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## An ESIPT-based highly selective and sensitive probe for the detection of hydrogen sulfide

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### ABSTRACT

A new excited state intramolecular proton transfer dye with red keto emission (620 nm) and remarkably large Stokes shift (240 nm) was discovered. Based on its unique red emission and large Stokes shift, it was developed to a novel fluorescent probe which can highly selectively and sensitively detect hydrogen sulfide.

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Hydrogen sulfide ( $H_2S$ ), well-known for its unpleasant rotten egg smell and traditionally considered as a toxic gas,<sup>1</sup> can be endogenously produced by enzymes such as cystathionine  $\beta$ -synthase, cystathionine  $\gamma$ -lyase, and 3-mercaptopyruvate sulfurtransferase in mammalian systems.<sup>1,2</sup> Nevertheless, recent studies have demonstrated that  $H_2S$  can work as gaseous signaling compound (gasotransmitter) with importance on a par with that of the other two known endogenous gasotransmitters, nitric oxide (NO) and carbon monoxide (CO).<sup>3</sup> Moreover,  $H_2S$  has been recognized for mediating a wide range of physiological effects, such as vasodilation,<sup>4</sup> anti-oxidation,<sup>5</sup> anti-apoptosis,<sup>6</sup> and antiinflammation.<sup>7</sup> Any imbalance in  $H_2S$  has also been recognized to connect to various diseases such as Alzheimer's and Down's syndrome.<sup>8</sup> Therefore, accurate and reliable measurement of  $H_2S$  concentrations is needed and can provide useful information to study the function of  $H_2S$  in depth.

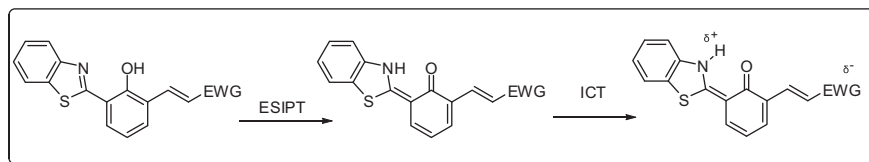
A number of techniques including polarography, gas chromatography, and colorimetry are available for the detection of  $H_2S$ .<sup>9</sup> However, these techniques require complicated procedures which do not allow for temporal monitoring and are destructive in nature. In recent years, fluorescent sensing has received great attention due to its simple operation and high sensitivity.<sup>10</sup> Thus, a fluorophore with a high quantum yield and large Stokes shift draws our interests. Recently, 2-(2-hydroxyphenyl) benzothiazole (HBT) and 2-(2'-hydroxyphenyl) benzoxazole (HBO) have received

considerable attention because of their separated dual fluorescence in a four-level cycle.<sup>11</sup> In the ground state, HBT adopts the enol (E) form stabilized by intramolecular hydrogen bonding. Upon photoexcitation at 320 nm, the excited enol ( $E^*$ ) is quickly converted into the excited keto ( $K^*$ ) tautomer by ESIPT on a subpicosecond time scale, which gives rise to an emission band ( $\sim 500$  nm) with a large Stokes shift ( $\sim 180$  nm). Nevertheless, the emission color of HBT/HBO is limited in the blue and green region, which may restrain the potential of their biological applications due to poor penetration and high photodamage.<sup>12</sup> Therefore, it is of great value to modify the structure of HBT/HBO and make the emission wavelength into the red region. On the other hand, many reported HBT/HBO derivatives still suffer from various shortcomings involving short emission wavelength, obvious hypochromatic shift, or the blockage of ESIPT process resulting in small Stokes' shift in strong polar solvents such as acetonitrile, methanol, and water.<sup>13</sup> Thus, it is challenging to tune the emission of HBT/HBO derivatives to longer wavelength, and still retain the ESIPT process for large Stokes' shift. To the best of our knowledge, among all the probes for  $H_2S$  detection based on ESIPT mechanism, rare of them have been found to have an emission exceed 600 nm, and most of them are at below 500 nm which may restrict their potential applications.<sup>14</sup> In this work, we present the development of HBTTP-S as a novel red fluorescent  $H_2S$  sensor based on 'turn-on' ESIPT mechanism (Scheme 1).

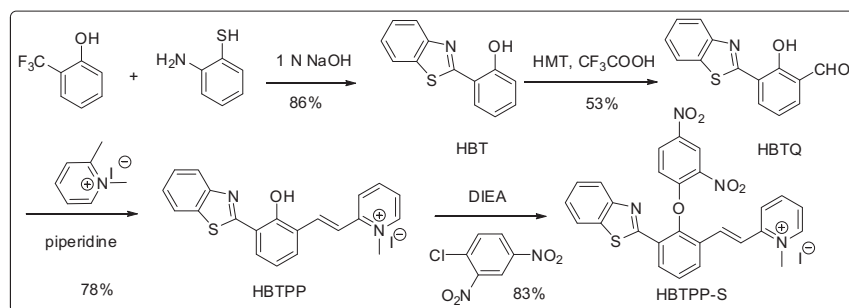
In a typical ESIPT process, upon photoexcitation, HBT can undergo fast proton transfer reaction in a sub picosecond time scale and imino nitrogen is converted into an amine group which

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Scheme 1. Our design strategy.



Scheme 2. Synthetic scheme of HBTPP-S.

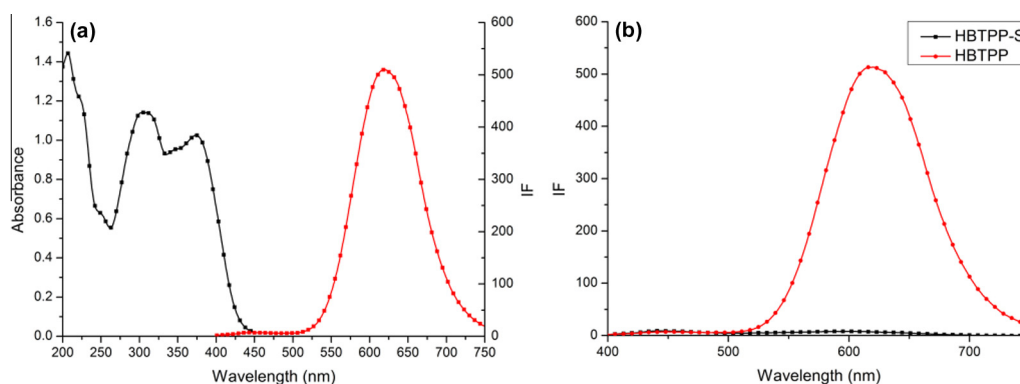


Figure 1. (a) Absorption and fluorescence spectra of HBTPP. (b) Fluorescence spectra of HBTPP and HBTPP-S. All absorption and fluorescence were recorded in a mixed solution of CH<sub>3</sub>CN/PBS (50:50, v/v, pH = 7.4, 10 mM).

can serve as an electron donor group.<sup>15</sup> As we all know, when a dye possesses an electron rich group conjugated to an electron deficient group as a push–pull structure, intramolecular charge transfer (ICT) from the donor to the acceptor will proceed upon excitation.<sup>16</sup> Thus, if we appended an electron acceptor group in the *ortho*-position of phenol through double bond, it is logical to expect that the amine group formed by ES IPT process is capable of effective charge transfer into the electron acceptor unit and triggers the strong push–pull ICT interaction. This ES IPT coupled ICT process may lead to dramatic changes in fluorescent properties involving red shift keto emission and large Stokes shift. Furthermore, the ES IPT process can be hampered by a specific protecting group. Such a protected phenol can be used as a ‘turn-on’ molecular probe for detection or imaging of an analyte that can react with the probe to remove the protecting group (Scheme 2).

To test the above-mentioned hypothesis, we judiciously constructed HBTPP by the condensation reaction between HBTQ and 1,2-dimethylpyridin-1-ium iodide. HBTQ was prepared by the modified Duff reaction starting from HBT, which was synthesized by the established literature procedure.<sup>17</sup> With HBTPP in hand, we developed a fluorescent probe by connecting with 4-chloro-1,2-dinitrobenzene known as the protecting group for tyrosine in peptide synthesis.<sup>18</sup> These compounds synthesized were fully characterized by the standard NMR and mass spectrometry.

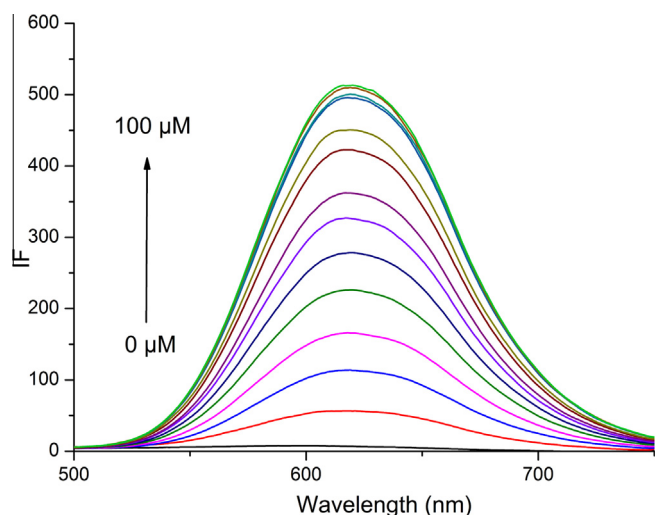


Figure 2. Emission spectra of probe HBTPP-S (5.0 μM) in a mixed solution of CH<sub>3</sub>CN/PBS (50:50, v/v, pH = 7.4, 10 mM) upon addition of NaHS with λ<sub>ex</sub> = 380 nm.

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