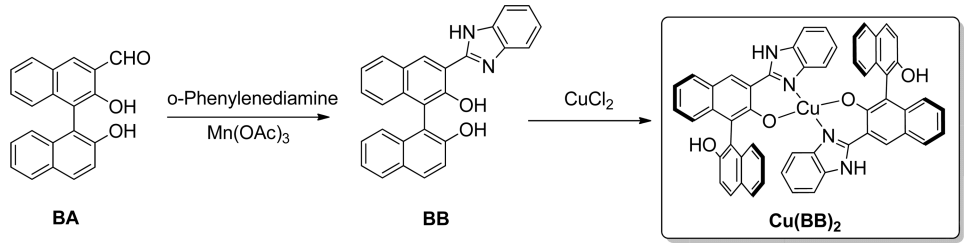
Scheme 1. Synthesis of the BINOL−Benzimidazole Ligand (BB) and Complex Cu(BB)$_2$ as a New Turn-on Fluorescence Probe for H_2S



different spectra shapes. This turn-on and ratiometric fluorescence probe has been demonstrated to be highly selective and sensitive.

EXPERIMENTAL SECTION

Materials. The chemicals and solvents were obtained from the commercial sources (Sigma-Aldrich or Aladdin) and used directly without further purification unless specified. The solvent *N*,*N*-dimethylformamide (DMF) was further purified before use by distillation using all-glass stills and was dried over molecular sieves before use. Aqueous solutions were all prepared using ultrapure water (18.2 MΩ·cm) from a Millipore water purification system, and all glassware was cleaned with ultrapure water and then dried before use. The compounds 2,2′-dihydroxy-[1,1′-binaphthalene]-3-carbaldehyde (BA) and $Mn(OAc)_3{\cdot}2H_2O$[34] was synthesized according to literature procedures.

Instrumentation and Methods. Fluorescence measurement was recorded on a PerkinElmer LS-55 luminescence spectrometer (Liantriant, U.K.) equipped with a plotter unit and a quartz cell (1 cm × 1 cm). UV−vis absorption was recorded at room temperature on a Shimadzu UV-2550 spectrometer. Photographs were taken with a canon 350D digital camera. pH values were measured by PHS-3C pH meter. ^{1}H NMR and ^{13}C NMR spectra were measured using a Varian Mercury-400 NMR spectrometer, and mass spectra were obtained on a Thermo Proteome X-LTQ MS mass spectrometer in ES positive or negative mode. The Fourier transform infrared (FTIR) spectra are obtained with a Thermo Scientific Nicolet iS10 spectrometer. Silica gel-60 (230−400 mesh) was used as the solid phases for column chromatography. Elemental analysis was performed using Germany Elementar VarioELIII. Thin-layer chromatography (TLC) was performed by using Merck F254 silica gel-60 plates.

pK_a Value Measurement. A 2.0 μL aliquot of the stock solution of probe in dimethyl sulfoxide (3.0×10^{-3} M) was added to a cuvette containing 2.0 mL of universal buffer solution by using a micro syringe to prepare 3.0 μM of probe solution, and the spectral changes in the fluorescence were measured as a function of the pH (4−11). The pK_a values of compound BB were calculated by linear regression analysis of the fluorescence data according to the following equation,[28] where R is the observed ratio (I_{517}/I_{iso}) at a given pH value. R_{max} and R_{min} are maximum and minimum limiting value of R, respectively, and c is the slope. I_a/I_b is the ratio of the fluorescent intensity in base (pH 10.0) to the intensity in acid (pH 5.0) at the wavelength chosen for the denominator of R.

$$\mathrm{pH} = \mathrm{p}K_a + c\left[\log\frac{(R - R_{min})}{(R_{max} - R)}\right] + \log\frac{I_a}{I_b}$$

Synthesis of Compound 3-(1*H*-benzo[*d*]imidazol-2-yl)-[1,1′-binaphthalene]-2,2′-diol (BB). $Mn(OAc)_3{\cdot}2H_2O$ (0.2 mmol) was added to a stirred solution of benzene-1,2-diamine (10.8 mg, 0.1 mmol) and compound BA (31.4 mg, 1 mmol) in acetic acid in a flask equipped with a dry-air inlet tube. The mixture was stirred at room temperature for 8 h. The reaction was monitored by TLC. Then the reaction was quenched by adding water and extracted with ethyl acetate. Combined organic layer was evaporated to dryness on a rotary evaporator. The solid was purified on silica gel chromatography eluted with dichloromethane/petroleum (1:1 v/v, R_f = 0.32 by TLC) to give the desired product BB (22.6 mg, 0.056 mmol, 56.2%). High-resolution mass spectrometry (HR-MS) (*m*/*z*): $(M-H)^-$ calcd for $C_{27}H_{17}N_2O_2$ 401.1296, found 401.1481. $(M+H)^+$ calcd for $C_{27}H_{19}N_2O_2$ 403.1441, found 403.1408. FT-IR (KBr, cm^{-1}): 3412 (br, s), 3250 (br, s), 3057 (s), 1636 (s), 1590 (m), 1504 (s), 1453 (s), 1393 (w), 1362 (w), 1340 (s), 1321(w), 1275 (s), 1254 (w), 1213 (w), 1151 (w), 966 (w), 935 (w), 907 (w), 853 (W), 778 (W), 737 (s). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.84 (t, *J* = 9.0 Hz, 2H), 7.58 (m, 2H), 7.37 (d, *J* = 8.9 Hz, 1H), 7.34−7.26 (m, 5H), 7.19 (m, 4H). ^{13}C NMR (400 MHz, CD_3OD) δ 157.46, 150.64, 137.16, 134.16, 128.16, 127.07, 125.82, 124.41, 122.82, 122.26, 120.96, 117.88, 112.76, 103.85. Anal. Calcd for $C_{27}H_{18}N_2O_2$: C, 80.58; H, 4.51; N, 6.96. Found: C, 80.52; H, 4.43; N, 6.89%.

Synthesis of Compound Cu(BB)$_2$. To a stirred solution of compound BB (50 mg, 0.12 mmol) in 10 mL of tetrahydrofuran (THF), NaH (6 mg, 0.15 mmol) was added at 0 °C (***Caution!*** *H_2 gas released*). The mixture was stirred for an hour and warmed to room temperature. Then the powder of anhydrous $CuCl_2$ (8 mg, 0.06 mmol) was slowly added to the above reaction mixture and stirred overnight. Removal of the solvents under reduced pressure gave a dark green residue, followed by extraction with ethanol (40 mL) to remove the insoluble impurities. Removal of ethanol under reduced pressure gave a brown residue. No suitable single crystal for X-ray crystal structural analysis was obtained by recrystallization in EtOH. Yield: 44.1 mg, 41 mmol, 82%. UV−vis: 319, 334, and 420 nm. Anal. Calcd for $C_{54}H_{34}CuN_4O_4$: C, 74.86; H, 3.96; N, 6.47. Found: C, 74.52; H, 4.11; N, 6.59%. FTIR (KBr, cm^{-1}): 3422 (br, s), 1623 (s), 1598 (s), 1559 (w), 1497 (m), 1461 (s), 1377 (m), 1359 (m), 1327 (w), 1284 (w), 1228 (m), 1152 (m), 983 (w), 951 (w), 896 (w), 859 (w), 779 (w), 753 (s), 622 (w), 432 (w). HR-MS: $(M+Na)^+$ calcd for $C_{35}H_{34}CuNaN_4O_4$ 888.1768, found 888.1660.

Procedure for Detecting Sulfide and Other Reactive Species. An aqueous stock solution of Na_2S (10 mM) was freshly prepared for further use. The solutions of cysteine (Cys), 3-mercaptopropionic acid (MPA), and ascorbic acid (AA) were prepared with concentrations of 10 mM in deionized water. Copper(II) chloride (1 mM) aqueous solution was prepared for preparation of probe. HOCl is freshly prepared with a stock concentration of 10 mM and determined on the basis of the Beer−Lambert law using the molar extinction coefficient of 100 $M^{-1}{\cdot}cm^{-1}$ (235 nm) at pH 6.2. A stock solution of 10 mM of H_2O_2 is freshly prepared, and the concentration of the solution is determined by measuring the absorbance at 230 nm using the molar extinction coefficient of 81 $M^{-1}{\cdot}cm^{-1}$. Hydroxyl radical ($OH^{\bullet}$) is generated in situ from Fenton reaction on mixing $FeSO_4{\cdot}7H_2O$ with 2 equiv of H_2O_2. The concentration of $OH^{\bullet}$ is estimated from the concentration of Fe^{2+}. Other ions or anions were prepared with a stock solution concentration of 10 mM.

RESULTS AND DISCUSSION

Compound BB was synthesized from one-pot reaction between 2,2′-dihydroxy-[1,1′-binaphthalene]-3-carbaldehyde (BA) and benzene-1,2-diamine using manganese triacetate as catalysts in HOAc (Scheme 1). The cloudy and heterogeneous reaction mixture of compound BA and benzene-1,2-diamine in HOAc became brown and homogeneous after 8 h of stirring at room

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temperature, indicating the completion of reaction. The desired compound BB was obtained in 56% yield as pale yellow solid after purification on column chromatography. The structure of compound BB was characterized with HR-MS, IR, and ^{1}H NMR as well as ^{13}C NMR (Figure S1−S4 in the Supporting Information). From the FT-IR results in Supporting Information, Figure S2, we can see that the overlapped strong broad peak of 3412 and 3250 cm^{-1} indicates the existence of hydroxyl group and N−H group. The vibration at 1636 cm^{-1} indicates the C═N bond in the imidazole ring. The two vibrations at 1275 and 1213 cm^{-1} can be attributed to C−N bond in the imidazole ring and Ar−O bond, respectively. The absorption spectra of compound BB showed four maximum absorption peaks at 283, 319, 334, and 384 nm, respectively. The fluorescence spectra showed one maximum emission peak at 590 nm, suggesting a large Stokes' shift of more than 200 nm (9093 cm^{-1}, Supporting Information, Figure S5). The Stokes' shift was larger than common fluorophores such as fluorescein, rhodamine, and BODIPY, as well as cyanine dyes, which is desirable for suppressing self-quenching, minimizing measurement errors, and increasing detection sensitivity to a great extent.[35,36]

The benzimidazole−Cu complex was synthesized from the reaction of compound BB with $CuCl_2$ in a 2:1 ratio in the presence of NaH in THF as shown in Scheme 1. The desired product was obtained with high yield and characterized with FT-IR, HR-MS, and UV−vis spectroscopies, as well as elemental analyses. From the FT-IR results (Figure S6 in the Supporting Information), we can see that the hydroxyl group vibration at 3250 cm^{-1} becomes less obvious, while the vibration band of C═N bond broadens and shifts to 1623 cm^{-1}, indicating the O and N atom participation in coordination bond formation. The Ar−H strong band at 737 cm^{-1} in compound BB blue-shifts to 753 cm^{-1}. In addition, the appearance of 622 and 432 cm^{-1} peak confirmed the formation of Cu−O and Cu−N bonds.[37] These results suggested that compound BB coordinated with Cu^{2+} through hydroxyl group and benzimidazole nitrogen atom. To better understand the binding mode of compound BB with Cu^{2+}, stoichiometric reaction and the electrospray ionization mass spectrometry (ESI-MS) spectra were systematically performed in the presence of Cu^{2+}. The fluorescence emission intensities of compound BB in the buffer solutions were completely quenched upon addition of 0.5 equiv of $CuCl_2$ (Supporting Information, Figure S7). Addition of more $CuCl_2$ up to 1 equiv did not further decrease the fluorescence, implying a 2:1 coordination of compound BB with Cu^{2+}. In addition, the Job's plot fluorescence titration revealed a break at 0.33, also suggesting the formation of 2:1 complexes (Supporting Information, Figure S8). Furthermore, the ESI-MS spectrum displays a dominating new peak at m/z = 888.16 (M + Na^+), which is consistent with the theoretical value of complex $Cu(BB)_2$ (Figure S9 in the Supporting Information). The result further indicates the formation of the complex with 2:1 stoichiometry binding of compound BB with Cu^{2+}.

We then evaluated the fluorescence response of compound $Cu(BB)_2$ toward sulfide in buffer solution at various pH values. As shown in Figure 1a, the fluorescence intensity at 590 nm of the $Cu(BB)_2$ in PBS 7.4 solution was gradually increased with the amount of S^{2-}. The orange fluorescence was easily visualized from the probe solution after sulfide addition. However, when compound $Cu(BB)_2$ was dissolved in phosphate-buffered solution (PBS) at pH 10.0, the fluorescence

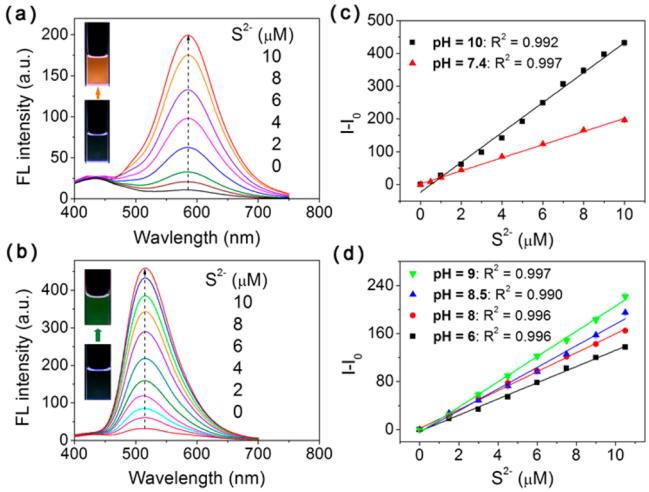

Figure 1. (a) Fluorescence spectra (λ_{ex} = 384 nm) of complex $Cu(BB)_2$ (1.5 μM) upon addition of S^{2-} (0−10 μM) at pH 7.4 in 50 mM PBS/DMF (4:1). (b) Fluorescence spectra (λ_{ex} = 384 nm) of complex $Cu(BB)_2$ (1.5 μM) upon addition of S^{2-} (0−10 μM) at pH 10 in 50 mM PBS/DMF (4:1). (c) The linearity of increased fluorescence intensity with the concentrations of added S^{2-} (0−10 μM) at pH 7.4 (red) and pH 10.0 (black). (d) The linearity of increased fluorescence intensity with the concentrations of added S^{2-} (0−10.5 μM) at various pH values in 50 mM PBS/DMF (4:1). I and I_0 are the fluorescence intensity of complex in the presence and absence of S^{2-}, respectively.

emission band was shifted to 517 nm and increased dramatically upon addition of sulfide. Meanwhile, the fluorescence color was changed to green as shown in Figure 1b. Interestingly, the increases in both emission bands were in a good linear relationship (R^2 = 0.997 and 0.992, respectively), which can be calibrated for quantification (Figure 1c). The limit of detection (LOD) was found to be 0.11 μM at pH 7.4 based on the definition of three times the deviation of the blank signal (3σ), which is comparable to those of other sulfide probes.[38−41] The fluorescence of probe $Cu(BB)_2$ can also be turned on by hydrogen sulfide following a dose−response manner at various pH values of 6.0, 8.0, 8.5, and 9.0 (Figure 1d and Figure S10 in the Supporting Information). It can be seen that although the enhanced fluorescence spectral shapes depend on pH values, the LODs for sulfide obtained at different pH values are very close (0.37 μM at pH 6, 0.13 μM at pH 8, 0.39 μM at pH 8.5, and 0.43 μM at pH 9.0). The result shows that the probe $Cu(BB)_2$ has the same reactivity to sulfide at different pH conditions, suggesting that the concentration of sulfide can be determined via the increased integrated fluorescence intensity.

The interaction between probe $Cu(BB)_2$ and sulfide was thoroughly examined with UV−vis absorption spectra. Apparently spectral changes were observed upon addition of Cu^{2+}. The absorption peaks at 319, 334, and 384 nm were decreased, while a new absorption peak around 420 nm appeared simultaneously (Figure 2), indicating the formation of the new Cu complex. The binding constant (K) derived from the fluorescence titration data was found to be 3.14×10^2 (R^2 = 0.993, Figure S11 in the Supporting Information) using Benesi−Hildebrand plot,[42] which suggested that compound BB exhibited weaker binding capacity than sulfide with Cu^{2+}, hence making the compound BB easily displaceable by S^{2-}. Actually, treatment of $Cu(BB)_2$ with S^{2-} gave the identical absorption spectrum of compound BB, implying release of

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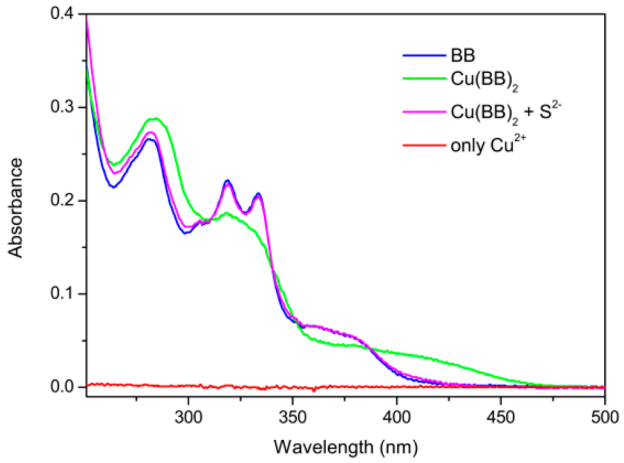

Figure 2. Absorption spectra of compound BB (3 μM), Cu^{2+} (1.5 μM), complex $Cu(BB)_2$ (1.5 μM) and the mixture of complex $Cu(BB)_2$ (1.5 μM) upon addition of S^{2-} (10 μM).

fluorescent compound BB from the complex by S^{2-}. Interestingly, the probe $Cu(BB)_2$ displayed an "ON−OFF−ON" loop in fluorescence when S^{2-} and Cu^{2+} were added alternately, with reversible formation−separation of the complex $Cu(BB)_2$ (Figure S12 in the Supporting Information). These results confirmed a displacement mechanism between the $Cu(BB)_2$ complex and target analyte S^{2-}.

In view of the release of fluorescent compound BB from the probe $Cu(BB)_2$ upon addition of sulfide, the interesting phenomenon of fluorescence response dependent on pH conditions can be explained by the spectroscopic properties of compound BB. The pH-dependent fluorescence properties of compound BB were presented in Figure 3a. Under acidic conditions of pH 5.0−7.0, the fluorescence properties were almost identical. When the pH value was increased from neutral

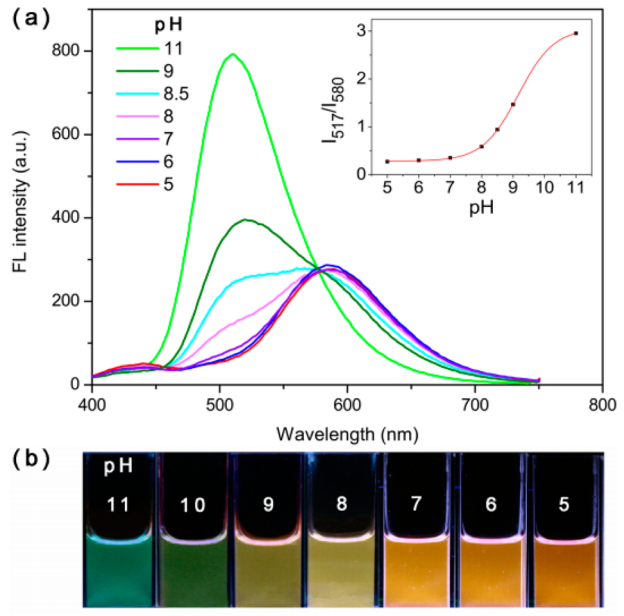

Figure 3. (a) pH dependence of the fluorescence intensity of compound BB (3 μM) in buffer solutions. (inset) The ratiometric calibration curve of I_{517}/I_{580} (intensity at 517 nm vs intensity at isoemissive point 580 nm). (b) Fluorescence color change of compound BB in PBS with varied pH value.

to basic (pH 7.0 to 11), however, the fluorescence peak exhibited remarkable hypsochromic shift from 590 to 517 nm as well as increased fluorescence intensity, resulting in an isoemission point at 580 nm. The spectral blue-shift is due to the deprotonation of phenolic hydroxyl group,[26] a well-known phenomenon in intramolecular hydrogen-bonded molecules.[43,44] The changes in the fluorescence intensity of the two emission wavelengths at 590 and 517 nm resulted in a continuous fluorescence color evolution (Figure 3b) from orange to green in sensitive response to the pH change from neutral to basic. Thus, compound BB showed great potential in fluorescence monitoring pH fluctuation under physiological conditions. Furthermore, the first pK_a value of the compound BB was estimated to be 8.21 from the titration curve of emission ratios (I_{517}/I_{580}) at isoemission point (I_{580}) and 517 nm (I_{517}), implying that the probe was more suitable for assessing basic media. The lower pK_a value than binaphthol (10.28) may be attributed to the benzimidazole group, a derivative of imidazole with general pK_a values at 5−6. It can be concluded that the BINOL group acts as the protonated form, while the benzimidazole group containing imidazole ($pK_a \approx 5.5$), which is usually used for acidic pH, acts as the protonation site.[28] That is to say, the fluorescence spectroscopic properties of compound BB under a wide pH range result from the combined contribution of BINOL and benzimidazole group. Although the compound BB exhibited tremendous fluorescence hypochromatic shift as well as the increased fluorescence intensity when the pH value changed from neutral to basic, there was almost no spectral change of the fluorescence peak at 590 nm in a range of physiological condition or acidic media. This property makes it a probable fluorescence precursor, which could be used in physiological pH condition.

The fluorescence properties of the complex $Cu(BB)_2$ probe were then investigated prior to the fluorescence response to sulfide in solution at various pH values. The probe $Cu(BB)_2$ has very weak fluorescence at pH values from 5.0 to 10.0 both at 517 and 590 nm (Figure 4a), indicating good stability in these buffer solutions. Time dependence of the fluorescence experiments was investigated in the absence and presence of 10 μM of S^{2-} (Figure S13 in the Supporting Information). The fluorescence intensity of $Cu(BB)_2$ immediately increased and reached the maximum value in 4 min upon the addition of 1 equiv of sulfide. Further prolonging the irradiation time to 30 min at 384 nm, the fluorescence intensity still keeps stable and constant, which suggested the good photostability of the system, indicating its fast response to sulfide and reliability for practical analysis in environmental and physiological conditions. Interestingly, distinct fluorescence spectra were obtained in the presence of sulfide at pH 5.0−10.0 (Figure 4b). The fluorescence intensity was increased conformably at 590 nm, while it increased continuously as the pH value changed from 5.0 to 10.0 at 517 nm, resulting in stepped ratio curve of $F_{517\ nm}/F_{590\ nm}$ from 0.3 to 3.0 (Figure 4c,d). This is in agreement with our observation that compound BB exhibits different fluorescence spectra in various pH values. It can also be concluded that upon addition of sulfide, compound BB was released from complex $Cu(BB)_2$, and thus the fluorescence was switched on. In addition, we can estimate the dominant species (S^{2-}, HS^-, or H_2S) by comparing the fluorescence spectra shapes and/or ratio of $F_{517\ nm}/F_{590\ nm}$ of the probe $Cu(BB)_2$ in solutions.

The fluorescence responses of the probe to other anions (AA, SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, NO_3^-, PO_4^{3-}, SCN^-, HCO_3^-,

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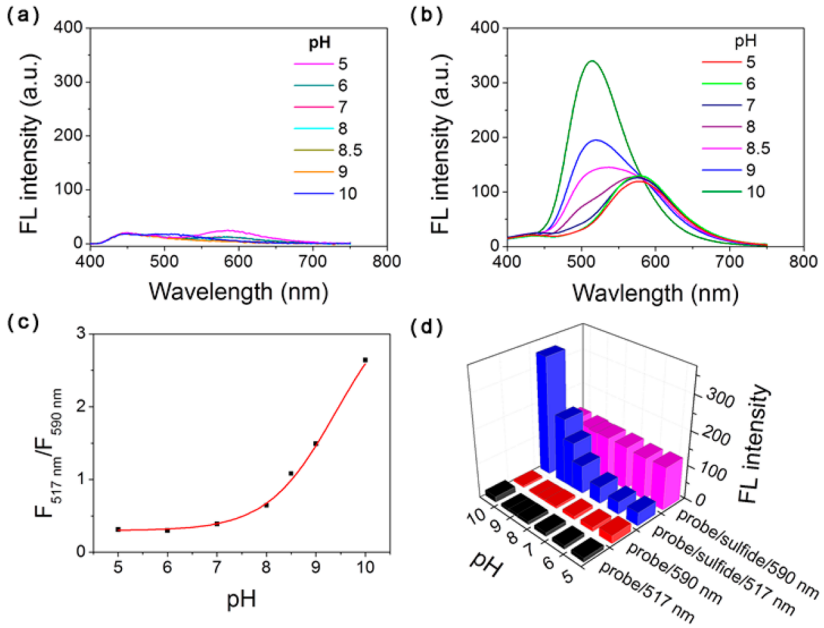

Figure 4. Fluorescence spectra (λ_{ex} = 384 nm) of complex $Cu(BB)_2$ (1.5 μM) in the absence (a) and presence (b) of S^{2-} (6 μM) and fluorescence ratio changes (c) at various pH values in 50 mM PBS/DMF (4:1). (d) The bars represent the fluorescence intensities of complex $Cu(BB)_2$ at 517 nm (black) and 590 nm (red) and complex $Cu(BB)_2$ with addition of sulfide at 517 nm (blue) and 590 nm (magenta), respectively.

N_3^-), biothiols (Cys, MPA), and reactive oxygen species or reactive nitrogen species (H_2O_2, HOCl, $O_2^{\bullet-}$, NO, $ONOO^-$) were carefully examined at the same conditions (Figure 5 and Figure S14 in the Supporting Information). Clearly, other species including the mercapto compounds cysteine and mercaptopronic acid showed no apparent fluorescence enhancement compared with sulfide. It can be seen that the copper complex $Cu(BB)_2$ probe displayed 20-fold fluorescence enhancements upon treatment with H_2S, while gave only threefold fluorescence increase upon the treatment of Cys or MPA, implying that the probe is capable of differentiating the inorganic sulfide and organic thiols. In addition, no apparent interference was obtained in fluorescence intensity of the probe solution in the presence of other potential coexisting species even at the concentration of 100 μM. The results imply the high selectivity of the complex probe for fluorescent identification of S^{2-} over other anions and species in assay conditions.

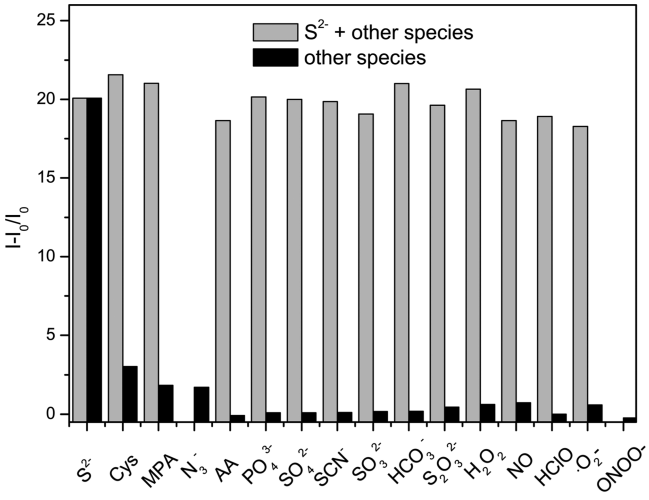

Figure 5. Effect of various species on the fluorescence intensity of complex $Cu(BB)_2$ in DMF/PBS 10 (1:4 v/v). The concentration of sulfide was 10 μM, and the concentration of other species was 100 μM. The gray bar represents the interference of common species with the fluorescence intensity for the detection of S^{2-}. I and I_0 are the fluorescence intensity of $Cu(BB)_2$ in the presence and absence of S^{2-}, respectively.

Because of the fast response of $Cu(BB)_2$ probe to sulfide in aqueous media, we wonder if it can be used for the detection of gaseous H_2S in air. To demonstrate the application, 1 mL of gas mixture containing H_2S was bubbled into the $Cu(BB)_2$ probe solution in EtOH by a syringe. The orange fluorescence from the solution quickly appeared and was easily visualized under a UV lamp (Figure 6a). We further demonstrated that the probe could be used for the visual monitoring of gaseous H_2S. First, a test paper strip was fabricated by dropping the probe solution on a piece of paper.[45] Such as-prepared test paper strips were exposed to gas samples containing different amounts of H_2S for 2 min. They were then illuminated under a UV lamp. It can be seen that different fluorescence colors were observed on the paper strips depending on the concentration of hydrogen sulfide (Figure 6b). The results showed a dose-responsive brightness to the concentrations of H_2S in the gas samples (Figure 6c). The visual detection limit was thus found as ~11.2 ppm with the test paper strips. These results suggest that the developed test papers immobilized with $Cu(BB)_2$ probe can be used for rapid and visual detection of gaseous H_2S in air.

CONCLUSIONS

In summary, a multifunctional fluorescence system was developed and demonstrated for fluorescence turn-on detection of hydrogen sulfide in a wide pH range. Combination of binaphthol and imizadole give a new fluorescent probe compound BB, which is highly sensitive to pH in basic media with apparent color change from orange to green. A turn-on fluorescence probe $Cu(BB)_2$ was obtained by further coordination with copper. The probe was demonstrated to be

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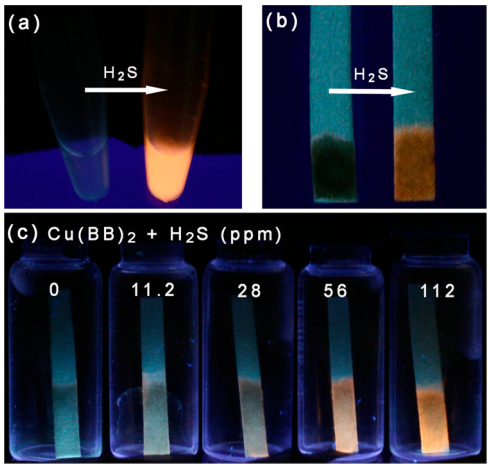

Figure 6. Visual detection of gaseous H_2S under illumination of a 365 nm UV lamp in the dark. (a) The fluorescence of $Cu(BB)_2$ probe solution was switched on immediately by bubbling H_2S with a syringe. (b) The test paper strip immobilized with $Cu(BB)_2$ probe exposure to H_2S atmosphere give obvious fluorescence color change. (c) The test paper strips were exposed in H_2S gas with different concentrations.

highly sensitive and selective for hydrogen sulfide detection in various pH conditions and can also be used for the identification of the dominant species of H_2S in aqueous solution. In addition, the probe $Cu(BB)_2$ has been developed for the visual detection of gaseous H_2S in air using a simple test paper strip. This concept reported herein could be extended to the detection of a wide range of organic and biological molecules through proper functional modification.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

ESI-MS, FT-IR, ^1H NMR, ^{13}C NMR, absorption, and fluorescence spectra of compound BB, FT-IR and ESI-MS spectra of $Cu(BB)_2$, fluorescence titration spectra and Job's plot study of compound BB with Cu^{2+}, fluorescence spectra of $Cu(BB)_2$ upon addition of hydrogen sulfide, as well as the kinetic curve and selectivity study. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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