## **Supporting Information for**

Highly Efficient Fluorescent Sensor of Explosive Peroxide Vapor via ZnO Nanorod Array Catalyzed Deboronation of Pyrenyl borate

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**General**: UV-vis absorption and fluorescence analysis conducted on a Jasco V-670 spectrophotometer and a Jasco FP 6500 spectrometer, respectively. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained from a Brucker DRX500 instrument, tetramethylsilane (TMS) was used as an internal standard. Mass spectra were recorded on BIFLEX III MALDI-TOF (Brucker Daltonics Inc.) and GCT-MS Micromass UK mass spectrometers. High vacuum infrared spectra were performed on Brucker VERTEX 70v via surface reflection-absorption model. Cyclic voltammetry experiments were performed with a CH Instruments electrochemical analyzer. The electrochemical behaviors of **TPA-PR**, **TPA-PR-Br**, **PR-BOR** and **TPA-PR-BOR** were investigated in a standard three electrode electrochemical cell with 0.1 M tetra-*n*-butylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in acetonitrile solution, (a glassy carbon working electrode, a platinum counter electrode and a saturated calomel electrode

(SCE) as a reference electrode) and the scanning rate was 100 mV/s under nitrogen at room temperature. All the films both on (10×20 mm) quartz plates and (10×20 mm) ordered vertical ZnO nanorod arrays substrates were spin-casted using 2500 rpm from their  $3\times10^{-3}$  M toluene solutions, and placed under vacuum for 1 hour before use. The fluorescence responses of films to various analytes were progressed by inserting the films into sealed vials (3.8 ml) at room temperature containing cotton and analytes, which prevents direct film analyte contact and helps to maintain a constant vapor pressure. The fluorescence time-course responses were recorded immediately after exposing the films to analytes by front-face ( $30^{\circ}$ ) detection.

**Materials:** TATP was obtained from Institution of Forensic Science, The Criminal Department of Shanghai Public Security Bureau. All solvents and reagents were obtained from commercial sources and used as received. Ordered vertical ZnO nanorod arrays substrates were prepared as described in our latest report: A mixture composed of 2.2 g zinc acetate dihydrate, 0.6 mL monoethanolamine, and 30 mL 2-methoxyethanol was stirred at 60 °C for 30 min, followed by being spin coated on quartz plates at 2000 rpm for 20 s. The seed layer was heated to 120 °C for 10 min without delay to decrease the fluidity and finally formed after 1 h post-annealing at 400 °C in air. Quartz plates with ZnO seed layer were then vertically inserted into the aqueous precursor solution and heated at a constant temperature of 90 °C (for 4 to 8 h) with continuous magnetic stirring to grow ZnO nanorod array. The precursor solution was composed of 0.02 mol/L zinc nitrate [Zn(NO<sub>3</sub>)<sub>2</sub>], 0.02 mol/L

hexamethylenetetramine [HMT, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>] and 0.4 wt % PVA whose polymerization degree



was 1800±100. Finally, ordered vertical ZnO nanorod array substrates were obtained:<sup>1</sup>

SEM of ordered ZnO nanorod array substrate (performed on Hitachi S-4700)

Synthesis



**1-bromopyrene (1):** To a methanol-ethyl ether solution of pyrene (2.02 g, 10 mmol) and hydrobromic acid (1.688 ml, 40 % aq., 11 mmol) was slowly added hydrogen peroxide (1.05 mL, 30% aq., 10 mmol) over a period of 15 mins at  $15^{\circ}$ C and stirred at room temperature for

12 hrs. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL×2), and washed with NaOH (1 M aq), water and brine. The organic layer was separated and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the residue was purified by gel column chromatography on silica gel to get white solid (2.7 g, yield 96%). <sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm)  $\delta$  8.428 (d, 1H, *J* =9Hz), 8.208 (m, 3H), 8.166 (d, 1H, *J*=9Hz), 8.082 (d, 1H, *J*=9Hz), 8.004 (m, 3H); MALDI-TOF MS: m/z 280.

1,6-dibromopyrene (2): To a methanol-ethyl ether solution of pyrene (8.5 g, 41.7 mmol) and hydrobromic acid (7.06 ml, 40 % aq., 46.1 mmol) was slowly added hydrogen peroxide (4.40 mL, 30% aq., 41.7 mmol) over a period of 1 hr at 15°C and stirred at room temperature for 24 hrs. The mixture was extracted with  $CH_2Cl_2$  (100 mL×2), and washed with NaOH (1 M aq), water and brine. The organic layer was separated and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the residue was purified by gel column chromatography on silica gel to get white powder (14 g, yield 93%), then fraction recrystalized in toluene to get needle-like crystal 1,6-dibromopyrene (6.7 g, yield 45%) and 1,8-dibromopyrene (6 g, yield 40%). **1,6-dibromopyrene:** <sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm) δ 8.429 (d, 2H, *J*=9Hz), 8.244 (d, 2H, J=8Hz), 8.084 (d, 2H, J=9Hz), 8.023 (d, 2H, J=8Hz); HRMS (ESI) calculated for C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub>, 357.8993, found 357.8998. **1,8-dibromopyrene:** <sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm) δ 8.493 (s, 2H), 8.230 (d, 2H, J=8Hz), 8.003 (m, 4H); HRMS (ESI) calculated for C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub>, 357.8993, found 357.8998.

**N-(4-bromophenyl)-N-phenylbenzenamine (3):** To a methanol-ethyl ether solution of triphenylamine (10 g, 40.8 mmol) and hydrobromic acid (6.89 ml, 40 % aq., 44 mmol) was slowly added hydrogen peroxide (4.28 mL, 30% aq., 40.8 mmol) over a period of 1 hr at 15 °C and stirred at room temperature for 24 hrs. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL×2), and washed with NaOH (1 M aq), water and brine. The organic layer was separated and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the residue was purified by gel column chromatography on silica gel to get white solid (12.7 g, yield 96%). <sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm)  $\delta$  7.314 (d, 2H, *J*=8.5Hz), 7.241 (t, 4H, *J*=7.5Hz), 7.067 (d, 4H, *J*=8Hz), 7.020 (t, 2H, *J*=7.5Hz), 6.938 (d, 2H, *J*=9Hz); MALDI-TOF MS: m/z 323.

**N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-N-phenylbenzenamine (4):** To a THF solution of **3** (8 g, 24.7 mmol) was added n-BuLi (18.8 mL, 3.3 g, 52.7 mmol) at -78°C, then added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19.8 mL, 18 g, 96.8 mmol ) dropwise, after stirring at this temperature for 2 hr, the mixture was cooled to room temperature and reacted for 18 hrs. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water and brine, and the organic layer was then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the residue was purified by column chromatography on silica gel to get white solid (7.6 g, yield 83%).<sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm)  $\delta$  7.650 (d, 2H, *J*=8.5Hz), 7.235 (m, 4H), 7.092 (d, 4H, J=7.5Hz), 7.014 (m, 4H), 1.328 (s, 12H); MALDI-TOF MS: m/z 384.

## N-(4-(1-bromopyren-6-yl)phenyl)-N-phenylbenzenamine (TPA-PR-Br): A mixture of 4 (5

g, 13.4 mmol), 2 (5.3 g, 14.7 mmol), potassium carbonate (8.29 g, 60 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (394 mg, 0.34 mmol) in 180 mL of toluene/H<sub>2</sub>O(2:1) was degassed for 30 min and then heated to reflux for 72 hrs. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 ml×3), and the organic layer was washed with water and brine, and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the residue was purified by column chromatography on silica gel to get slightly yellow powder (4.3 g, yield 60%), and then recrystallized in CH<sub>2</sub>Cl<sub>2</sub>/ethanol to get slightly yellow crystal 3 g. <sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm)  $\delta$  8.431 (d, 1H, J=9Hz), 8.296 (d, 1H, J=9Hz), 8.221 (t, 2H, J=8Hz), 8.168 (d, 1H, J=9Hz), 8.020 (d, 1H, J=9Hz), 7.976 (d, 2H, J=8.5Hz), 7.478 (d, 2H, J=8Hz), 7.308 (t, 4H, J=8Hz), 7.226 (t, 6H, J=9Hz), 7.061 (t, 2H, J=7Hz); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  147.69, 147.24, 138.28, 134.61, 131.34, 130.49, 130.17, 129.97, 129.36, 129.02, 128.52, 128.26, 126.98, 126.20, 125.77, 125.24, 125.21, 124.68, 124.47, 123.14, 119.85; HRMS (ESI) calculated for C<sub>34</sub>H<sub>22</sub>BrN, 523.0936, found 523.0944.

N-(4-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyren-6-yl)phenyl)-N-phenylbenzen amine (TPA-PR-BOR): To a THF solution of TPA-PR-Br (1.5 g, 2.8 mmol) was added

5.9 -78℃. n-BuLi (2.15)mL. 0.37 mmol) at then added g, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.75 mL, 1.6 g, 8.6 mmol ) dropwise, after stirring at this temperature for 2 hr, the mixture was cooled to room temperature and reacted for 12 hrs. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with water and brine, and the organic layer was then dried over anhydrous MgSO4. The solvent was removed and the residue was purified by column chromatography on silica gel to get slightly yellow powder (1.4 g, yield 86%), and then recrystallized in CH<sub>2</sub>Cl<sub>2</sub>/ethanol to get slightly green crystal 0.9 g. <sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm)  $\delta$  9.068 (d, 1H, J=9Hz), 8.526 (d, 1H, J =7.5Hz), 8.317 (d, 1H, J=9Hz), 8.225 (d, 1H, J=8Hz), 8.140 (d, 1H, J=7Hz), 8.124 (d, 1H, J=5.5Hz), 8.016 (d, 1H, J=9Hz), 7.987 (d, 1H, J=8Hz), 7.494 (d, 2H, J=7.5Hz), 7.300 (t, 4H, J=7.5Hz), 7.224 (t, 6H, J=9Hz), 7.050 (t, 2H, J=7Hz), 1.496 (s, 12H); <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>, ppm) δ 147.76, 147.05, 137.66, 136.82, 133.97, 133.29, 131.42, 130.00, 129.33, 127.86, 127.80, 127.49, 127.39, 126.53, 125.05, 124.99, 124.70, 124.61, 123.82, 123.24, 123.03, 83.88, 25.07; HRMS (ESI) calculated for C<sub>40</sub>H<sub>34</sub>BNO<sub>2</sub>, 571.2683, found 571.2690.

**1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (PR-BOR):** To a THF solution of **1** (2.5 g, 8.9 mmol) was added n-BuLi (6.8 mL, 1.2 g, 19 mmol) at -78°C, then added 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.2 mL, 6.5 g, 34.9 mmol) dropwise, after stirring at this temperature for 1 hr, the mixture was cooled to room temperature and

reacted for 12 hrs. The mixture was extracted with  $CH_2Cl_2$  and washed with water and brine, and the organic layer was then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the residue was purified by column chromatography on silica gel to get slightly yellow solid (2.5 g, yield 86%).<sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm)  $\delta$  9.061 (d, 1H, *J*=9Hz), 8.526 (d, 1H, *J*= 8Hz), 8.223-8.107 (m, 5H), 8.057 (d, 1H, *J*=9Hz), 7.992 (t, 1H, *J*=7.5Hz), 1.494(s, 12H); MALDI-TOF MS: m/z 328.

**N-phenyl-N-(4-(pyrenyl)phenyl)benzenamine (TPA-PR):** A mixture of **PR-BOR** (0.61g, 1.85 mmol), **3** (0.6 g, 1.85 mmol), potassium carbonate (1.33 g, 9.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (64 mg, 0.05 mmol) in 20 mL of toluene/H<sub>2</sub>O(2:1) was degassed for 30 min and then heated to reflux for 36 hrs. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 ml×3), and the organic layer was washed with water and brine, and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed and the residue was purified by column chromatography on silica gel to get white solid (0.6 g, yield 73%). <sup>1</sup>H NMR (500M, CDCl<sub>3</sub>, ppm)  $\delta$  8.284 (d, 1H, *J*=9Hz), 8.156-8.218 (m, 3H), 8.082 (s, 2H), 7.992-8.053 (m, 3H), 7.499 (d, 2H, *J*=8.5Hz), 7.304 (t, 4H, *J*=7.5Hz), 7.226 (t, 6H, *J*=8Hz), 7.055 (t, 2H, *J*=7Hz); HRMS (ESI) calculated for C<sub>34</sub>H<sub>23</sub>N, 445.1831, found 445.1836.

## Supporting results and discussion:

1. Characterization of the reaction between **PR-BOR** and  $H_2O_2$  in THF:



After reaction, the product **PR-OH** was characterized by <sup>1</sup>H NMR and HRMS.

<sup>1</sup>H NMR: (500M, CDCl<sub>3</sub>, ppm) δ 8.012 (9H, broad) 5.646 (s, 1H).

HRMS (ESI) calculated for C<sub>16</sub>H<sub>10</sub>O, 218.0732, found 218.0735.



2. Discussion of the reaction between **PR-BOR** film and  $H_2O_2$  vapor:

Figure S1. (a) Absorption and time-course fluorescent spectra changes of **PR-BOR** during reaction with hydrogen peroxide in THF solution, (blue line:  $5 \times 10^{-6}$  M **PR-BOR**; red line:  $5 \times 10^{-6}$  M **PR-OH**; green line:  $5 \times 10^{-6}$  M **PR-BOR** after reaction with  $7 \times 10^{-2}$  M hydrogen

peroxide for 20 minutes.) (b) Absorption and fluorescent spectra of **PR-BOR** (blue), dissolved hydrogen peroxide exposed **PR-BOR** film (green) and **PR-OH** (red) in THF solution. The hydrogen peroxide exposure time was 300 s.

**Figure S1a** showed the real time spectral changes of **PR-BOR** upon reaction with  $H_2O_2$  in solution. During the 20 minutes reaction, emission peaks of **PR-BOR** at 379 nm and 399 nm decreased successively along with the appearance of two new emission peaks at 387 nm and 408 nm, as well as two new absorption peaks at 364 nm and 385 nm. By comparison with the spectra of **PR-OH**, it could be concluded that these new peaks arose from **PR-OH**. Therefore, the new absorption and emission peaks of  $H_2O_2$  exposed **PR-BOR** film dissolved in solution as shown in **Figure S1b** (green line) could directly demonstrate that the same reaction took placed between **PR-BOR** film and  $H_2O_2$  vapor, and this reaction lead to the fluorescence quenching of **PR-BOR** film as shown in **Figure 1** of the text.

3. Discussion of substitute effects:





**Figure S2.** The CV curves of **TPA-PR**, **TPA-PR-Br**, **PR-BOR** and **TPA-PR-BOR** on glassy carbon substrates at a sweep rate of 100 mV s<sup>-1</sup>.

**Table S1**. Spectroscopic and electrochemical properties of **TPA-PR**, **TPA-PR-Br**, **PR-BOR** and **TPA-PR-BOR**.

	Abs, $\lambda_{max}$ (nm)		PL, $\lambda_{max}$ (nm)		НОМО	LUMO	∠E	Φ
	solution	film	solution	film	(eV)	(eV)		
TPA-PR	361	378	463	453	-5.60	-2.74	2.86	0.90
TPA-PR-Br	374	-	476	-	-5.67	-2.92	2.75	0.39
PR-BOR	350	354	379, 399, 421	480	-5.90	-2.87	3.03	0.32
			(weak)	(broad)				
TPA-PR-BOR	376	385	476	472	-5.62	-2.93	2.69	0.83

As shown in **Table S1**, In contrast with **PR-BOR**, the absorption spectra of **TPA-PR-BOR** both in solution and film were red-shifted more than 20 nm, while the emission spectra red-shifted to 476 nm in solution but blue-shifted to 472 nm in film state. The blue-shifted emission in film state of **TPA-PR-BOR** indicated  $\pi$ - $\pi$  interaction of pyrenyl units which resulted in severe excimer emission at 480 nm was suppressed. In addition, the emission of **TPA-PR-BOR** exhibited only a single peak in comparison with that multiple peaks of **PR-BOR** in solution. And for **TPA-PR-BOR**, the fluorescence emission of film at 472 nm was even blue-shifted compared with its highly diluted solution (10<sup>-8</sup> M, 476 nm), thus it should not arise from the excimer of pyrene but the emission of **TPA-PR-BOR** molecule. The fluorescence quantum yield of **TPA-PR-BOR** increased significantly from 0.32 to 0.83 and the energy band gap decreased from 3.03 to 2.69 by the introduction of TPA unit. These results indicated TPA unit could not only reduce the excimer emission of pyrene, but also modulate the emission wavelength, fluorescence quantum yield and energy gap for its propeller spatial structure and electron donating character. Furthermore, the extreme broad emission at 480 nm of **PR-BOR** in the film state obviously arises from the excimer emission of pyrene by comparing with its multiple emission peaks (379 nm, 399 nm and 421 nm) in solution. In addition, in contrast with the emission in solution, **TPA-PR** in film state was just blue-shifted with a peak at 453 nm rather than the excimer emission of pyrene at 480 nm. This result suggested the excimer emission of pyrene in film state was suppressed by introducing TPA unit as we described above.

In contrast with **TPA-PR**, by introducing bromine substitute (**TPA-PR-Br**) the absorption and emission were all red-shifted 13 nm with fluorescence quantum yield decreased from 0.90 to 0.39 in solution; moreover, band-gap obtained from CV curves decreased 0.11 eV. Additionally, **TPA-PR-Br** showed very weak fluorescence after fabricating onto film state. These results indicated bromine atom lead to the severe heavy-atom effects of fluorescence (significant fluorescence quantum yield decrease), as well as influenced the energy-gap (a little lower HOMO and much lower LUMO) via its electron-drawing ability and partially delocalizing its lone pairs of electrons to pyrene. By substituting bromine unit with BOR group, **TPA-PR-BOR** showed distinct fluorescence quantum yield increase as well as a little higher HOMO and similar LUMO in comparison with **TPA-PR-Br**. These results were attributed to the removing of heavy-atom effect (distinct fluorescence quantum yield increase) and the conjugation of unoccupied *p*-orbit of boron atom with pyrene which acts similarly as the electron-drawing/feedback of bromine atom (similar energy-gap between **TPA-PR-Br** and **TPA-PR-BOR**).

4. Detailed discussion and deduction of reaction degree equation:





**Figure S3.** (a) Absorption and time-course fluorescence spectra changes of **TPA-PR-BOR**  $(1 \times 10^{-7} \text{ M})$  during reaction with hydrogen peroxide  $(7 \times 10^{-2} \text{ M})$  in THF solution. (b) Absorption and fluorescence spectra of **TPA-PR-BOR** (blue), dissolved hydrogen peroxide exposed **TPA-PR-BOR** on quartz plate (green) and on ordered vertical ZnO nanorods substrate (red) in THF solution. The hydrogen peroxide exposure time was 300 s. (c) time-course degree of reaction between **TPA-PR-BOR** and hydrogen peroxide in THF solution. The positions of red star-spots were determined by corresponding reaction degree of **TPA-PR-BOR** on Quartz plate after exposure to hydrogen peroxide vapor.

Reaction:



As illustrated in **Figure S3a**, the appearance of peak at 440 nm was due to the emission of reaction product **C**, According to the Lambert-Beer's law, the concentration of **C** was direct proportion with the absorption intensity in high diluted solution, and herein the concentration of product **C** was highly diluted since the concentration of reactant **A** was  $1 \times 10^{-7}$ M. In

addition, the quantum yield of C should be a constant for the solution condition and equipment parameter had not changed during the test. Therefore, the amount of increased fluorescence intensity at 440 nm was direct proportion with the concentration of C during the reaction. As a result, according to **Figure S3a**, we obtained the equation of time-course degree of reaction like this:

$$D = \frac{I_t - I_0}{I} \qquad (1)$$

Where *D* is the degree of reaction,  $I_t$  is time-course fluorescence intensity of 440 nm,  $I_0$  is fluorescence intensity of **TPA-PR-BOR** at 440 nm before adding hydrogen peroxide, *I* is the fluorescence intensity at 440 nm minus  $I_0$  when reaction completed.

As a result, by measuring time-course fluorescence spectra changes of **TPA-PR-BOR** during reaction as in **Figure S3a**, time-course degree of reaction was obtained as shown in the **Figure S3c**. (black squares)

Moreover, according to the reaction,

$$-\frac{dC_A}{dt} = kC_A C_B \qquad (2)$$

Where *k* is the reaction constant,  $C_A$  and  $C_B$  are concentration of **A** and **B** In this reaction  $C_B >> C_A$ ,

$$-\frac{dC_A}{dt} = k'C_A \qquad (3)$$

Integrate,

$$-\int_0^t d(\ln C_A) = \int_0^t k' dt \qquad (4)$$

Therefore,

$$\frac{C_{A_{t}}}{C_{A_{0}}} = e^{-k't} \longrightarrow \frac{C_{A_{0}} - C_{A_{t}}}{C_{A_{0}}} = 1 - e^{-k't} \quad (5)$$

Where  $C_{A0}$  and  $C_{At}$  are concentrations of **A** at the time of 0 and t. Hence, we can get equation of time-course degree of reaction like this:

$$D = \frac{C_{A_0} - C_{A_t}}{C_{A_0}} = 1 - e^{-k't} \qquad (6)$$

The data (black squares) of **Figure S3c** were well-fitted by equation **6** and the constant k' was determined to be 0.05232 (error  $\pm 2\%$ ).

Owing to the deduction we have discussed above, Film state reaction between **TPA-PR-BOR** and H<sub>2</sub>O<sub>2</sub> vapor could be characterized by dissolving H<sub>2</sub>O<sub>2</sub> exposed **TPA-PR-BOR** film in solution. And after dissolving H<sub>2</sub>O<sub>2</sub> exposed **TPA-PR-BOR** film both on ZnO nanorod array and on quartz plate as shown in **Figure S3b**, the absorption and emission spectra of **TPA-PR-BOR** on ZnO nanorod array showed the reaction was completed while **TPA-PR-BOR** on quartz plate reacted partially. By measuring the emission intensity at 440 nm, the reaction degree of **TPA-PR-BOR** on ZnO nanorod array and on quartz plate were determined to be 100% and 30% in 300 s, respectively. Later, we found the reaction of **TPA-PR-BOR** on ZnO nanorod array have already been completed in 100 s as illustrated in **Figure S3c**.

5. High vacuum reflection-absorption infrared spectra of ZnO nanorod array before and after exposure to peroxides:



**Figure S4.** High vacuum infrared spectra of the ZnO nanorod array before (black) and after exposure to hydrogen peroxide (red) and TATP (green) vapor.

Nanostructured ZnO is a promising photonics material for its wide band gap (3.4 eV), large exciton binding energy (60 meV) and radiation hardness. Though its photooxidation catalysis which related with the surface-defect emission was widely studied,<sup>2</sup> the photooxidation catalysis mechanism on the surface of ZnO nanoparticals has not been well resolved. Bohle et al. reported that after UV radiation exposure, ZnO might lead to the formation of hydrogen peroxide and subsequently the surface of ZnO nanoparticle was oxidated in colloidal solution as below:<sup>3</sup>

1. 
$$\operatorname{ZnO} + \operatorname{O}_{2(g)} \xrightarrow{k_{ads}} \operatorname{ZnO}(O_2)_{x+y}$$
  
2.  $\operatorname{ZnO}(O_2)_{x+y} + 2 \operatorname{e}_{CB^-} + 2H^+ \xrightarrow{hv} \operatorname{ZnO}(O_2)_y + H_2O_2$   
3.  $2 \operatorname{ZnO} + H_2O_2 \longrightarrow 2 \operatorname{ZnO}(OH)_y$ 

They proposed this catalytic activity was accounted for the difficulty in complete extinction of defect emission. Therefore, in our illustration, the ZnO nanorod-peroxide "complex" and its catalysis of the deboronation reaction might work as follows:

1. 
$$2 ZnO + R'_2O_2 \longrightarrow 2 ZnO(OR')^*$$
  
2. TPA-PR-BOR  $\xrightarrow{ZnO(OR')^*}_{k_{cat}}$  TPA-PR-OR'+ R'O-BOR

First, peroxide interacts with ZnO nanorod to form highly reactive intermediate ZnO(OR')\*, later, it will rapidly bind with TPA-PR-BOR to afford non-emissive TPA-PR-OR'.

## Reference:

- D. F. Zhu, Q. Chen, Y. Y. Fu, C. He, L. Q. Shi, X. Meng, C. M. Deng, H. M. Cao and J. G. Cheng, ACS Nano, 2011, 5, 4293-4299.
- (a) D. W. Bahnemann, C. Kormann and M. R. Hoffmann, J. Phys. Chem. B, 1987, 91, 3789-3798.
   (b) A. van Dijken, E. A. Meulenkamp, D. Vanmaekelbergh and A. Meijerink, J. Phys. Chem. B, 2000, 104, 4355-4360.
   (c) N. S. Norberg and D. R. Gamelin, J. Phys. Chem. B, 2005, 109, 20810-20816.
- 3. D. S. Bohle and C. J. Spina, J. Am. Chem. Soc., 2007, 129, 12380-12381.