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A chromogenic dioxetane chemosensor for hydrogen sulfide and pH dependent off–on chemiluminescence property

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ABSTRACT

In this paper, a rapid and highly selective chromogenic naked eye detection of hydrogen sulfide was achieved by a 1,2-dioxetane based chemiluminescent probe in aqueous media at pH 7.4. Chemiluminescence property of the probe can be modulated depending on the pH value of medium.

1. Introduction

The emission of light produced by a chemical reaction is described as chemiluminescence and this phenomenon is utilized in nature frequently and referred to as bioluminescence [1–5]. The most known bioluminescence assay is derived from firefly luminescence that arises from luciferase catalyzed aerobic oxidation of luciferin [6]. Among the most popular chemiluminescent substrates such as oxalate esters, luminol, acridinium esters, 1,2-dioxetanes have received a great deal of attention due to their unique emission properties [7,8]. Following the synthesis of a first member of dioxetanes by Kopecky and Mumford, many four-membered ring peroxide derivatives have been synthesized [9]. The unimolecular or catalyzed decomposition of 1,2-dioxetanes result in chemiluminescence emission. The unimolecular thermal decomposition of 1,2-dioxetanes having uncharged substituents can be explained with concerted and biradical mechanisms. In the thermally induced concerted mechanism, two carbonyl products which one of them is in the singlet or triplet excited state are formed directly via homolytic cleavage of the C—C and O—O bonds of four membered ring. In the biradical mechanism, an intermediate singlet biradical, which can yield carbonyl products, is formed [10,11]. The latter decomposition mechanism of 1,2-dioxetanes is the chemically initiated intramolecular charge transfer induced chemiluminescence (CTICL) of dioxetanes. In the CTICL mechanism, decomposition is catalyzed by substrates such as a base or a metal ion. Generally the hydroxyphenyl group is often used as an aromatic electron donor. The deprotanation of hydroxy phenyl group leads to formation of an anionic phenolate group which causes intramolecular charge transfer (CT). The CT occurs from phenolate to the O—O of dioxetanes in order to induce decomposition into respective excited species [11].

Redox active sulfur containing molecules which are known as reactive sulfur species (RSS) play crucial roles via oxidation or reduction of biomolecules under physiological conditions [12–17]. One member of this family is hydrogen sulfide (H_2S) which has a characteristic foul odor of rotten egg. Since endogenously produced H_2S has significant roles in biological signaling and metabolic process such as modulation of neurotransmission, cardiovascular protection, regulation of cell growth, stimulation of angiogenesis, detection of this molecule attracts growing interest in literature [17–25].

A chromogenic chemosensor generally transduces a chemical signal into a color change and this type of sensing attracted much attention last two decades [25–30]. In this study, we designed and synthesized a novel fast responding 1,2-dioxetane based a chromogenic probe **6** for sensing H_2S. After the design of probe **6**, it was synthesized in six steps. The detection of H_2S was achieved successfully by probe **6** and the highly selective sensing process can be monitored by a color change of solution with naked eye and also via appearance of a new absorbance band in electronic absorption spectra at pH 7.4. On the other hand, chemiluminescence of probe **6** obtained at pH 12.4 since it decomposed at this pH value.

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0925-4005/

2. Materials and methods

2.1. Materials

4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) was purchased from Sigma–Aldrich. Sodium hydroxide solution (0.1 mol/L) was added to aqueous HEPES (100 mmol/L) to adjust the pH to 7.4. Spectrophotometric grade solvents were used for spectroscopy experiments. Flash column chromatography (FCC) was performed by using glass columns with a flash grade silica gel (Merck Silica Gel 60 (40–63 μm)). Reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates (Merck Silica Gel PF-254), visualized by UV-Vis light. All organic extracts were dehydrated over anhydrous Na_2SO_4 and concentrated by using rotary evaporator before being subjected to FCC. All other chemicals and solvents were supplied from commercial sources and used as received.

2.2. Instruments

A pH meter (Oakton, manufactured by Eutech instruments) was used to determine the pH. Ultraviolet–visible (UV–vis) spectra were recorded on a Varian Cary 100 UV–vis spectrophotometer. Chemiluminescence measurements were done on a Varian Eclipse spectrofluorometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Spectrospin Avance DPX 400 spectrometer using $CDCl_3$ as the solvent. Chemical shifts values are reported in ppm from tetramethylsilane as internal standard. Spin multiplicities are reported as the following: s (singlet), d (doublet), m (multiplet). HRMS data were acquired on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS.

2.3. Synthesis of compounds

2.3.1. Synthesis of 3-benzyloxybenzaldehyde (**1**)

3-Hydroxy benzaldehyde (1 g, 8.19 mmol) was dissolved in dry THF. When reaction mixture was cooled to 0 °C, triethylamine (TEA) (1.71 mL, 12.2 mmol) was added and mixed for 20 min. After the addition of catalytic amount of 4-(dimethylamino)pyridine (DMAP), benzoyl chloride (1.38 mL, 12.2 mmol) was added dropwise to the reaction mixture and it was left to stir at room temperature. The progress of the reaction was monitored by thin layer chromatography (TLC). When TLC showed no starting material, reaction was concentrated to half of it. The residue was diluted with ethyl acetate (EtOAc) and extracted with brine. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc/Hexane (1:5, v/v) as the eluent. Compound **1** was obtained as white solid (1.41 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 10.04 (s, 1*H*), 8.23 (d, *J* = 8.4 Hz, 2*H*), 7.78–7.82 (m, 2*H*), 7.57–7.69 (m, 2*H*), 7.51–7.57 (m, 3*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1, 164.8, 151.5, 137.8, 133.9, 130.24, 130.21, 129.0, 128.71, 128.69, 127.9, 127.3, 122.5 ppm.

2.3.2. Synthesis of 3-benzyloxybenzaldehyde dimethyl acetal (**2**)

Compound **1** (1 g, 4.42 mmol), 2,2′-dimethoxypropane (1.2 mL) and catalytic amount of *p*-toluenesulfonic acid was mixed at 75 °C. The progress of the reaction was monitored by TLC. When TLC showed no starting material, reaction was concentrated to half of it. The residue was diluted with EtOAc and extracted with brine. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc/Hexane (1:5, v/v) as the eluent. Compound **2** was obtained as white solid (745 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.24 (d, *J* = 8.49 Hz, 2*H*), 7.65 (t, *J* = 7.41 Hz, 1*H*), 7.39–7.55 (m, 5*H*), 7.23 (d, *J* = 8.0 Hz, 1*H*), 5.48 (s, 1*H*), 3.37 (s, 6*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 151.0, 140.0, 133.6, 130.1, 129.5, 129.3, 128.6, 124.2, 121.7, 120.2, 102.2, 52.5 ppm. MS (TOF-ESI): *m*/*z*: Calcd for $C_{16}H_{16}O_4$: 295.09408 $[M + Na]^+$, Found: 295.09078 $[M + Na]^+$, Δ = 11.18 ppm.

2.3.3. Synthesis of dimethyl 1-methoxy-1-(3-benzyloxyphenyl) methyl phosphonate (**3**)

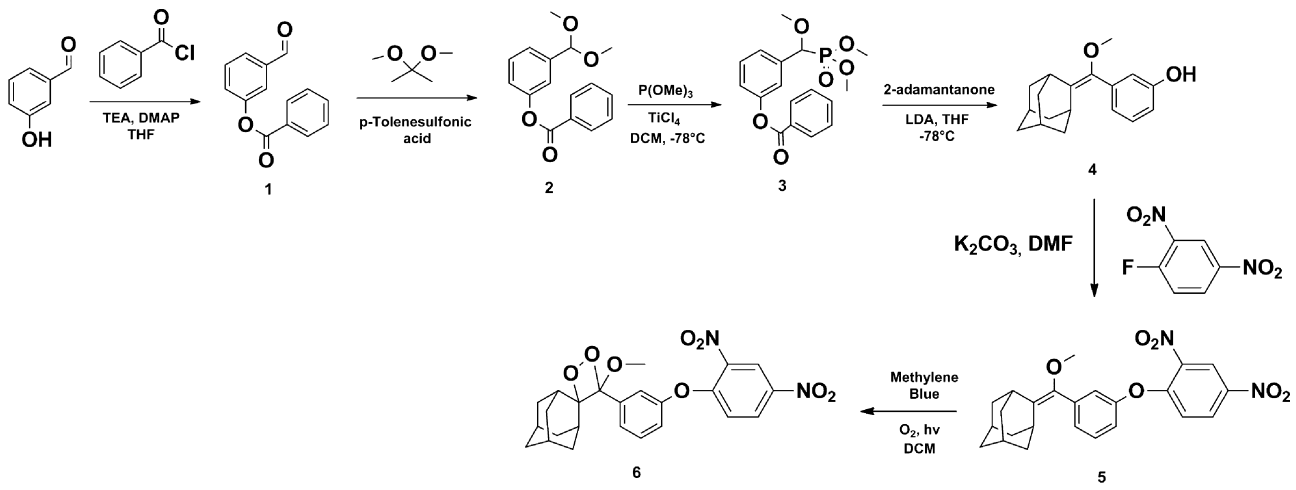
Trimethyl phosphite (0.3 mL, 2.58 mmol) was added to the solution of compound **2** (500 mg, 1.84 mmol) in DCM at −78 °C under argon. 15 min later, $TiCl_4$ (0.3 mL, 2.58 mmol) was added dropwise to the reaction mixture at −78 °C. The mixture was stirred for 30 min before allowing it to room temperature and stirred at room temperature for further 1 h. After the addition of aqueous methanol (2:1), reaction mixture was diluted with DCM and extracted first with saturated solution of $NaHCO_3$ then with brine. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc as the eluent. Compound **3** was obtained as white solid (583 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.22 (d, *J* = 8.27 Hz, 2*H*), 7.66–7.68 (m, 1*H*), 7.52–7.55 (m, 2*H*), 7.48 (t, *J* = 7.86 Hz, 1*H*), 7.38 (d, *J* = 7.74 Hz, 1 h), 7.34 (s, 1*H*), 7.24 (d, *J* = 8.01 Hz, 1*H*), 4.60 (d, *J* = 15.8 Hz, 1*H*), 3.74 (dd, *J* = 7, 10, 6*H*), 3.45 (s, 3*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 151.19, 151.16, 136.1, 133.6, 130.1, 129.6, 129.5, 128.6, 125.4, 125.3, 121.97, 121.94, 121.19, 121.14, 80.7, 79.0, 59.0, 58.8, 53.98, 53.92, 53.8, 53.7 ppm. MS (TOF-ESI): *m*/*z*: Calcd for $C_{19}H_{17}O_6P$: 373.07657 $[M + Na]^+$, Found: 373.07657 $[M + Na]^+$, Δ = 12.27 ppm.

2.3.4. Synthesis of 1-(2-adamatylidene)-1-methoxy-1-(3-hydroxyphenyl) methane (**4**)

Lithiumdiisopropyl amide (1.8 mL, 3.07 mmol) was added dropwise to the reaction mixture of compound **3** (430 mg, 1.23 mmol) dissolved in 1 mL dry THF at −78 °C under argon. After stirring of the reaction mixture for 45 min, 2-adamantanone (166 mg, 1.11 mmol) dissolved in dry THF was added dropwise to the reaction mixture at −78 °C under Ar. Reaction was left to stir at room temperature overnight. After pouring it into phosphate buffer (0.2 M, pH 7), it was extracted with EtOAc. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc/Hexane (1:5, v/v) as the eluent. Compound **4** was obtained as white solid (312 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.17 (s, br, 1*H*), 7.09 (t, *J* = 7.83 Hz, 1*H*), 6.81 (s, 1*H*), 6.70–6.77 (m, 2*H*), 3.24 (s, 3*H*), 3.15 (s, 1*H*), 2.57 (s, 1*H*), 1.67–1.85 (m, 14*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 142.8, 136.7, 132.4, 129.1, 121.8, 115.9, 114.6, 57.7, 39.1, 39.0, 37.1, 32.2, 30.3, 28.2 ppm. MS (TOF-ESI): *m*/*z*: Calcd for $C_{18}H_{22}O_2$: 271.16926 $[M + H]^+$, Found: 271.16357 $[M + H]^+$, Δ = 13.59 ppm.

2.3.5. Synthesis of 1-(2-adamatylidene)-1-methoxy-1-(3-(2,4-dinitrophenoxy) phenyl) methane (**5**)

Compound **4** (100 mg, 0.37 mmol) was dissolved in 1 mL DMF and K_2CO_3 (153 mg, 1.11 mmol) was added and the reaction mixture was stirred for 5 min at room temperature. 2,4-dinitro-1-fluoro-benzene (68.9 mg, 0,37 mmol) was added and the reaction mixture was left to stir at room temperature. The progress of the reaction was monitored by TLC. When TLC showed no starting material, the residue was diluted with EtOAc and extracted with brine. Combined organic phases were dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel flash column chromatography using EtOAc/hexane (1:5, v/v) as the eluent. Compound **5** was obtained as white solid (143.6 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.88 (d, *J* = 2.08 Hz, 1*H*), 8.36 (dd, *J* = 2.95, 9.23 Hz, 1*H*), 7.47 (t, *J* = 7.75 Hz, 1*H*), 7.31 (s, 1*H*), 7.07–7.12 (m, 3*H*), 3.34 (s, 3*H*), 3.26 (s, 1*H*), 2.66 (s, 1*H*), 1.77–2.01 (m, 14*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 153.5,



Scheme 1. Synthesis of probe **6**.

142.1, 141.4, 139.5, 138.64, 130.2, 128.8, 127.4, 122.0, 119.2, 118.6, 58.0, 39.1, 38.9, 37.0, 32.3, 30.3, 28.1. MS (TOF-ESI): *m*/*z*: Calcd for $C_{24}H_{24}N_2O_6$: 435.15616 $[M-H]^-$, Found: 435.15452 $[M-H]^-$, Δ = 3.77 ppm.

2.3.6. Synthesis of 4′-methoxy-4′-(3-(2,4-dinitrophenoxy) phenyl)spiro [adamantine-2,3′-[1,2]-dioxetane (6)

Compound **5** (143.6 mg, 0.37 mmol) was dissolved in DCM. Methylene blue (5 mg) was added to the reaction mixture which was irradiated while oxygen gas was passing through it. The progress of the reaction was monitored by TLC. When TLC showed no starting material, the mixture was concentrated under vacuo and the residue was subjected to the silica gel flash column chromatography by using DCM as the eluent. Compound **6** was obtained as white solid (162.8 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.88 (t, *J* = 2.59 Hz, 1*H*), 8.36 (dt, *J* = 2.65, 9.24 Hz, 1*H*), 7.60 (m, b, 4*H*), 7.21–7.24 (m, 1*H*), 6.99 (d, *J* = 9.23 Hz, 1*H*), 3.27 (s, 3*H*), 3.05 (s, 1*H*), 2.12 (s, 1*H*), 1.90–1.50 (m, 14*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 153.8, 141.6, 139.6, 138.1, 130.6, 128.8, 122.1, 121.4, 118.1, 111.2, 50.0, 36.2, 34.7, 33.2, 32.9, 32.1, 31.6, 31.4, 25.9 ppm.

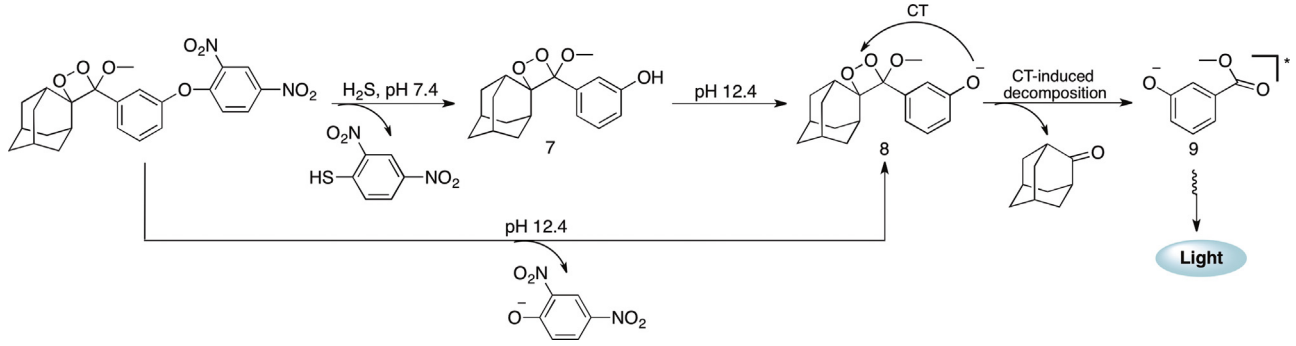
3. Results and discussions

3.1. Synthesis of probe 6

The synthetic route toward probe **6** is depicted in Scheme 1. Initially 3-hydroxybenzaldehyde was converted to a benzoyl derivative **1** to prevent any polymerization reaction during the preparation of dimethyl acetal **2**. After that, dimethyl acetal **2** was synthesized by using 2,2′-dimethoxypropane and toluene-4-sulfonic acid as a catalyst. Then ||-methoxy phosphonate **3** was obtained in the presence of trimethyl phosphite and $TiCl_4$ as a Lewis acid. Subsequent treatment of the phosphonate **3** to the Wittig–Horner reaction with 2-adamantanone yielded compound **4**. Then compound **5** was synthesized by the reaction between **4** and 1-fluoro-2,4-dinitrobenzene under basic conditions through nucleophilic substitution. Finally, 1,2 dioxetane derivative **6** was synthesized with the [2 + 2] cycloaddition of singlet oxygen $^1O_2$ on enol ether of compound **5** (Scheme 2).

3.2. Electronic absorption spectra for H_2S detection

The first important observation was the colorimetric change in the solution of probe **6** in the presence of Na_2S (a commonly employed H_2S donor) at pH 7.4. The concentration ratios of S^{2-}, HS^- and H_2S are determined by the pH of the buffer. The time dependent electronic absorption spectra were examined for 100 μM probe **6** in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C) (Fig. 1a and b). Upon addition of 10 equiv. of H_2S (in HEPES buffer, 100 mM) at pH 7.4 a new absorption band appeared at 468 nm immediately, within a minute, and reached equilibrium after about 30 min. The decomposition of probe **6** with H_2S at pH 7.4 resulted in the release of dinitrothiophenol group which is responsible for appearance of a new absorbance band at 468 nm in electronic absorption spectrum. Titration with varying concentrations of H_2S in HEPES buffer (100 mM, pH 7.4) clearly showed a progressive increase of the absorption intensity. For titration experiment, the electronic absorption spectra were collected 10 min after the each addition of H_2S (Fig. 1c) and the color change was easily distinguishable with naked eye.



Scheme 2. Proposed sensing and decomposition mechanism of probe **6**.

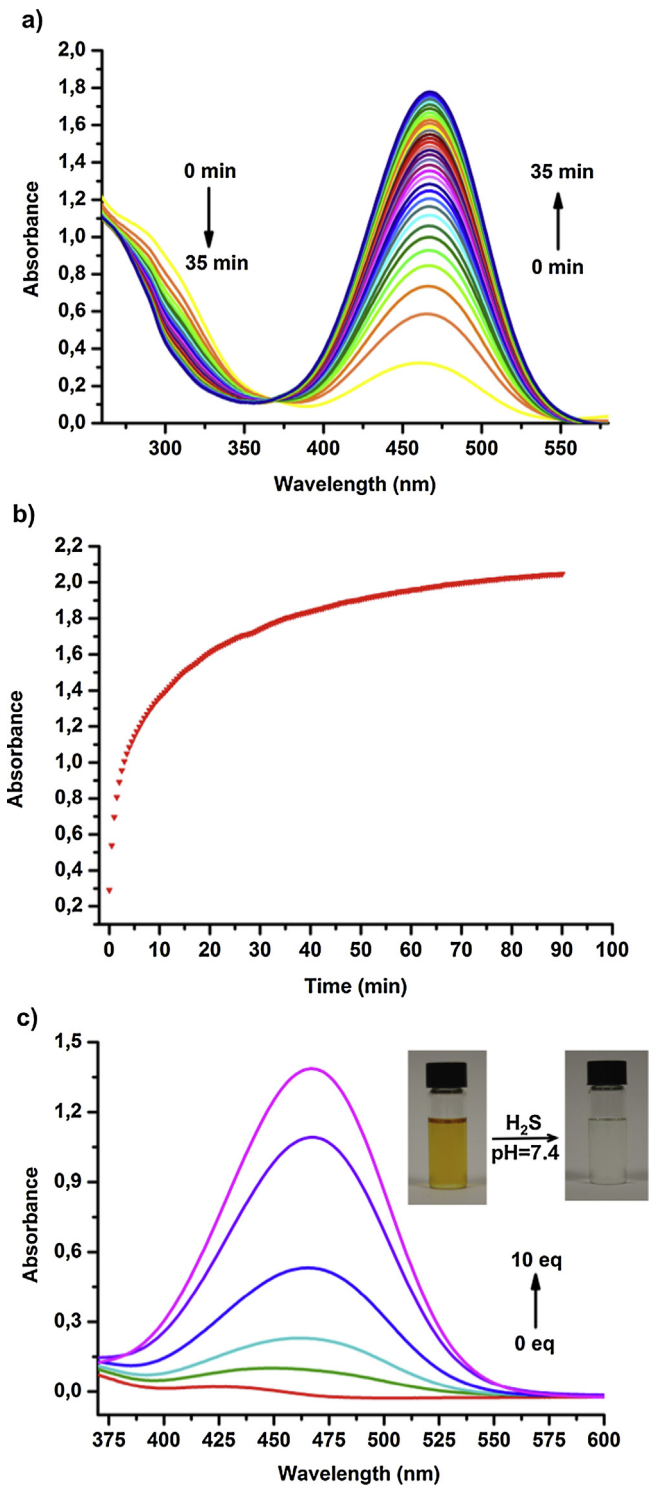


Fig. 1. (a) Time dependence of electronic absorption spectra of 100 μM probe **6** in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C) with 10 equiv. H_2S. (b) Time dependence of electronic absorption spectra of probe **6** (100 μM) in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C) with 10 equiv. H_2S at 468 nm. (c) The electronic absorption spectra of probe **6** (100 μM) in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C) in the presence of 0–10 equiv. H_2S in HEPES buffer (100 mM, pH 7.4).

3.3. Chemiluminescence measurements

Once H_2S solution in HEPES buffer at pH 7.4 was added the solution of probe **6** in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C), a dark yellow chromogenic change was observed within the first minute due to the release of dinitrothiophenol group.

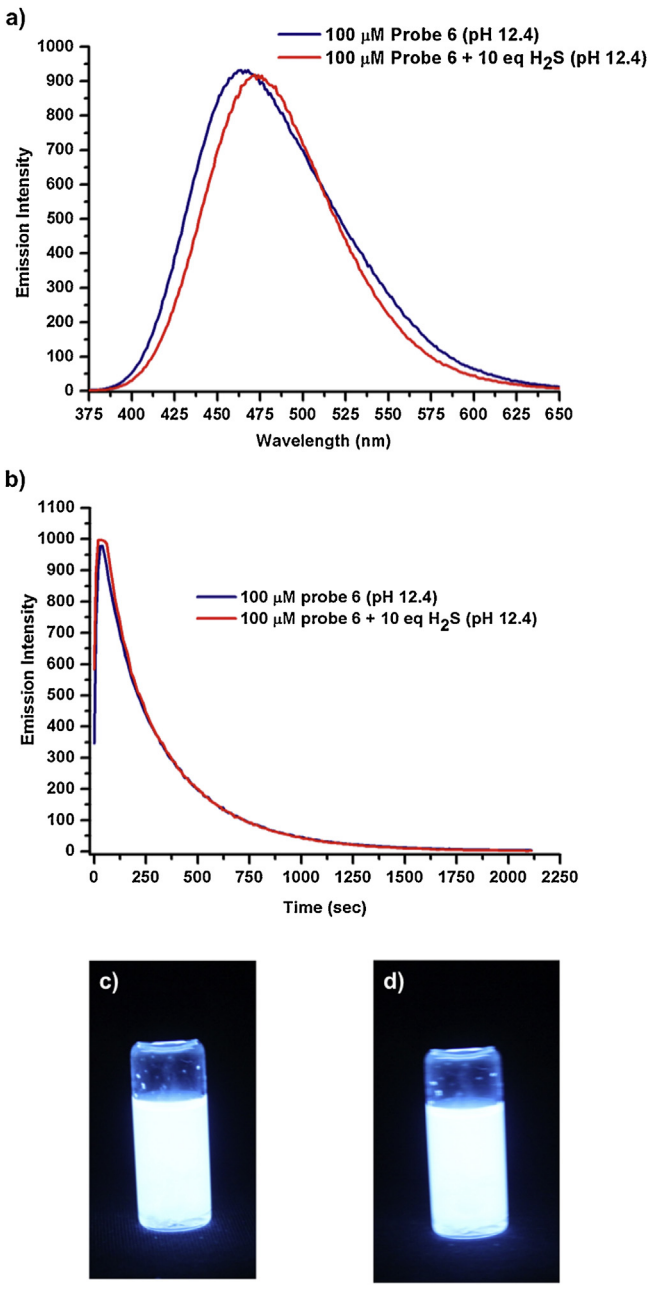


Fig. 2. (a) Light emission spectra of probe **6** (100 μM) in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C) with10 equiv. H_2S (in HEPES buffer, 100 mM) at pH 12.4 and without H_2S at pH 12.4. (b) Time dependence of chemiluminescence spectra of probe **6** (100 μM) in 9 DMSO-1 HEPES buffer (100 mM, pH 7.4) with 10 equiv. H_2S and without H_2S at pH 12.4. (c) The digital photograph of chemiluminescence of probe **6** in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C) with 10 equiv. H_2S at pH 12.4. (d) The digital photograph of chemiluminescence of probe **6** in 100 mM HEPES buffer/DMSO (1:9, v/v, 25 °C) at pH 12.4.

However, luminescence cannot be observed since compound **7** was not deprotonated at pH 7.4 (chemiluminescence off). To that end, the pH of solution was adjusted to 12.4 by NaOH solution (10 N) and because of decomposition of **8** via intramolecular charge transfer, luminescence of solution was observed (chemiluminescence on). On the other hand, when pH of probe **6** (100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C) was reached to pH 12.4 without adding any H_2S solution, almost same luminescence value was measured (Fig. 2a–d). The only difference between two cases are substances which are released. Thus, an on–off chemiluminescence was achieved by probe **6** depending on pH of the medium.

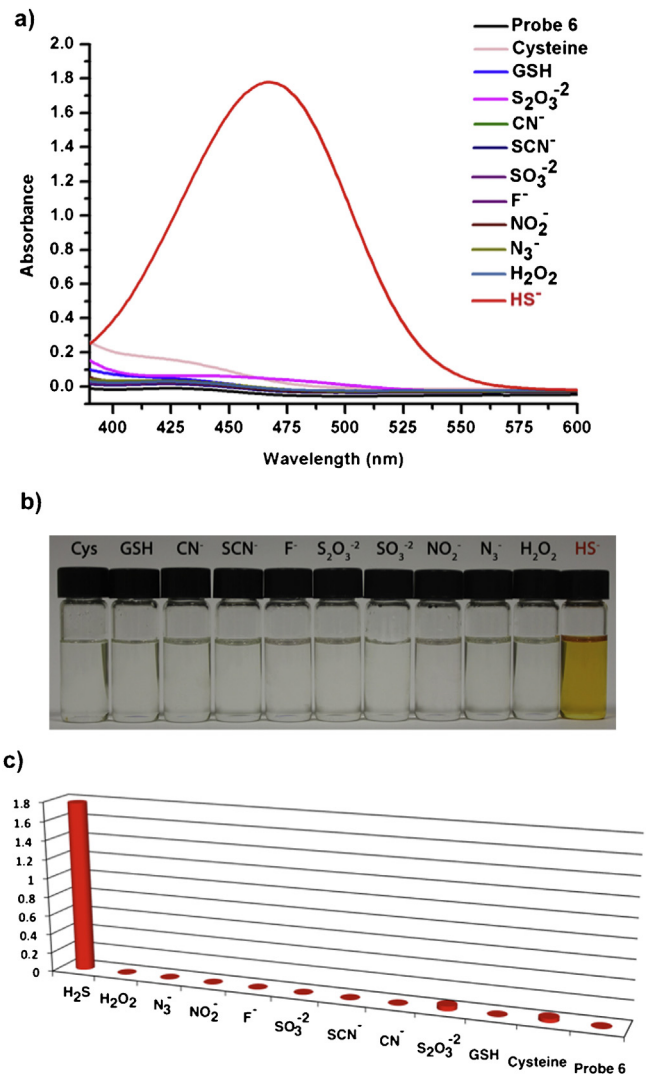


Fig. 3. (a) The electronic absorption spectra of 'probe **6** + H_2S' and 'probe **6** + various related species' (H_2S and other species were 10 equiv. in HEPES buffer 100 mM, pH 7.4). Probe **6** concentration was 100 μM in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C). (b) Digital photograph shows the appearance of the solutions under ambient light. Probe concentrations were 100 μM, H_2S and other related species were added at 10 equiv., all in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C). Photograph was taken 10 min after the addition of all species.

3.4. Selectivity over other related species

Further, we evaluated the selectivity of probe **6** by treating with other related species, including various reactive sulfur species and representative anions (Fig. 3a and b). Only probe **6** promoted significant absorbance change at 468 nm, conforming the high selectivity of probe **6** for H_2S. The electronic absorption spectra were taken 10 min after the addition of all species. Also digital photograph in Fig. 3b shows that the color changes of 100 μM probe **6** solutions (in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C)) which were prepared by adding 10 equiv. solutions of glutathione (GSH), cysteine (cys), H_2O_2, KCN, $Na_2S_2O_3$, KSCN, Na_2SO_3, KF, NaN_3, $NaNO_2$ and H_2S in 100 mM HEPES buffer/DMSO (1:9, v/v, pH 7.4, 25 °C). The digital photograph was taken 10 min after the addition of solutions. Thus, as shown in digital photograph (Fig. 3b), a highly selective and very fast naked eye colorimetric detection of H_2S is possible. Also the spectacular difference between H_2S and the other related species in terms of absorbance is clearly shown in the bar graphs (Fig. 3c).

3.5. Proposed decomposition mechanism

All experiments are in complete agreement with the following mechanisms described in Scheme 1. Once H_2S solution in HEPES buffer at pH 7.4 was added, the thiolysis of the dinitrophenyl ether yielded mixed **7** and dinitrothiophenol which mainly caused new absorption band namely a dark yellow color change. The HR-ESI mass spectral analysis in the negative mode clearly shows the release of dinitrothiophenol group (Fig. S17). At pH 12.4, the deprotanation of hydroxy phenyl group of **7** leads to an anionic phenolate group. The negatively charged phenolate group causes intramolecular charge transfer (CT) from phenolate to O—O of dioxetanes to induce decomposition into excited **9** which returns to the ground state through light emission and release adamantanone. Furthermore, when the pH of probe **6** was adjusted pH 12.4, the removal of dinitrophenolate group which was confirmed by HR-ESI mass spectrometry (negative ion mode) (Fig. S19) results in the formation of deprotonated **8** which decomposed to give the excited compound **9** that returns to the ground state through light emission in the same way.

4. Conclusion

In summary, we synthesized a novel fast responding 1,2-dioxetane derivative probe **6** for sensing of H_2S. For chromogenic chemosensing processes, a new absorption band appeared at 468 nm due to the release of dinitrothiophenol group in the presence of H_2S, and highly selective and sensitive naked eye chemosensing process was observed for H_2S. Also when pH of solution was adjusted to 12.4, strong chemiluminescence of solution was obtained due to the removal of dinitrothiophenol or dinitrophenolate groups. The demonstrations shown in this work are significant since the synthesis of a dioxetane based highly selective, sensitive and rapid chromogenic H_2S detection and modulation of chemiluminescence character by pH was presented for the first time.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2014.04.101.

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