

## Supporting Information for

# A Fluorescence Ratiometric Sensor for Trace Vapor Detection of Hydrogen Peroxide

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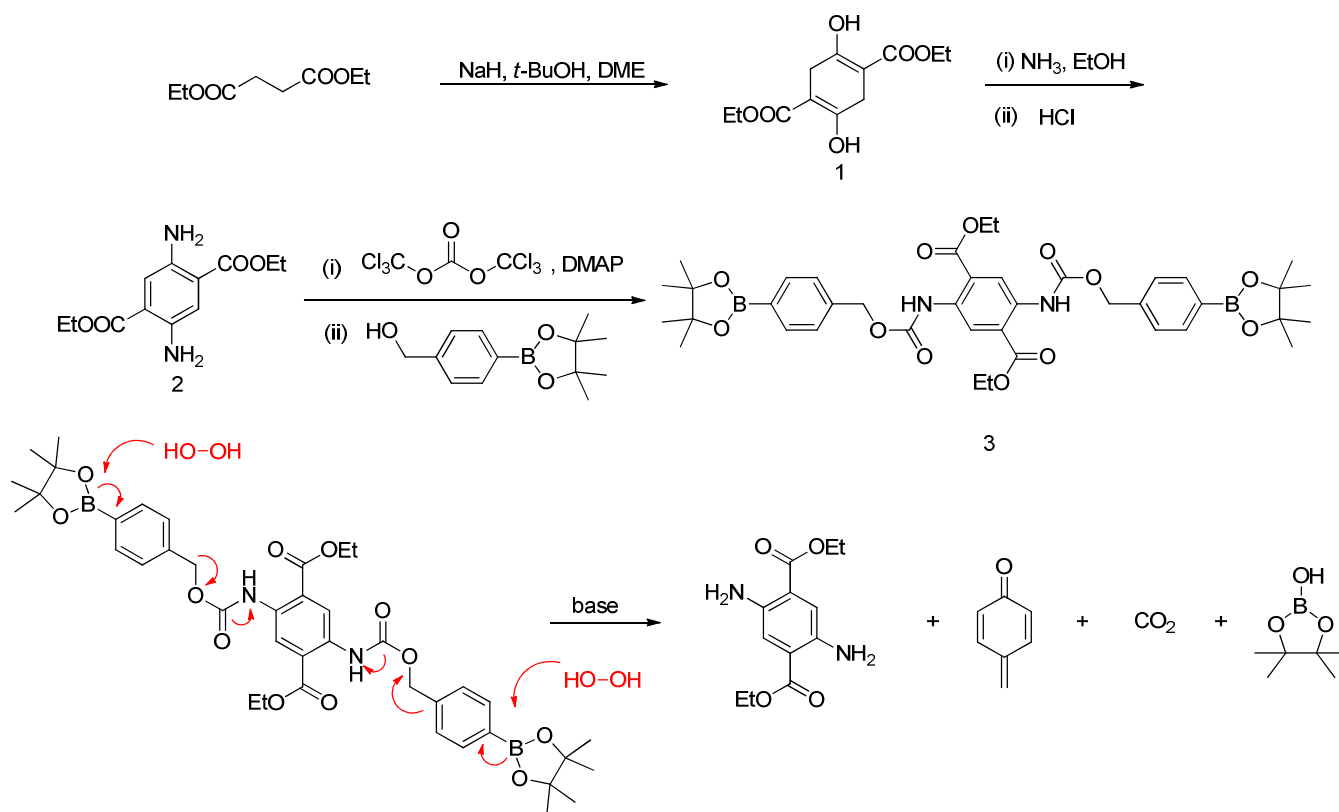
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**Scheme S1** The synthetic route of sensor molecule DAT-B (3), and the possible mechanism<sup>1</sup> of the reaction between DAT-B and  $\text{H}_2\text{O}_2$ .

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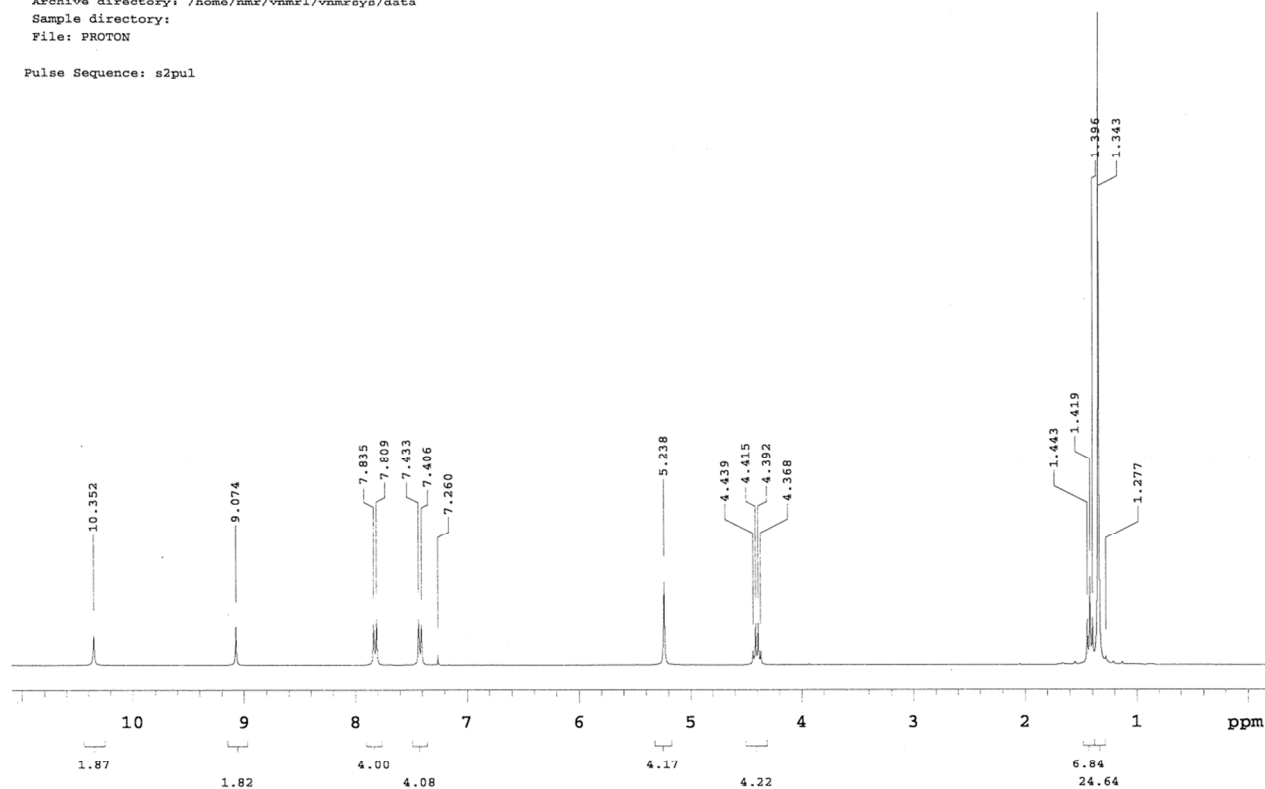


Figure S1 <sup>1</sup>H NMR spectrum of DAT-B.

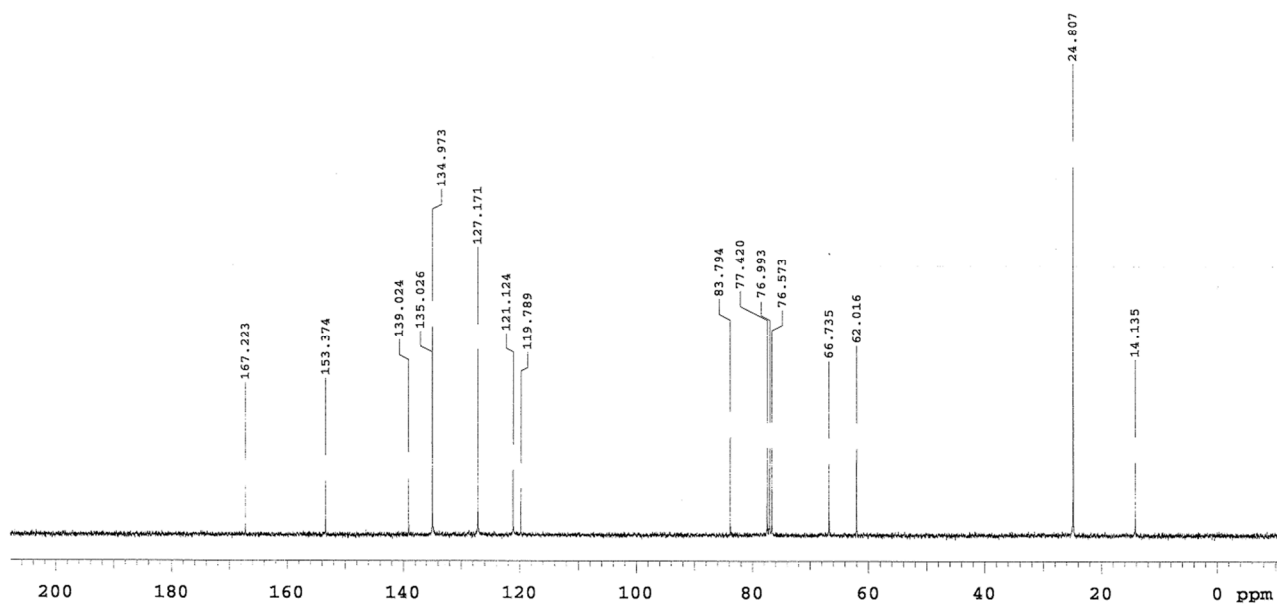
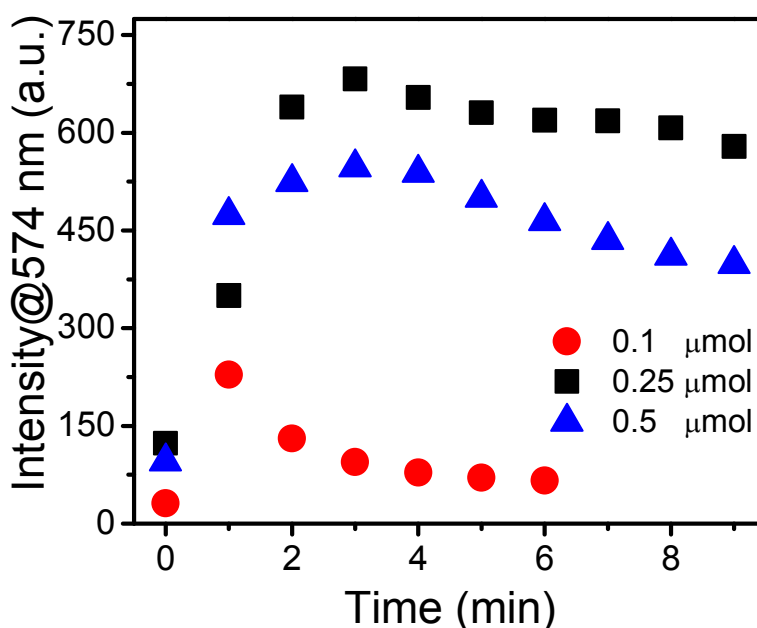


Figure S2 <sup>13</sup>C NMR spectrum of DAT-B.

## 1. Other experimental details

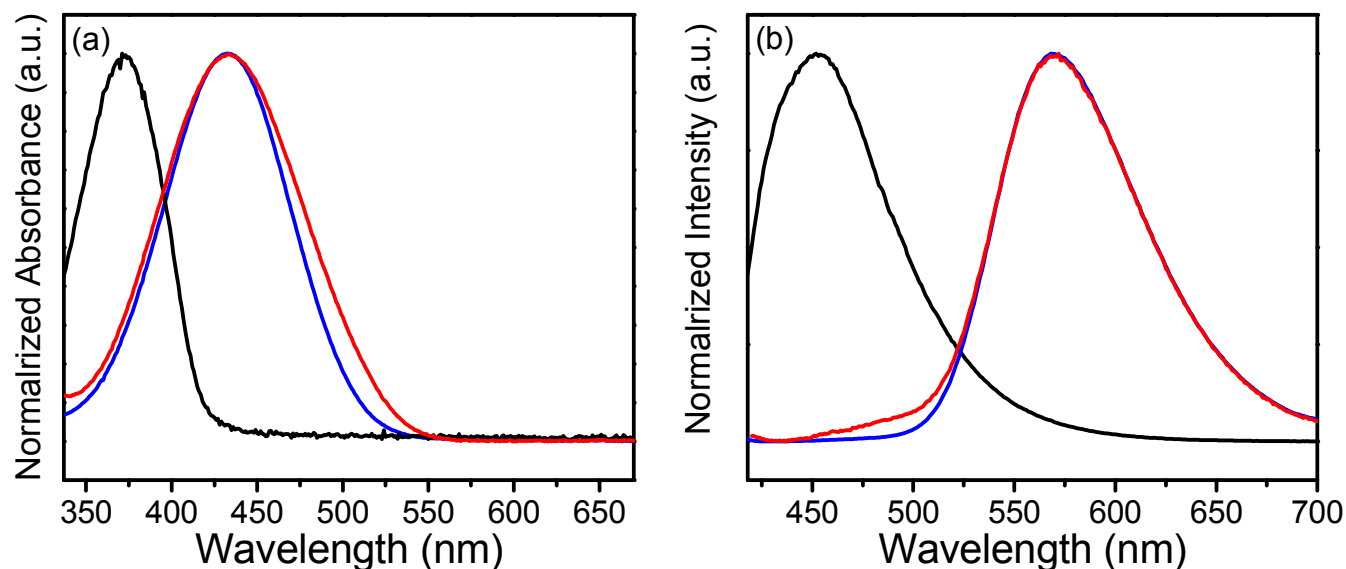
**Dispersion of sensor molecules on quartz slide.** To adjust the molar amount of DAT-B loading, various concentrations of DAT-B in ethanol were prepared and used: 0.02, 0.01 and 0.004 mol/L. Uniform solid film of DAT-B sensor molecules within the solid film is indicated by the uniform emission density shown in the emission photography of the quartz slide after exposure to the  $\text{H}_2\text{O}_2$  vapor (Scheme 1b). As shown in Figure S3, the film with 0.25  $\mu\text{mol}$  DAT-B gives the largest fluorescence change upon exposure to  $\text{H}_2\text{O}_2$  vapor, which indicates the optimal sensor molecule amount used in this study.



**Figure S3** Time course of the fluorescence intensity change measured at 574 nm for DAT-B coated quartz slide at different molar amount (0.1  $\mu\text{mol}$ , red; 0.1  $\mu\text{mol}$ , black; 0.5  $\mu\text{mol}$ , blue,  $1.0 \times 1.0 \text{ cm}^2$ ) with the same TBAH/DAT-B ratio (5:1) upon exposure to 225 ppm  $\text{H}_2\text{O}_2$  vapor.

**Absorption and Fluorescence spectra of DAT-B before and after reaction with  $\text{H}_2\text{O}_2$  in solution.** In situ UV-vis absorption and fluorescence spectral measurements were performed in a DAT-B solution in ethanol ( $1 \times 10^{-5}$  mol/L, in the presence of  $1 \times 10^{-3}$  mol/L TBAH) before and after addition of  $\text{H}_2\text{O}_2$  ( $1 \times 10^{-2}$  mol/L). As shown in Figure S4a, the absorption peak of DAT-B moved from 371 nm to 433 nm

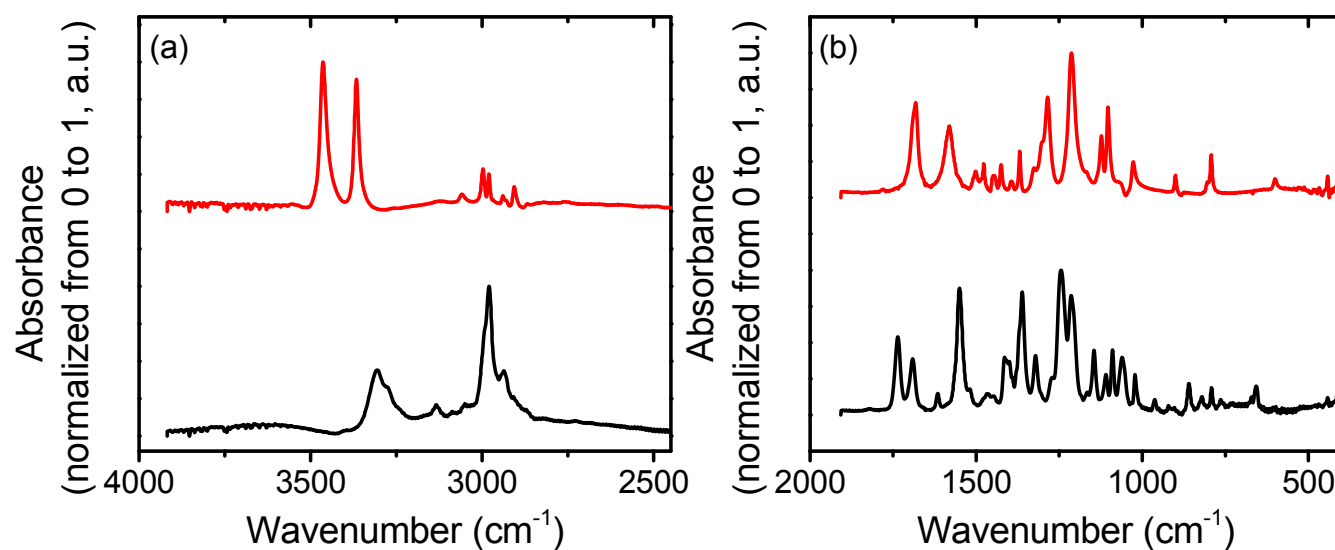
upon reaction with  $\text{H}_2\text{O}_2$ , which indicates the characteristic intramolecular charge transfer (ICT) band of DAT-N. Meanwhile, the emission peak of DAT-B was shifted from 452 nm to 570 nm upon reaction with  $\text{H}_2\text{O}_2$ , also characteristic of the ICT band of DAT-N. Both the absorption and fluorescence spectra of the reacted state of DAT-B match well the spectra of pure DAT-N solution, clearly indicating the  $\text{H}_2\text{O}_2$  mediated conversion of DAT-B to DAT-N as presented in Scheme S1.



**Figure S4** Absorbance (a) and fluorescence (b) spectra of DAT-B solution in ethanol ( $1 \times 10^{-5}$  mol/L, in the presence of  $1 \times 10^{-3}$  mol/L TBAH) before (black) and after (red) addition of  $\text{H}_2\text{O}_2$  ( $1 \times 10^{-2}$  mol/L). For comparison, pure DAT-N solution in ethanol (blue,  $1 \times 10^{-5}$  mol/L, in the presence of  $1 \times 10^{-3}$  mol/L TBAH) is also presented.

**IR spectra of DAT-B and DAT-N.** The IR spectra of DAT-B before and after reaction with  $\text{H}_2\text{O}_2$  (converting to DAT-N) were measured to demonstrate the function group changing. As shown in Figure S5, the CO-NH vibration of DAT-B ( $3300, 1733 \text{ cm}^{-1}$ ) shifted to  $3463$  and  $1579 \text{ cm}^{-1}$ , which are characteristic of the  $-\text{NH}_2$  vibration. Concurrently, the C-B vibration in DAT-B<sup>2</sup> ( $1056 \text{ cm}^{-1}$ ) disappears when converted into DAT-N. These IR spectral changes explicitly demonstrate the function group change from boronate group to amino group as illustrated in Scheme 1a.

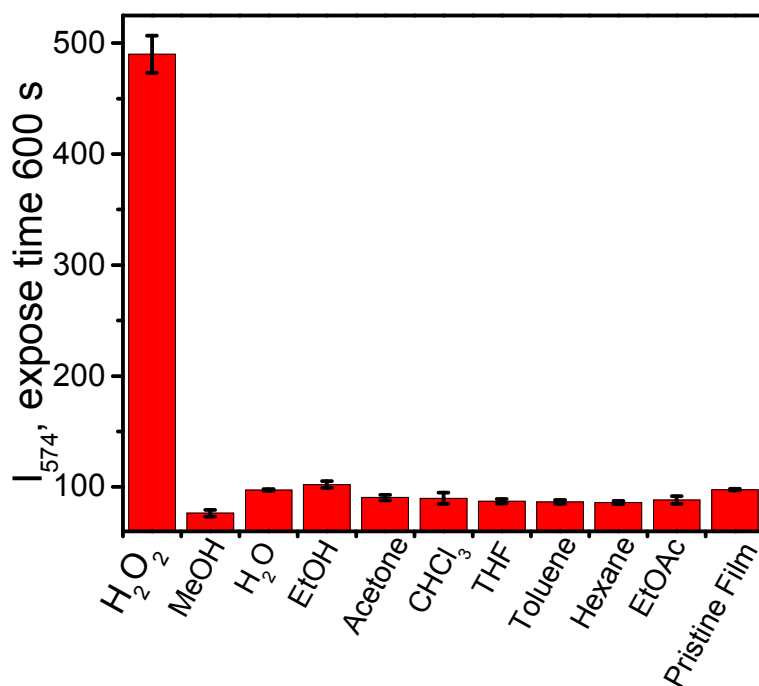
The IR spectra were measured by mixing DAT-B or DAT-N within KBr pellet. DAT-N used for IR measurement was made from the reaction of DAT-B with  $\text{H}_2\text{O}_2$  in a solution. Briefly, a solution of DAT-B (100 mg, 0.13 mmol, in 20 mL ethanol) was added in 4 mL  $\text{H}_2\text{O}_2$  (35 wt%), followed by stirring at room temperature for 4 h. The reaction solution was then diluted with ethyl acetate, extracted with brine and water, and dried over  $\text{Na}_2\text{SO}_4$ . After removal of solvent, the crude product was purified by flash chromatography (methylene chloride/ethyl acetate = 10:1) on silica gel to give 18 mg orange product, yield 54%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz, ppm):  $\delta$  = 7.29 (2 H, s, Ar-H), 4.30-4.38 (4 H, q,  $\text{CH}_2$ ), 1.37-1.42 (6 H, t,  $\text{CH}_3$ ). The NMR data matches well the data obtained from the pure DAT-N synthesized separately through the route in Scheme S1.



**Figure S5** IR spectra of DAT-B (black) and DAT-N (red) in 3900-2400 (a) and 1900-400 (b)  $\text{cm}^{-1}$  range.

**Selectivity test.** The sensor DAT-B coated quartz slides (containing 0.25  $\mu\text{mol}$  DAT-B and 1.25  $\mu\text{mol}$  TBAH,  $1.0 \times 1.0 \text{ cm}^2$ ) were exposed to the saturated vapor of various common solvents such as methanol (131,000 ppm), water (31,000 ppm), ethanol (89,000 ppm), acetone (260,000 ppm), chloroform (140,000 ppm), THF (173,000 ppm), toluene (26,000 ppm), hexane (130,000 ppm), ethyl acetate (100,000 ppm), to validate the selectivity of the sensor molecule. The increase in fluorescence

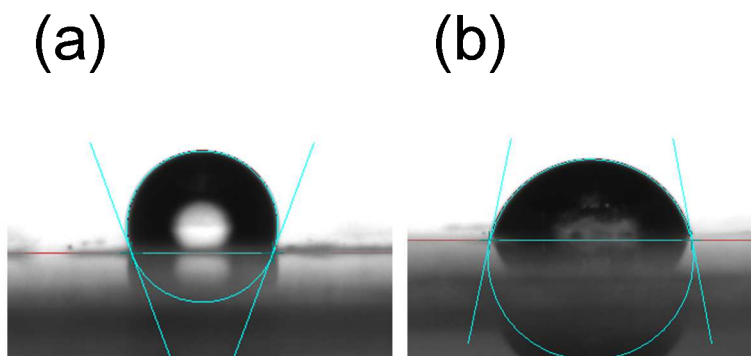
intensity was measured at 574 nm over DAT-B coated quartz slide (the same component as used in Scheme 1) after 10 min exposure to 225 ppm  $\text{H}_2\text{O}_2$  vapor, in comparison to that upon exposure to the saturated vapor of the common solvents. The minimum change of the fluorescent peak at 574 nm after extensive exposure to these highly concentrated solvents vapors (three orders of magnitude higher than  $\text{H}_2\text{O}_2$  vapor used in this experiment) demonstrates that sensor molecule DAT-B is highly selective towards  $\text{H}_2\text{O}_2$ .



**Figure S6** The selectivity plot of DAT-B (quartz slide containing 0.25  $\mu\text{mol}$  DAT-B and 1.25  $\mu\text{mol}$  TBAH,  $1.0 \times 1.0 \text{ cm}^2$ ) over saturated vapor of common solvents and 225 ppm  $\text{H}_2\text{O}_2$  vapor. The exposure time was fixed at 10 min; the error bars are based on the standard deviations of the data.

**Contact angle measurement of DAT-B and DAT-B/TBAH film.** The contact angle measurement of DAT-B (0.25  $\mu\text{mol}$ ,  $1.0 \times 1.0 \text{ cm}^2$ ) and DAT-B/TBAH film (0.25  $\mu\text{mol}$  DAT-B/1.25  $\mu\text{mol}$  TBAH,  $1.0 \times 1.0 \text{ cm}^2$ ) was performed to determine the surface hydrophilicity of as prepared film. The surface of DAT-B is hydrophobic and the contact angle is  $109.9^\circ \pm 0.6^\circ$ . After the addition of TBAH, the surface of the blended film is tuned to hydrophilic and the contact angle is decreased to  $80.9^\circ \pm 2.6^\circ$ . This

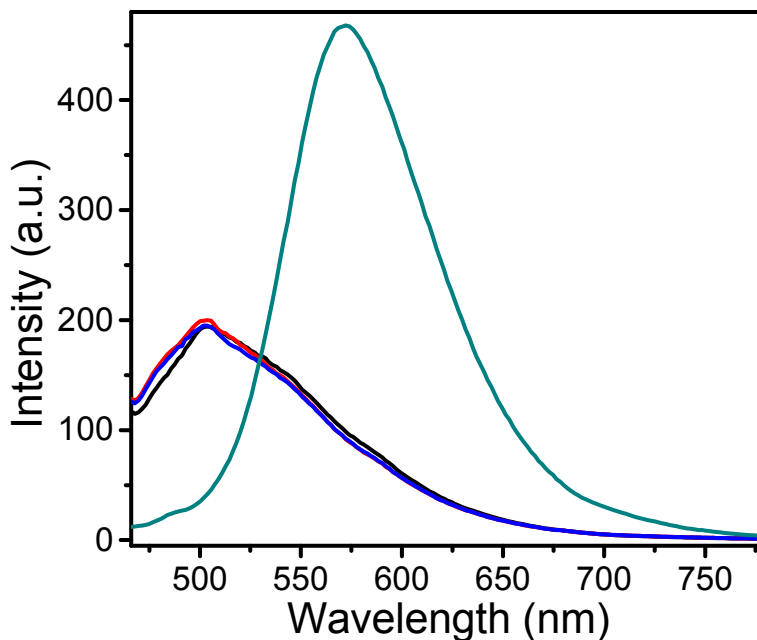
change in contact angle demonstrates another benefit of the addition of TBAH, i.e. the formation of hydrophilic film surface that increases the intake of  $\text{H}_2\text{O}_2$  vapor in humid air.



**Figure S7** Contact angle measurement of DAT-B film ( $0.25 \mu\text{mol}$ ,  $1.0 \times 1.0 \text{ cm}^2$ ) and DAT-B/TBAH film ( $0.25 \mu\text{mol}$  DAT-B/ $1.25 \mu\text{mol}$  TBAH,  $1.0 \times 1.0 \text{ cm}^2$ ).

**Sensor stability test on quartz slide.** The DAT-B coated quartz slide sample was prepared according to the method described above, and fluorescence spectra were measured at different time intervals after preparation (Figure S8), which did not show significant change in fluorescence spectra or intensity within the experimental investigation period. The same quartz slide was then exposed to 225 ppm  $\text{H}_2\text{O}_2$  vapor for 5 minutes, followed by measurement of the fluorescence spectrum.



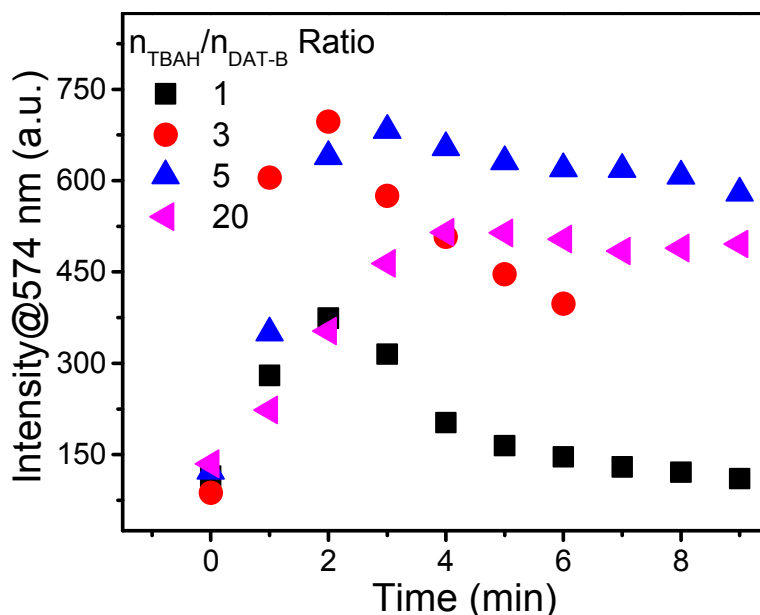


**Figure S8** The fluorescence spectra of the DAT-B coated quartz slide (containing 0.25  $\mu\text{mol}$  DAT-B and 1.25  $\mu\text{mol}$  TBAH,  $1.0 \times 1.0 \text{ cm}^2$ ): freshly prepared film (black), after 24 hours (red), after 7 days (blue), and after exposure to 225 ppm  $\text{H}_2\text{O}_2$  vapor for 5 min (green),  $\lambda_{\text{ex}} = 427 \text{ nm}$ .

**Time course of sensor response in solid films.** To find the optimal concentration of TBAH (or molar ratio TBAH/DAT-B) that would give the fastest sensor reaction, we measured the time course of the fluorescence intensity change at 574 nm for the sensor films drop cast on quartz slides. The optimization experiments were performed for the sensor films drop cast on quartz slides as shown in Figure S9, where the time course of the fluorescence intensity change was measured at 574 nm for DAT-B dispersed on a quartz slide (containing 0.25  $\mu\text{mol}$  DAT-B) upon exposure to  $\text{H}_2\text{O}_2$  vapor fixed at 225 ppm. Four series of measurements were performed over the quartz slides containing the same molar amount of DAT-B, but different amounts of TBAH, i.e., at molar ratios of TBAH/DAT-B: 1, 3, 5 and

20. The testing experiment was performed by hanging the loaded quartz slide in the saturated vapor of  $\text{H}_2\text{O}_2$  (225 ppm) above 10 mL of 35 wt %  $\text{H}_2\text{O}_2$  solution sealed in a 50 mL jar. The fluorescence emission evolved at different time intervals was measured by Agilent Eclipse spectrophotometer. As shown in Figure S9, the fluorescence intensity increased the fastest and reached the highest intensity value at TBAH/DAT-B ratio of 5, which was determined as the optimal molar ratio for fabricating the sensor composite. The slower sensor response observed at higher TBAH/DAT-B ratio (e.g., 20) is likely due to the excessive TBAH decreasing the concentration of DAT-B molecule on surface, thus limiting the sensor molecules' interaction with  $\text{H}_2\text{O}_2$  vapor.

For the measurements performed under varying vapor concentrations of  $\text{H}_2\text{O}_2$  (shown Figure 4), the experiment was performed by hanging the loaded quartz slide in the saturated vapor of  $\text{H}_2\text{O}_2$  generated in a 26.5 L container, where approximately 1 L of  $\text{H}_2\text{O}_2$  solution (diluted down to various concentrations) was put in a and sealed for 12 hours to reach the equilibrium vapor pressure. The equilibrium vapor pressure corresponding to a specific diluted concentration of  $\text{H}_2\text{O}_2$  solution was deduced from the literature.<sup>3</sup> The experimental process was following our previous report.<sup>4</sup> In this study, various diluted concentrations of  $\text{H}_2\text{O}_2$  solution were obtained by diluting the commercial 35 wt % solution with pure water 100, 200, 1000, 2000, and 10000 times, which produce saturated (equilibrium) vapor pressures of  $\text{H}_2\text{O}_2$  of 1000, 500, 100, 50 and 10 ppb, respectively.



**Figure S9** Time course of the fluorescence intensity change measured at 574 nm for DAT-B coated quartz slides (containing 0.25  $\mu\text{mol}$  DAT-B mixed with different amount of TBAH,  $1.0 \times 1.0 \text{ cm}^2$ ) upon exposure to 225 ppm  $\text{H}_2\text{O}_2$  vapor ( $\lambda_{\text{ex}} = 427 \text{ nm}$ ). Shown in this plot are results of four slides containing the same molar amount of DAT-B, but different amounts of TBAH, i.e., at molar ratios of TBAH/DAT-B: 1 (black), 3 (red), 5 (blue) and 20 (purple).

**Fitting of the data presented in the Figure 3b.** The data presented in Figure 3b can be fitted following the reaction kinetics equation,<sup>5</sup>

$$\Delta I = K'(1 - e^{-Kt}) \quad (1)$$

where  $\Delta I$  is the increase in fluorescence intensity measured at 574 nm,  $K$  and  $K'$  are constants with  $K$  related to the surface reaction rate of DAT-B with  $\text{H}_2\text{O}_2$ , the given vapor pressure of  $\text{H}_2\text{O}_2$  and the total amount of DAT-B, and  $K'$  is referred to the ratio of the fluorescence intensity to the molar fraction of DAT-B (with respect to the total starting amount of DAT-B). Derivation of equation (1) is based on the surface reaction kinetics, i.e. the rate of producing DAT-N is proportional to the surface density (or molar fraction) of unreacted DAT-B<sup>4</sup>. The fitting gives  $K' = 378.93$ ,  $K = 0.0588$ , with a  $R^2 = 0.9698$ .

**Fitting of the data presented in Figure 4.** Assuming a quasi-equilibrium was reached within 10 min exposure (as implied from the result in Figure 3b) to H<sub>2</sub>O<sub>2</sub> vapor, the results shown Figure 4 should follow the Langmuir adsorption model (the film on quartz slide used here is the same with Figure 3, containing 0.25 μmol DAT-B and 1.25 μmol TBAH, 1.0 × 1.0 cm<sup>2</sup>). First, the surface adsorption of H<sub>2</sub>O<sub>2</sub> (i.e., the reacted fraction of sensor molecules,  $X$ ) is related to the vapor pressure of H<sub>2</sub>O<sub>2</sub> as described by the Langmuir Equation,

$$X = \frac{b \cdot [\text{H}_2\text{O}_2]}{1 + b \cdot [\text{H}_2\text{O}_2]} \quad (2)$$

Where  $b$  is a constant,  $[\text{H}_2\text{O}_2]$  is the vapor pressure (concentration) of H<sub>2</sub>O<sub>2</sub>.

The fluorescence emission intensity is proportional to the concentration of sensor molecules converted. Then, we have

$$\Delta I = \frac{a \cdot b \cdot [\text{H}_2\text{O}_2]}{1 + b \cdot [\text{H}_2\text{O}_2]} \quad (3)$$

Where  $a$  is a proportional constant.

The fitting gives  $a = 3.65 \times 10^6$ ,  $b = 9.67 \times 10^{-8}$  with a  $R^2 = 0.9732$ .

The standard deviation of the emission intensity measurement shown in Figure 4 was about 0.9 (a.u.).

The threshold of detectable emission can be set at an intensity level three times of the standard deviation of the noise floor, that's  $\Delta I = 2.7$ . Then, the corresponding detection limit can be determined by using the above equation and substituting  $\Delta I$  with 2.7. This gives a detection limit of H<sub>2</sub>O<sub>2</sub> vapor at 7.7 ppb.

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**sensors for H<sub>2</sub>O<sub>2</sub> vapor**

Reference	Limit of detection /exposure time	Response time at 1 ppm H <sub>2</sub> O <sub>2</sub> exposure
<i>J. Mater. Chem.</i> <b>2008</b> , <i>18</i> , 5134-5141. (ref. 21)	3 ppb / 8 h	800 s (1.2 ppm)
<i>Chem. Commun.</i> <b>2013</b> , <i>49</i> , 11779-11781. (ref. 22)	2.9 ppb / 5 min	0.86 s
This work	7.7 ppb / 10 min	< 0.5 s

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**Table S2. Sensor performance comparison between our sensor and other types of sensors for H<sub>2</sub>O<sub>2</sub> vapor**

Sensor technique	Limits of detection / exposure time	Response time at 1 ppm H <sub>2</sub> O <sub>2</sub> exposure
Colorimetric (ref. 16)	400 ppb / 10 s	n/a
Chemiresistor (ref. 10)	50 ppb / minutes	n/a
Electrochemistry (ref. 30)	6 ppb / 2 min	n/a
This work	7.7 ppb / 10 min	< 0.5 s

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