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Synthesis and property study of phenanthroimidazole based hydrosulphite fluorescent probe

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Abstract. Phenanthrenequinone and terephthalaldehyde work as raw materials to fabricate TM1 in which phenanthroimidazole works as matrix. Aldehyde group react with hydrosulphite (HSO_3^-) to produce addition product, in which electron gain or loss varies and intramolecular charge transfer (ICT) happens, leading to changes of absorption spectrum. According to this mechanism, HSO_3^- could be detected. Convenience, fast response time and long lifespan are advantages of the novel fluorescent probe.

1. Introduction
Sodium hydrogen sulfite could inhibit enzymatic browning and non-enzymatic browning processes in food, it has been widely used as food additives for a long time [1-3]. However, sodium hydrogen sulfite would induce asthma and allergy under certain concentration that should be strictly controlled [4]. In addition, huge amount of sulfur dioxide was produced and released in industrial manufacture, making sulfite a wide-spread pollutant in modern environment. Thus, it's urgent to build up an excellent analytical method with fast response, high sensitivity and good selectivity to detect hydrosulphite in environment and food.

In recent years, receptors conducting fluorescence sensing and detection to anion has great applications in environment, chemistry, biology and medicine, thus gains wide-spread attention and a wide variety of fluorescent probes based on anion come out. Nevertheless, only few chemical sensors and probes could test hydrosulphite and sulfur dioxide. Most of them are traditional ones that purely depend on emission intensity as signal, in which results are easily affected by concentration of probes, variation of equipment and outer environment [4,5]. Ration-dependent fluorescent probes could depend on ratios under different intensities as signals, and they could maintain high sensitivity and correct undesirable factors from environment while under quantitative measurement, such as photobleaching, concentration of probes, pH, temperature, polarization and stability of light etc. In this work, prepared TM1 probes could react with HSO_3^- to produce adduct, change electron gain or loss and inhibit ratio-dependent fluorescent response caused by ICT.

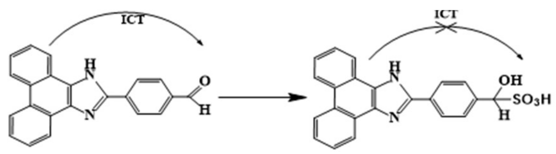

Figure 1. Reaction mechanism of TM1 probes and HSO_3^-

2. Experimental

2.1. Instrument
F7000 fluorospectro photometer, Agilent 1100 Liquid Chromatogram-mass spectrometer, CAY-300 ultraviolet spectrophotometer, Infrared spectrometer, Rotary evaporator, Circulating water vacuum pump, Vacuum drying oven, Column chromatography, UV Lamp, Magnetic stirrer.

2.2. Reagents
Phenanthrenequinone, terephthalaldehyde, glacial acetic acid, ammonium acetate, pyrrolidine, PBS buffer, dichloromethane.

2.3. Fabrication of TM1 fluorescent probes
Add 0.1664g phenanthrenequinone, 0.3215g terephthalaldehyde, 1.23g ammonium acetate to 15ml glacial acetic acid, then add them to flask, stirred for 2h under 95 ℃. After that, cooling and filtration, watered by glacial acetic acid, 10% sodium bicarbonate and deionized water successively for three times. Then we get khaki powder, dried to get crude product 0.1464g, 56.48% yield.

Purification: Let the crude powder isolated by neutral aluminium oxide to get 0.1g yellow solid powder. (eluant: dichloromethane/petroleum ether=1/1,v/v), Data of NMR: 1H NMR (300 MHZ , DMSO-d6) 13.73 (s,1H-NH), 10.09 (s, 1H, CHO), 8.86-8.87 (d,J=3.0, 1H, Ar-H), 8.52-8.58 (m, 4H, Ar-H), 8.13-8.15 (d,J=7.0 Hz, 2H, Ar-H), 7.70-7.76 (m,4H, Ar-H), 13C NMR (75 MHz, DMSO-D6):1=121.8, 123.9, 125.3, 126.2, 127.8, 128.1, 130.0, 135.2, 135.9, 147.5, 192.3 ppm. MS(ESI), m/z [M+H]+ : 323.3, calcd, 323.4.

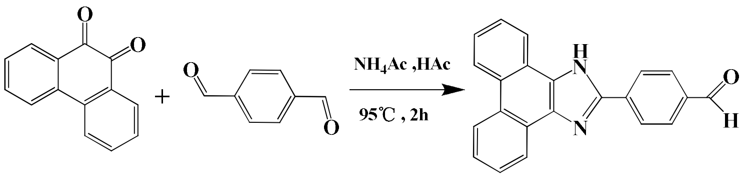

Figure 2. Fabrication of TM1 probes

2.4. Measurement method
Add 0.2 ml CTAB, 0.1ml PBS7.4, 0.5ml 2.0mmoL^{-1} solution of TM1 successively, and different concentration of $NaHSO_3$. Stewing under room temperature for 30 min and then conducting ultraviolet spectrophotometer and fluorescence spectra scanning. Parameter of fluorescence spectra: λex = 320 nm, λem =350-650 nm, Ex, Em:3 nm, 5 nm.

3. Results and discussion

3.1. Design of TM1 and mechanisms of stimuli-response
This experiment test the molecular morphology of TM1 probes before and after reaction with hydrosulphite. Later we find that retention time of TM1 is around 6 min, ion peak under ionization source of ESI was m/z 323.2; Retention time of TM and HSO_3^- is 2.1 min, excimer ion peak is m/z 405. Addition reaction between hydrosulphite and aldehyde group increase 81 of molecular mass, molecular

hydrophilcity increase a lot too, thus the retention time was brought forward which is in consistent with deduction in theory.

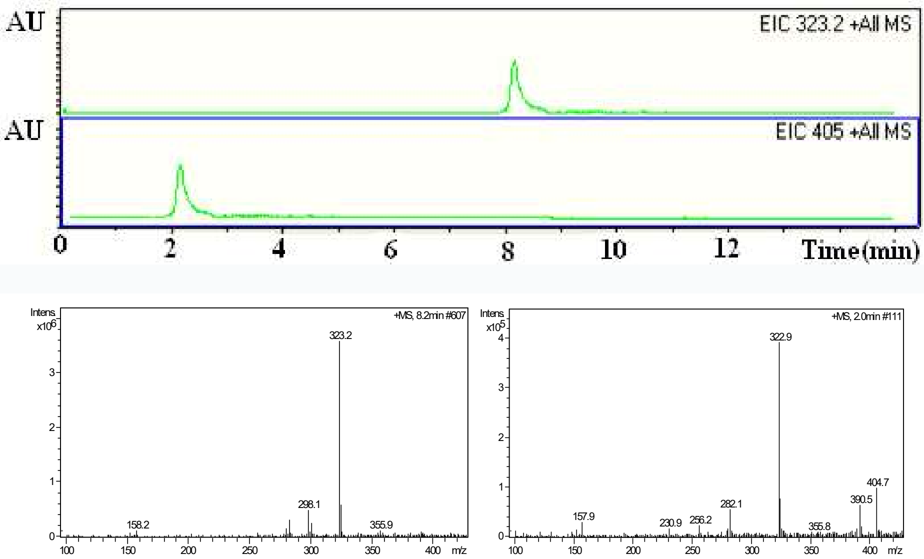

Figure 3. Results of LC and mass spectrometry: before and after reaction between TM1 and hydrosulphite

3.2. Research of TM1 spectrum

This experiment study spectrum of TM1 and TM1+ HSO_3^- depending on three dimensional fluorescence, and we find that the biggest excitation and emission wavelengths of TM1 are around 380 and 510 nm, while product after reaction with HSO_3^- reach at 300nm and 400 nm, thus we could develop a kind of ration-responsive fluorescence analytical method.

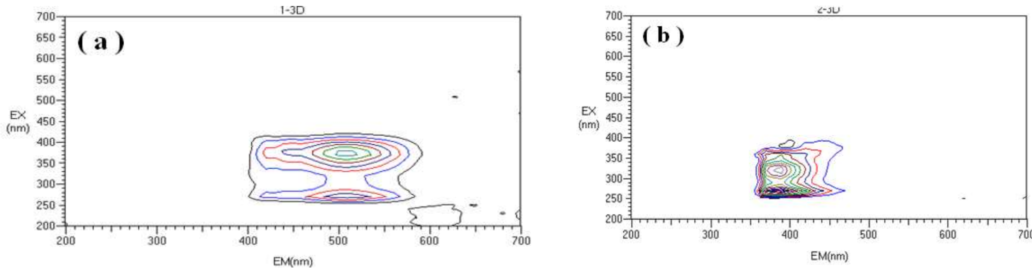

Figure 4. Compound of TM1 probe (A) and 3D spectrum after addition of $NaHSO_3$ (B)

3.3. Selectivity of method

In the experiment we test selectivity of TM1 and HSO_3^-. Under the same conditions, adding same amount of HSO_3^-,F^-,Cl^-,Br^-,I^-,NO_3^-, Ac^-,SCN^-, SO_4^{2-},CO_3^{2-},HPO_4^{2-} to solution of TM1 and scanning the emission spectrum. The results indicate only HSO^{3-} can make TM1 solution show obvious adsorption peak, while solution contained other anion cannot show apparent adsorption peak, the same to emission spectrum. Thus the results strongly indicate TM1 own good selectivity to HSO_3^-.

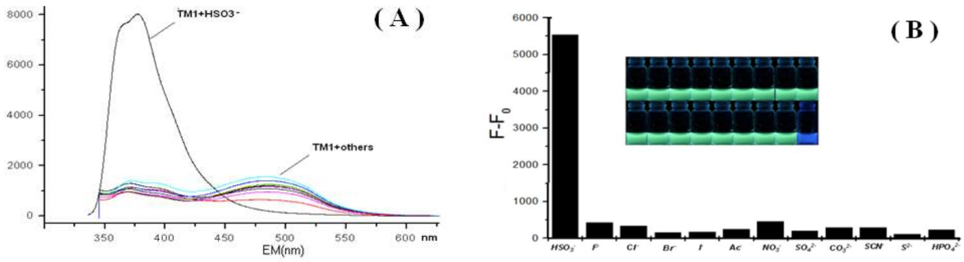

Figure 5. Responsive results of TM1 to different anions (A) and histogram of F-F0

Moreover, the experiment test fluorescent spectrum of TM1 reacting with different concentrations of HSO_3^-. There is a typical fluorescence peak at 525nm for TM1, and with the increase of TM1 there is a new fluorescence peak at 380nm and stronger intensity, meanwhile intensity of fluorescence emission at 525nm decreases continuously. From the above results, aldehyde group in TM1probe react with HSO_3^- causing decrease of electronic absorption ability, appearance of ICT, thus blue shift of emission wavelength happened, decrease at 525nm and increase at 380nm. Ratio-responsive fluorescence analytical method was established to test HSO_3^- according to it.

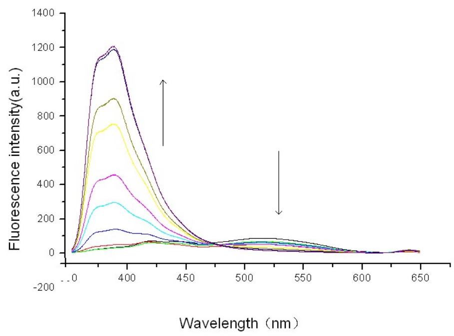

Figure 6. Emission spectrum of TM1 reacting with different concentrations of HSO_3^-

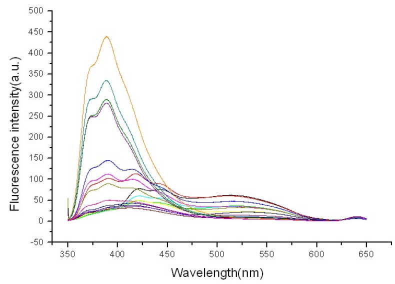

Figure 7. Fluorescence emission spectrum of TM1 reacting with HSO_3^- under different organic solvent

3.4. Optimization of experimental conditions

3.4.1. Influence of different amount of solvent to reaction system. Dimethylamino formamide and PBS (pH=5.0, 30mM) work as reaction medium, testing influence to florescence response by composition of reaction system. As shown in Figure7, florescence intensity has the most apparent variation when DMF: PBS=1:1; Thus this ration is the best dosage of organic solvent.

3.4.2. Influence of reaction time. The experiment test reaction dynamics of TM1 and HSO_3^-, and results indicate the fluorescence intensity increase in a short time after the addition of HSO_3^- to TM1, thus finishing reaction in 5s. As time goes by, fluorescence intensity could maintain at a steady level, thus ration-responsive fluorescent analytical method based on TM1 could achieve rapid detection of HSO_3^-.

3.5. Characteristic of analytical method

Under selected most appropriate conditions, there is a linear correlation between fluorescence intensity and concentration of HSO_3^- within 10-500 μ m, the detection limit is 2 μ m; parallel determination for 7 times, RSD is 4.5%.

4. Conclusion

Phenanthroimidazole works as matrix to fabricate a kind of fluorescence probe that could be used to test TM1. There is an obvious increase of fluorescent ration-response at 380/525nm before and after reaction. According to it, TM1 could work as ration-response probe to test HSO_3^-. Based on TM1 we establish a kind of analytical method that has fast response capacity, good selectivity and sensibility, temperate reaction conditions, which could be widely used for detection of HSO_3^-.

Acknowledgments

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