

Expeditious Base-free Solid-State Reaction between Phenyl Boronates and Hydrogen Peroxide on Silica Gel

*Li Zhang, Qianqian Chen, Li Yang, Yining He, Keke Guo, Jialin Yang, and Ji-Min Han**

State Key Laboratory of Explosion Science and Technology of China, Explosion Protection and Emergency Disposal Technology Engineering Research Center of the Ministry of Education, Beijing Institute of Technology, 5 Zhongguancun South Street, Haidian District, Beijing, 100081, China. Email: hanjimin@bit.edu.cn

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1. Materials and General Instrumentations

All raw materials and reagents were obtained from commercial suppliers (Alfa Aesar, Aldrich, Weiss), and the purity is the analytical grade. C6NIB was synthesized according to the steps in literature and undergoes further separation and purification and other post-processing procedures.

The aluminum foil-based silica gel plate (200 ~ 300 mesh, thickness 0.2 mm, type G) was purchased from commercial manufacturers (KEPNO) and used as received.

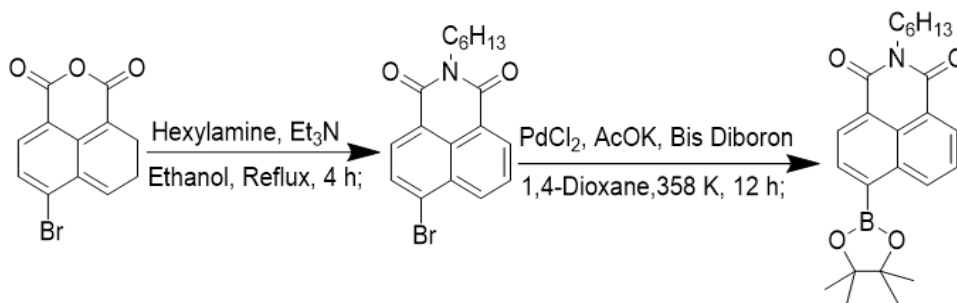
C6NIB was dissolved with chloroform as the solvent, and TBAH was dissolved with ethanol as the solvent. The preparation of the experimental reagents (the concentration of C6NIB, the molar ratio of C6NIB to TBAH) were all measured with pipettes, and were prepared in a 20 mL centrifuge bottle, and the additional solvent is ethanol.

The aluminum foil-based silica gel plates were cut into a size of 20 mm × 20 mm as the test substrate base, the 35 μ L of solution was dropped onto the center of the test substrate base with a pipette gun, and was allowed to evenly spread and dry to complete the preparation of the test substrate. 35 μ L 0.5 mol/L C6NIB solution was dropped and treated on the silica gel substrate, before it formed a round shape deposition with a diameter of 13 mm. By calculating the molecular weight and molecular volume in the solution, we roughly estimated the thickness of the formed boronate thin film as around 100 nm if the film was deposited on a smooth surface. Because the surface roughness (Ra) of silica gel substrate is larger than 100 μ m and its surface morphology is relatively irregular, the thickness and the surface roughness of C6NIB film in this study is neglectable and hard to be estimated.

The 30% H₂O₂ aqueous solution was added in a 20 mL beaker with lid at room temperature overnight to obtain saturated H₂O₂ vapor. The H₂O₂ vapor was obtained by taking the headspace gas of solution and the concentration as well as the gas pressure can be calibrated in the reported literature¹. The test substrates were placed in the headspace gas and in full contact with H₂O₂ in the beaker mentioned above.

The fluorescence emission spectrum was tested using a RF-6000 fluorescence spectrophotometer from Shimadzu. The SEM image was tested using a JSM-IT300 Scanning Electron Microscope from JEOL. The ¹H and ¹³C NMR spectra were recorded on a Bruker 500 FT-NMR spectrometer (400 MHz for ¹H and 75 MHz for ¹³C). The UV Absorbance spectrum was tested using a PerkinElmer Lambda 650R spectrophotometer with a build-in universal reflection accessory. The spectra were collected with unpolarized light incident at ~ 45° with respect to the surface and integrated for 0.1 s and at a resolution of 1 nm. The spectra collected were converted and shown as extinction measured as $-\log(R_0/R)$, where R is the reflectance of the loaded sample substrate and R_0 is the reflectance of the unload silica gel plate substrate.

2. Synthesis of the Phenyl Boronate Compound C6NIB



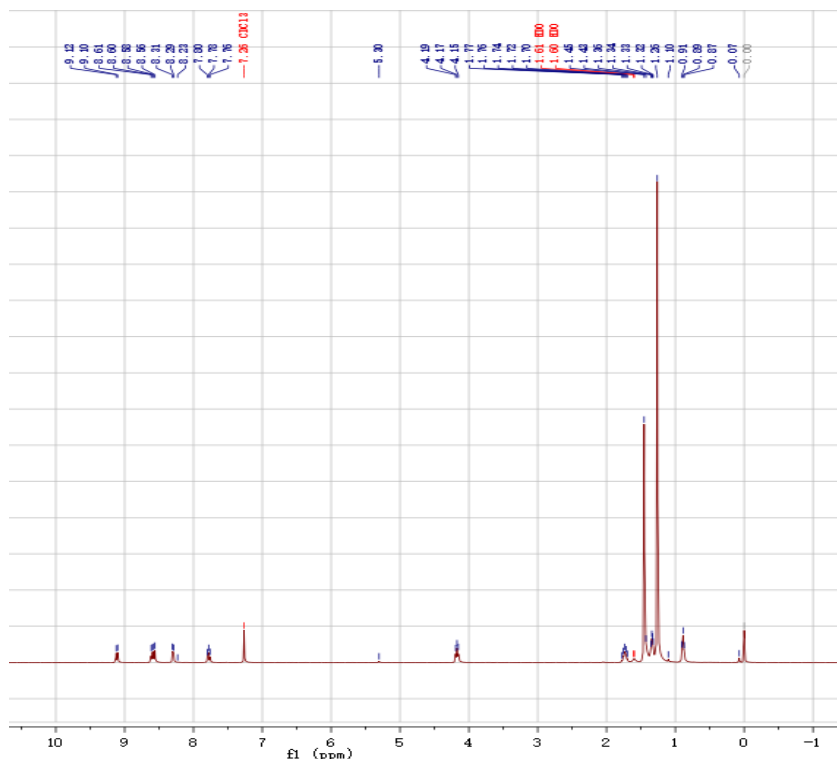
Scheme S1. The synthetic route of C6NIB.

The synthesis of the substance C6NIB used for detection was following the modified steps in the literature². As shown in Scheme S1, the synthesis contains two steps.

The synthesis of the intermediate product C6NIBr. 4-Bromo-1,8-naphthalic anhydride (1.0 g, 3.6 mmol), hexylamine (383.0 mg, 3.8 mmol), and triethylamine (10 mL) were added into anhydrous ethanol (50 mL) and refluxed for 4 h. The reaction mixture was evaporated under reduced pressure and then purified through column chromatography on silica gel with hexane/ethyl acetate (5:1, v/v) as eluent. The intermediate product C6NIBr was obtained as white crystal (1.10 g, 85 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 8.52-8.55 (1 H, m, Ar-H), 8.39-8.43 (1 H, m, Ar-H), 8.27-8.29 (1 H, d, *J* = 7.8 Hz, Ar-H), 7.90-7.93 (1 H, d, *J* = 7.8 Hz, Ar-H), 7.71-7.76 (1 H, m, Ar-H), 4.07-4.13 (2 H, t, *J* = 7.2 Hz, CH₂), 1.66-1.71 (2 H, m, CH₂), 1.29-1.40 (6 H, m, CH₂), 0.84-0.8 (3 H, t, CH₃). ¹³C NMR (CDCl₃, 75 MHz, ppm): δ 163.32, 163.29, 132.90, 131.76, 130.94, 130.88, 129.95, 128.65, 127.87, 122.90, 122.05, 40.51, 31.45, 27.91, 26.70, 22.49, 14.00.

The synthesis of the substance C6NIB. The intermediate product C6NIBr (360.0 mg, 1.0 mmol) was then mixed with anhydrous potassium acetate (588.0 mg, 6.0 mmol), bis(pinacolato)diboron

(560.0 mg, 2.2 mmol), [PdCl₂(dppf)] (73.0 mg, 10 mol %), and dppf (55.0 mg, 10 mol %) in dioxane (20 mL). The mixture was degassed by three freeze-pump-thaw cycles and then heated at 358 K for 12 hours. After cooling to room temperature, the reaction mixture was partitioned between water and dichloromethane. The aqueous phase was extracted with 20 mL dichloromethane for 3 times and then combined with the original dichloromethane phase. This dichloromethane solution was washed with brine twice and then washed with water, followed by drying with Na₂SO₄. After rotary evaporate under reduced pressure to remove excess solvent, the residue was purified through column chromatography on silica gel with hexane/ethyl acetate (5:1, v/v) as eluent. The product was obtained as white powder (180 mg, 44 %). ¹H NMR (CDCl₃, 400 MHz, ppm): δ = 9.05-9.08 (1 H, m, Ar-H), 8.50-8.56 (2 H, m, Ar-H), 8.24-8.26 (2 H, d, *J* = 7.2 Hz, Ar-H), 7.71-7.76 (1 H, t, *J* = 7.2 Hz, Ar-H), 4.11-4.16 (2 H, t, *J* = 7.2 Hz, CH₂), 1.71 (2 H, m, CH₂), 1.30-1.35 (6 H, m, CH₂), 0.85-0.90 (3 H, t, CH₃). ¹³C NMR (CDCl₃, 75 MHz, ppm): δ 164.16, 164.14, 135.66, 135.11, 134.77, 130.70, 129.59, 127.69, 126.95, 124.62, 122.51, 84.48, 40.43, 31.50, 27.96, 26.74, 24.91, 22.50.



Scheme S2. ^1H NMR spectrum of C6NIB.

C6NIB is only weakly fluorescent in the UV region, where the quantum yield is only 0.6% under basic condition. However, upon reaction with H_2O_2 the aryl boronate group of C6NIB is transformed to phenol. The weak blue-fluorescent naphthalimide backbone transition was converted to electron donor-acceptor (push-pull) C6NIO/C6NIO $^-$ structure, which turns on the charge transfer transition and fluorescent emission in the longer wavelength band. Because the pristine C6NIB molecule has close to zero emission in the charge transfer band, extremely high turn-on ratio will be obtained if the reaction with H_2O_2 is monitored in the long wavelength domain.

3. Studies on silica gel surface properties

The silica gel sample used in the following test was scraped off from the aluminum-foil based

silica gel plate without any special treatment.

Specific Surface Area (S_{BET}) - N_2 Adsorption. The specific surface area (BET) was measured with an Autosorb iQ Station 2 outfitted with the micropore option by Quantachrome Instruments, running version 4.0 of the ASWin software package, using the adsorption of N_2 at the temperature of 77.35 K. Prior to measuring, the 0.2179 g sample was degassed at 423.15 K for 2 h and finally outgassed to 10^{-5} Torr.

The BET test shows that the specific surface area (S_{BET}) of the silica gel sample is $166.5 \text{ m}^2/\text{g}$, which shows the large surface area of the silica gel.

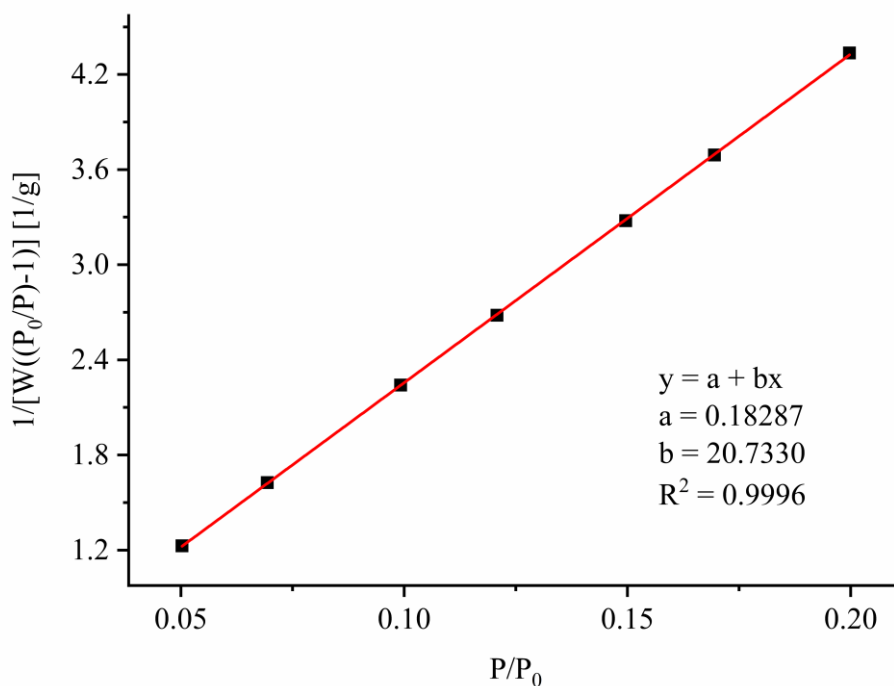


Fig. S1 BET fit for the N_2 adsorption isotherm of the silica gel.

Water Vapor Sorption Isotherm. Water vapor sorption isotherm was measured with an automated Vstar 3-0000-1000-XS from Quantachrome Instruments, running version 1.1.12 of the

VstarWin Software package. Prior to measuring, the samples were degassed at 423.15 K for 2 h and finally outgassed to 10^{-5} Torr, approximately 0.0706 g silica gel measured at a temperature of 298.15 K.

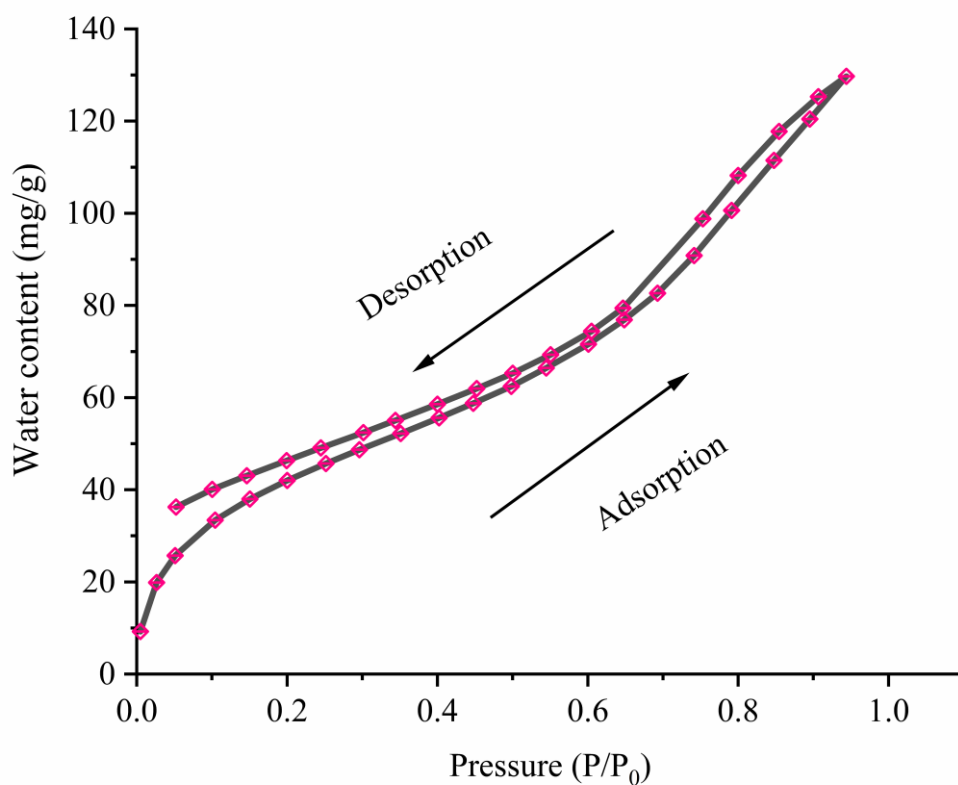


Fig. S2 Water vapor sorption isotherm of the silica gel.

The Water Vapor Sorption test confirmed the outstanding water adsorption capacity of the silica gel.

4. Additional Experimental Details

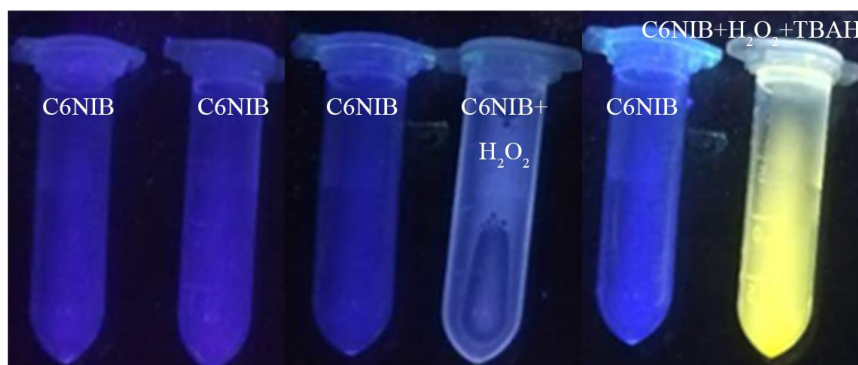


Fig. S3. Picture of the reaction of C6NIB with H₂O₂ in chloroform solution ($\lambda_{ex} = 358$ nm).

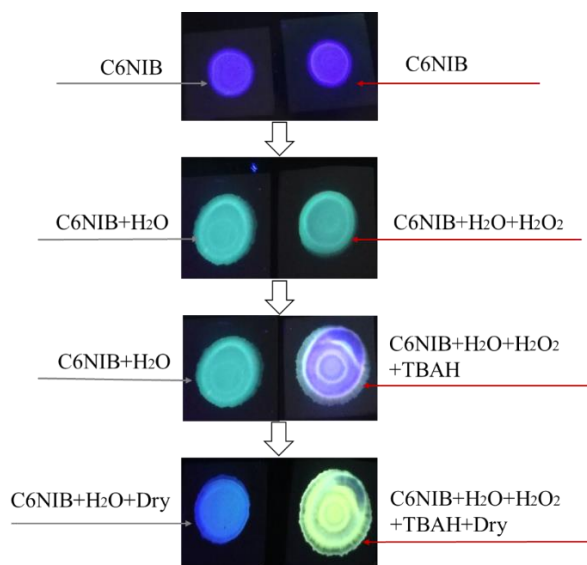


Fig. S4. Pictures of the qualitative exploration of the influence of H₂O on the silica gel surface ($\lambda_{ex} = 358$ nm)

We prepared two silica gel plates test substrates of the same specification. One of the test substrates was added by liquid H₂O droplet before drying, while the other substrate was treated sequentially by H₂O, H₂O₂ gas, and TBAH solution before drying. For each step of operation, the

substrates were taken under the UV analyzer for observation. The operation steps and qualitative analysis results are shown in Fig. S4.

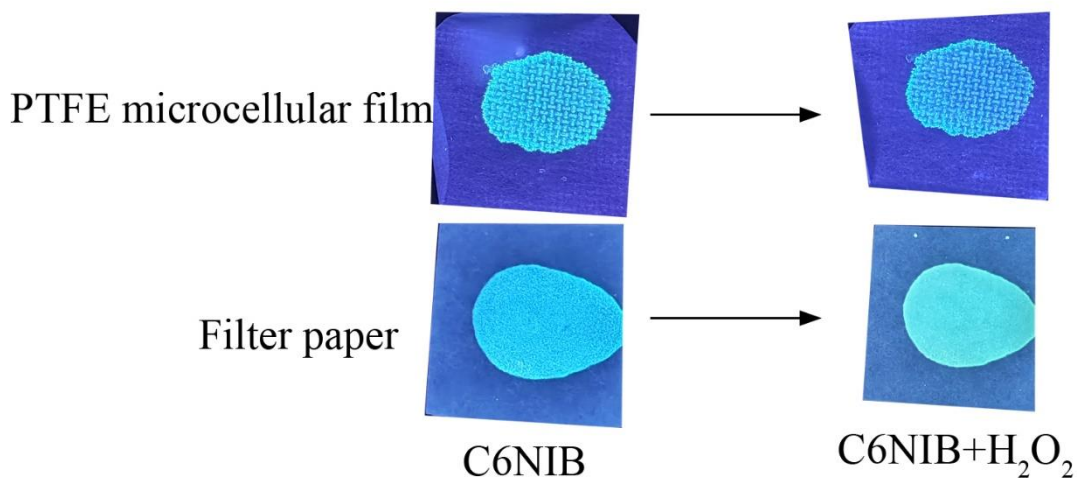


Fig. S5. Pictures of the reaction of C6NIB with H₂O₂ on PTFE microcellular film and filter paper. (λ_{ex} = 358 nm)

Silica gel has large surface area, continuous porosity, and hydrophilic interface, showing strong polarity. The PTFE microcellular film and the filter paper have the large surface area, continuous porosity, but lack of hydrophilic interface and strong polarity compared to silica gel. As shown in Fig. S5, the reaction had almost no fluorescence emission due to the non-polarity PTFE microcellular film; the same result was observed on the filter paper.

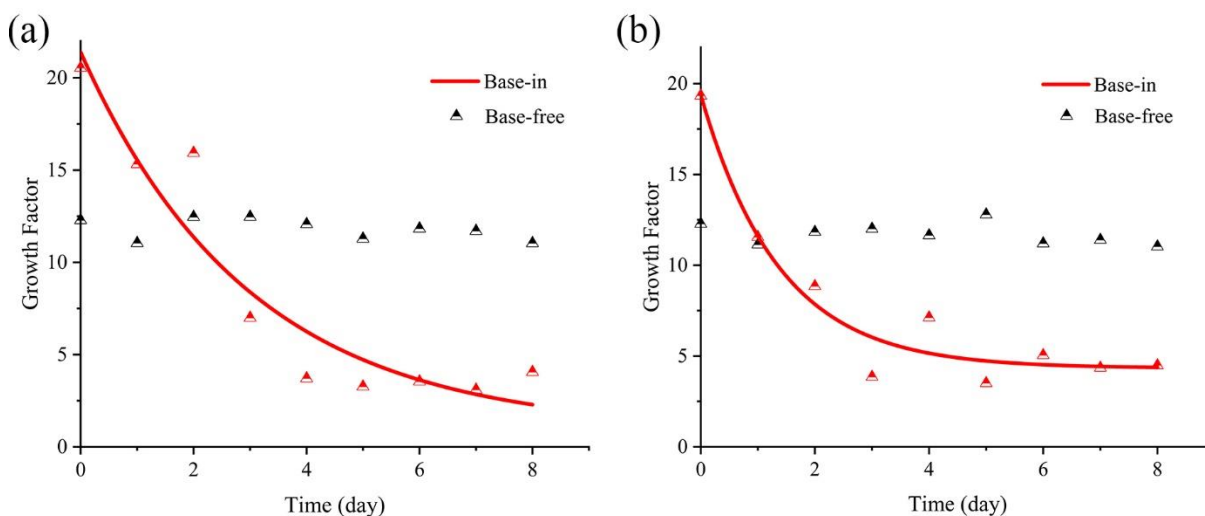


Fig. S6. The growth factor plots of base-in test substrate (red line, after nonlinear fitting) and base-free test substrate (black line) in (a) oxygen-in packaging, and (b) oxygen-free packaging ($\lambda_{ex} = 458$ nm). The C6NIB concentration was 2 mmol/L, and the reaction time with H_2O_2 is 15 s.

We prepared base-free test substrate dripping with 2.0 mmol/L C6NIB, as well as base-in test substrate with TBAH: C6NIB = 2 (mole ratio) where the concentration of C6NIB was maintained at 2.0 mmol/L. One group was oxygen-in packaging, and the other was oxygen-free packaging. The solid-state fluorescence spectra of the different time were collected through the saturated H_2O_2 steam blowing for 15 s into the test substrate. The decline of fluorescence detection performance of test substrates with and without alkali in eight days are shown in Fig. S6. As shown by the red dots and red lines of Fig. S6(a) and (b), Compared to day 0, the detection efficiency of day 8 decreased by 80.28% and 76.85% for the oxygen-in packaging, and the oxygen-free packaging, respectively. The fitting formula of oxygen-in and oxygen-free packaging of base-in test substrate is: $y = A_1 e^{-\frac{x}{t_1}} + y_0$. Where $A_1 = 20.5$, $t_1 = 3.0$, $y_0 = 0.9$ in the case of oxygen-in packaging; $A_1 = 15.0$, $t_1 = 1.4$, $y_0 = 4.3$, in the case of oxygen-free packaging, which means the response performance of

base-in test substrate to H_2O_2 under oxygen-free storage can reach more than 4.7 times of that under oxygen-in storage, when the storage time is long enough. As shown in the black dots of Fig. S6(a) and (b), the growth factor of the oxygen-in packaging base-free test substrate fluctuated between 11.03 and 12.46; after 8 days, the growth factor decreased only 10.18% compared to the day 0. The growth factor of the oxygen-free packaging test substrate fluctuated between 11.02 and 12.79; after 8 days, the growth factor only decreased 10.17% compared to day 0.

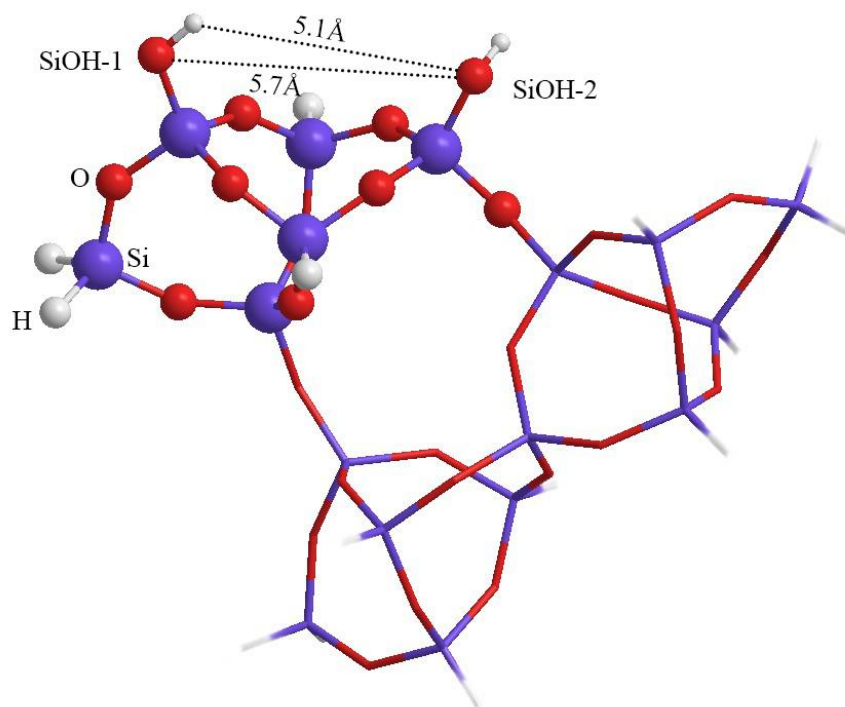


Fig. S7. The structure of silica gel surface interacting Si-OH surface group pairs. Bond distances are given in Å.

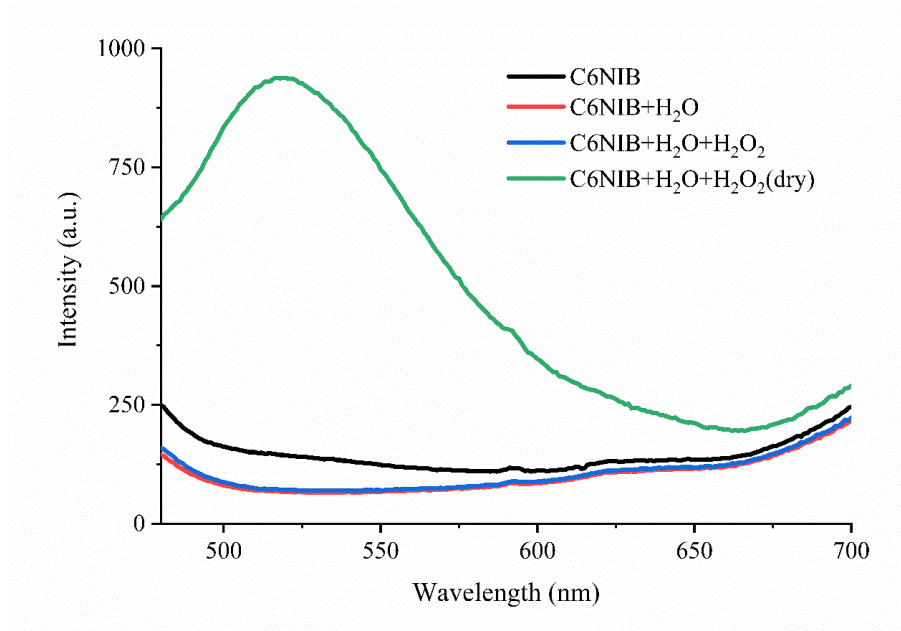


Fig. S8. Effect of dropping water before blowing H₂O₂ vapor on C6NIB on silica gel. ($\lambda_{ex} = 458$ nm)

35 μ L C6NIB was dropped onto the silica gel plate, the following operations were performed, and the solid-state fluorescence spectra were tested successively: H₂O was dropped, saturated H₂O₂ vapor was blown for 15 s, and the test substrate was left to dry. After drying, the test substrate had a fluorescence emission peak at 522 nm and a growth factor of 13.2. The results show that C6NIB can hardly react with H₂O₂ on silica gel in wet state.

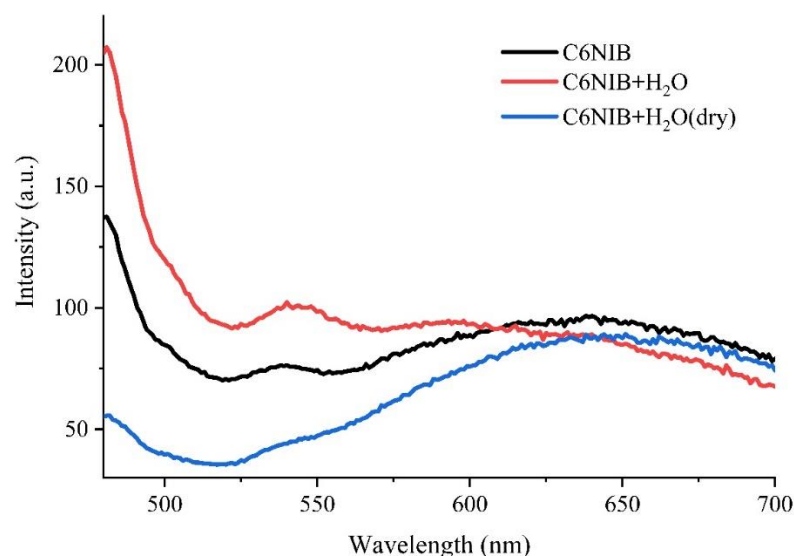


Fig. S9. Effect of water on fluorescence emission of C6NIB on silica gel plate.

35 μL C6NIB was dropped onto the silica gel plate, the following operations were performed, and the solid-state fluorescence spectra were tested successively: H_2O was dropped, the test substrate was left to dry. After drying, the test substrate had no fluorescence emission peak nor a growth factor. The result shows that there is no additional fluorescence emission peak during the dripping and drying process, the effect of water on the silica gel surface can be ignored.

5. References

1. S. L. Manatt and M. R. R. Manatt, *Chem. Eur. J.* 2004, **10**, 6540 – 6557.
2. M. Xu, J. M. Han, Y. Zhang, X. Yang and L. Zang, *Chem. Commun.* 2013, **49**, 11779.