Supporting Information

Gas-Solid Aldol Condensation Reaction in Confined Space of Metal Organic Framework for Formaldehyde Detection

Qi-Long Wu,[a] Man-Xiu Nie,[a] Qian Liu,[a] Jian rui Feng,[b] Jian-Wei Ren,[a] Jiong-Peng Zhao,*[a] and Fu-Chen Liu*[a]

1. Material Synthesis and Characterization:

Chemicals:

All chemical reagents were used of analytical reagent grade without any further purification. KOH, $Tb(NO_3)_3{\bullet}6H_2O$, 2-methylimidazole, $Zn(NO_3)_2{\bullet}6H_2O$ were purchased from Tianjin Heowns Biochemical Technology Co., Ltd. Acetylacetone, methanol, ethanol, acetone, formaldehyde (FA), aldehyde, biformyl, benzene, tluene were acquired from Tianjin Chemical Reagent Co., Ltd.

Experimental Section:

Synthesis of ZIF-8: $Zn(NO_3)_2{\bullet}6H_2O$ (1.47g) and 2-methylimidazole (3.25g) were dissolved in 100 mL of methanol, and the solution was stirred at the room temperature for 24 hours. The product was collected by centrifugation (8000 rpm), washed three times by ethanol and dried in vacuum at 60 °C for overnight.

Synthesis of $Tb(acac)_3(H_2O)_2.H_2O$: KOH (0.2g) and acetylacetone (0.4g) were dissolved in 20mL of CH_3OH under vigorously stirring for 30min at 80 °C. Then 0.43g of $Tb(NO_3)_3{\bullet}6H_2O$ was added into the above solution，and 5mL of deionized water was subsequently injected into the solution, finally crystallized in the refrigerator at 4 °C for overnight.

Synthesis of Tb@ZIF-1: KOH (0.4g) and acetylacetone (0.8g) were dissolved in 40mL of CH_3OH under vigorously stirring for 30min at 80 °C. Then 0.86g of $Tb(NO_3)_3{\bullet}6H_2O$ was added into the above solution，and 8mL of deionized water was subsequently injected into the solution, thus the precursor solution was obtained for further use. 2-methylimidazole (3.25g) and $Zn(NO_3)_2{\bullet}6H2O$ (1.47g) was poured into the precursor solution and stirred for 15min. The product was collected by centrifugation (8000 rpm, 1 min), washed with methanol for twice, and steeped in 50 mL acetone for three days, finally dried in vacuum at 60 °C for overnight.

Synthesis of Tb@ZIF-2: The preparation procedure was same as Tb@ZIF-1, except that KOH (0.4g) and acetylacetone (0.8g) were replaced with KOH (0.2g) and acetylacetone (0.4g).

Synthesis of Tb@ZIF-3: The preparation procedure was same as Tb@ZIF-1, except that KOH (0.4g) and acetylacetone (0.8g) were replaced with KOH (0.1g) and acetylacetone (0.2g).

Synthesis of Tb@ZIF-4: The preparation procedure was same as Tb@ZIF-1, except that KOH (0.4g) and acetylacetone (0.8g) were replaced with KOH (0.05g) and acetylacetone (0.1g).

Detection of different solvents: The fluorescence spectra of Tb@ZIF-1 or $Tb(acac)_3(H_2O)_2$ powder (30mg) was measured before treated with different solvents. Where-after, the Tb@ZIF-1 or or $Tb(acac)_3(H_2O)_2$ powder was added with 20μL of aldehyde solution (40 wt%) or Deionized water carefully and recorded fluorescence again after drying.

Preparation of different concentration of FA vapor: The concentration of FA vapor was calculated from Henry's law by the following equation:

$$C = \frac{mH}{40\% \times MV \times 10^{-3} \times 101.325}$$

Where C (ppm) is the concentration of FA vapor, m (mg) is the mass of FA solution, $H=3\times10^{-5}$ kPa·m^3/mol is the the Henry's law constant of FA, M (g/mol) is the molecular weight of FA, V (mL) is the volume of injected deionized water.

For example, 25mg FA solution (40 wt%) was dissolved in 100mL of deionized water, then heated at 30 °C for more than 1h and obtained 1ppm of FA vapor. The others concentration of FA vapor are prepared by same method.

Fabrication of luminescent films: The substrates were successively cleaned with 0.1M HCl, acetone and ethanol. The Tb@ZIF-1, 2, 3, 4 films were prepared by spin-coating method through dropping the methanol suspensions of Tb@ZIF-1, 2, 3, 4 (0.5mg/mL) onto the pre-cleaned substrate which was fixed on a spin coater (2000 rpm, 30s). The spin-coating process was repeated twice with 15μL, and then the film was dried at room temperature.

Gas sensing: The luminescent spectra of the Tb@ZIF-1 film was measured before exposure to different atmosphere. Then, the film was carefully placed into a sealed container which contains 80mL of a given solution (different concentrations of FA vapors) for 30 min at 30 °C, and the film was subsequently taken out and quickly measured fluorescence again. The test of other gas such as water, benzene, toluene, methanol, ethanol and acetone was very like that of FA but with corresponding pure solvent vapour conditions. In addition, the Tb@ZIF-(1-4) films were placed into a sealed glass bottle with 80 mL of 1ppm of FA solution for different times at 30 °C, and then its emission spectrum was taken again rapidly.

The limit of detection (LOD) for FA vapors was calculated by equation：

$$\mathrm{LOD}=3\sigma/k$$

where σ is the standard deviation the residual from the regression line and k is the slope of the calibration curve.

Materials characterization:

The Powder X-ray diffraction (PXRD) was recorded with Rigaku Ultima IV. Scanning Electron Microscope (SEM) was taken by Germany MERLIN Compact scanning electron microscope at 10kV. Fourier Transform Infrared spectrometer (FT-IR) was recorded using a Bruker Vertex 70 spectrometer. Solid state UV-Vis diffuse reflectance spectra were measured on a Hitachi U-3310 ultraviolet-visible spectrophotometer. Fluorescent emission spectra of the solid samples were obtained on Cary Eclipse Fluorescence Spectrophotometer. The contents of Tb were determined by ICP on Optima 2100DV.

2. Supporting Figures

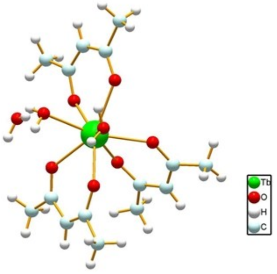

Figure S1. The structure of Tb(acac)$_3$(H$_2$O)$_2$·H$_2$O.

Table S1 Crystallographic crystal data for Tb(acac)$_3$(H$_2$O)$_2$ • H$_2$O

Chemical formula	$C_{15}H_{25}O_8Tb \cdot H_2O$
Formula weight	510.28
Space group	$P\ 2_1/n$
a/Å	8.4737 (18)
b/Å	22.078 (3)
c/Å	11.2744 (14)
β/Å	100.650 (15)
V/Å^3	2072.9 (6)
Z	4
GOF	1.003
D/g cm^{-3}	1.635
μ/mm^{-1}	3.451
T/K	293
Ra/wRb	0.0961 (0.1340)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths [Å] for Tb(acac)$_3$(H$_2$O)$_2$·H$_2$O.

Tb1—O4	2.431 (9)
Tb1—O2	2.360 (9)
Tb1—O3W	2.439 (8)
Tb1—O3	2.330 (9)
Tb1—O5	2.396 (8)
Tb1—O2W	2.485 (9)
Tb1—O6	2.376 (9)
Tb1—O1	2.363 (8)

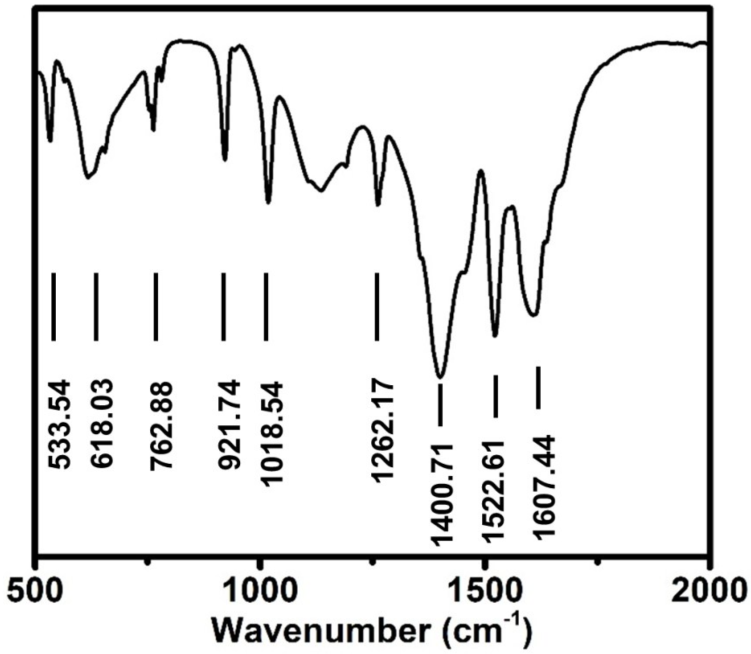

Figure S2. FT-IR spectra of Tb(acac)$_3$(H$_2$O)$_2$·H$_2$O.

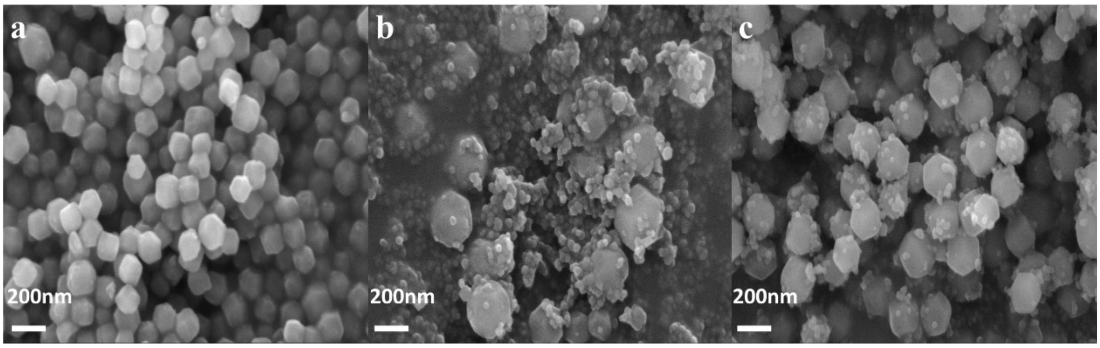

Figure S3. a-c) SEM images of Tb@ZIF-2,3,4.

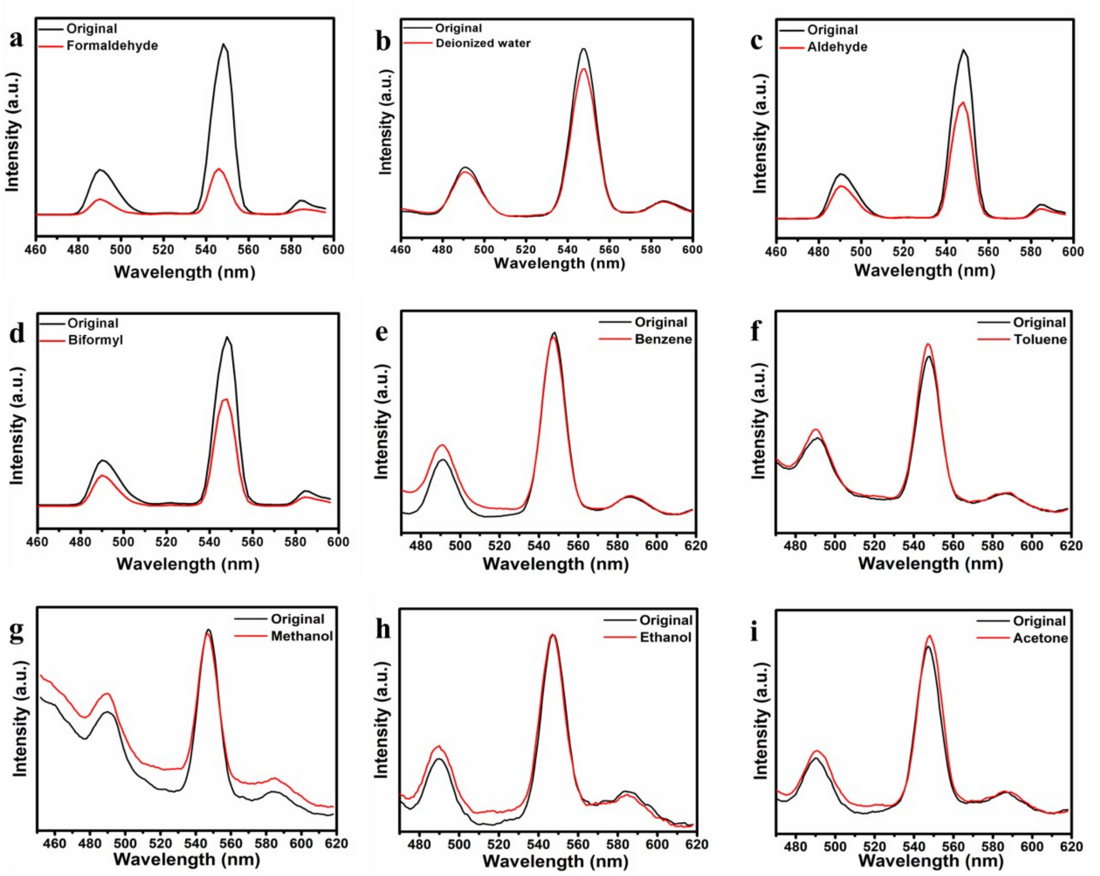

Figure S4. a-d) The FL spectras of Tb@ZIF-1 before and after (red line) treated with FA, deionized water, aldehyde and biformyl. e-i) The FL spectrums of Tb@ZIF-1 films before and after (red line) exposure to various indoor polluted gas atmosphere including benzene, toluene, methanol, ethanol, acetone for 30 min.

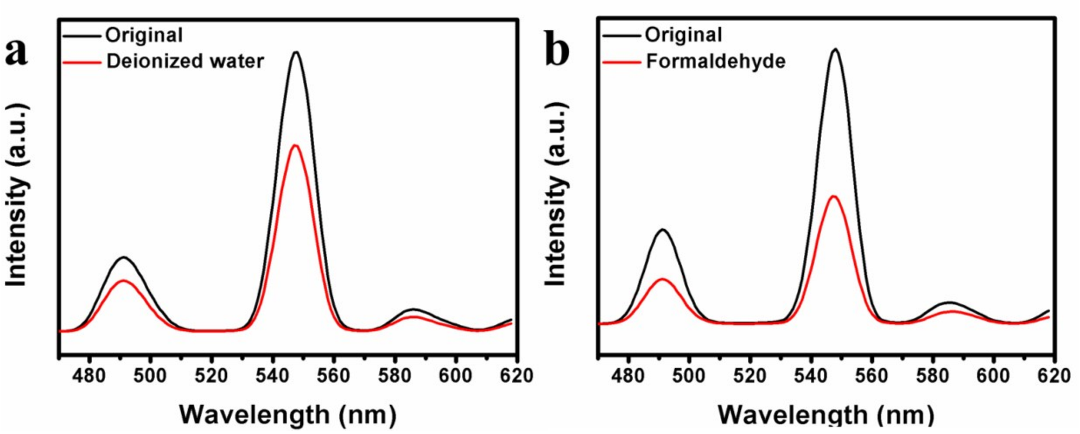

Figure S5. The FL spectrums of $Tb(acac)_3$ before and after (red line) treated with deionized water and FA.

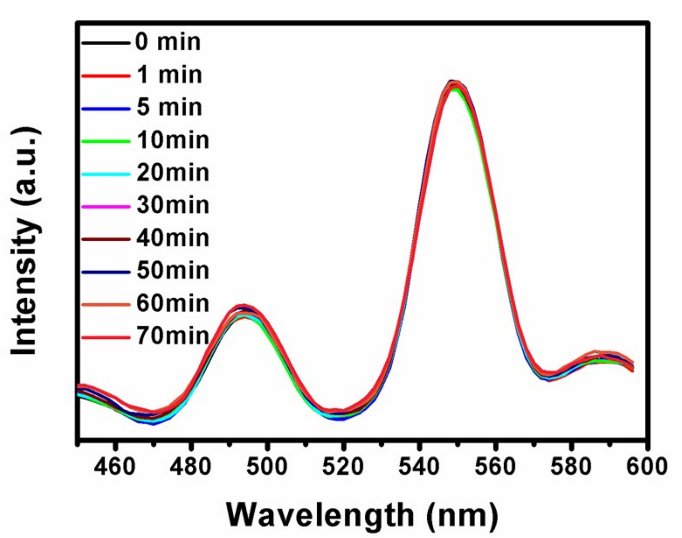

Figure S6. The FL spectrums of Tb@ZIF-1 film on exposure to water vapor at various time intervals (λ_{ex} = 320 nm).

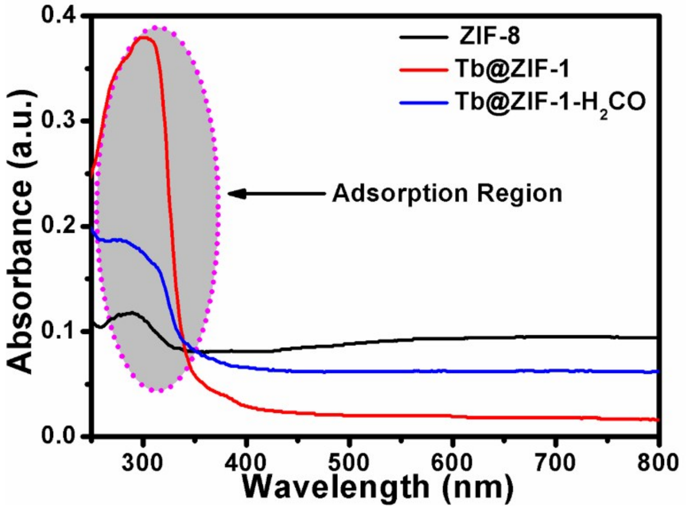

Figure S7. UV–visible absorption spectra of ZIF-8, Tb@ZIF-1 and Tb@ZIF-1-H_2CO.

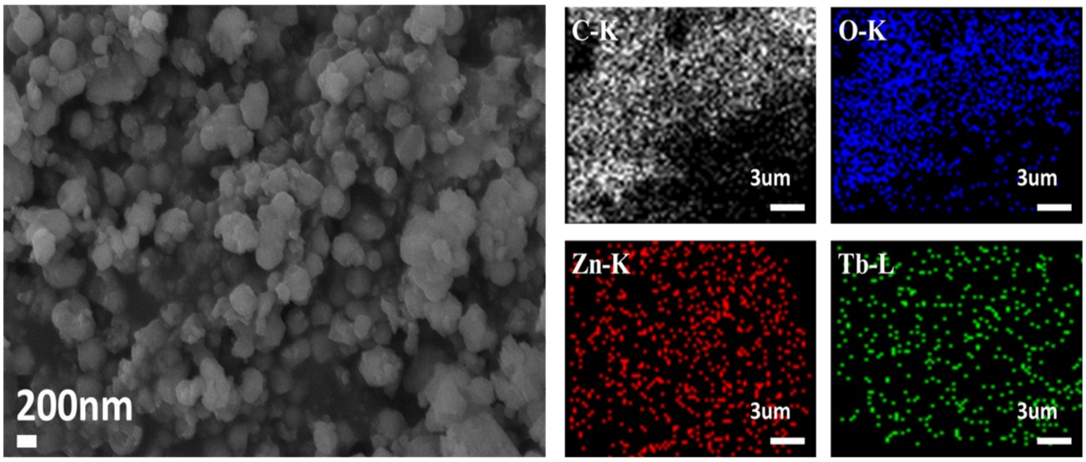

Figure S8. SEM images and EDS mapping results of Tb@ZIF-1-H_2CO.

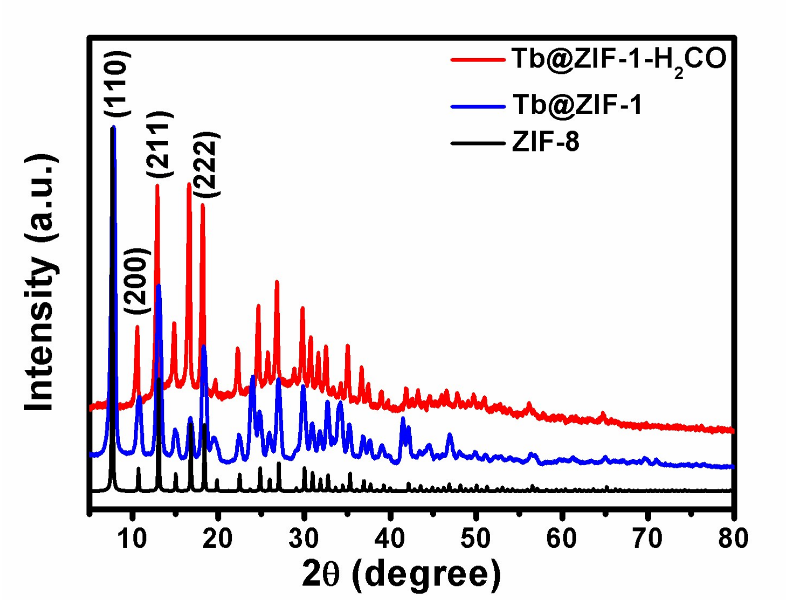

Figure S9. PXRD patterns of pure ZIF-8, Tb@ZIF-1 and Tb@ZIF-1-H_2CO.

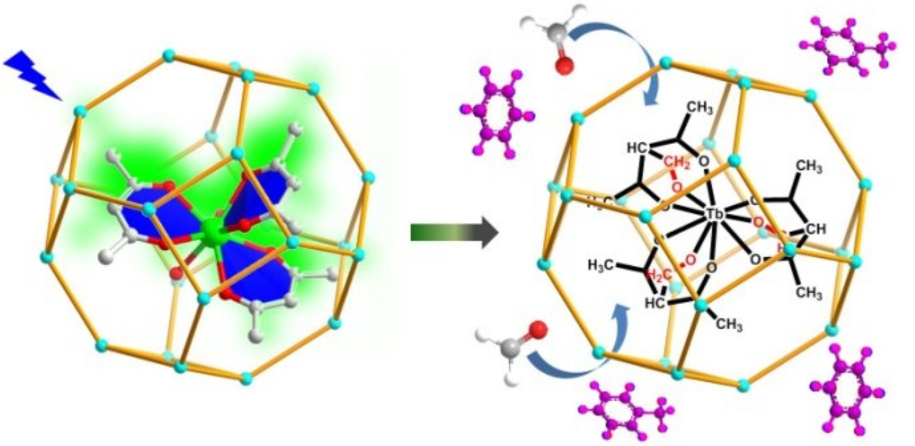

Figure S10. The fluorescent quenching breakdown of the antenna effect of the Tb@ZIF exposed in FA atmosphere.

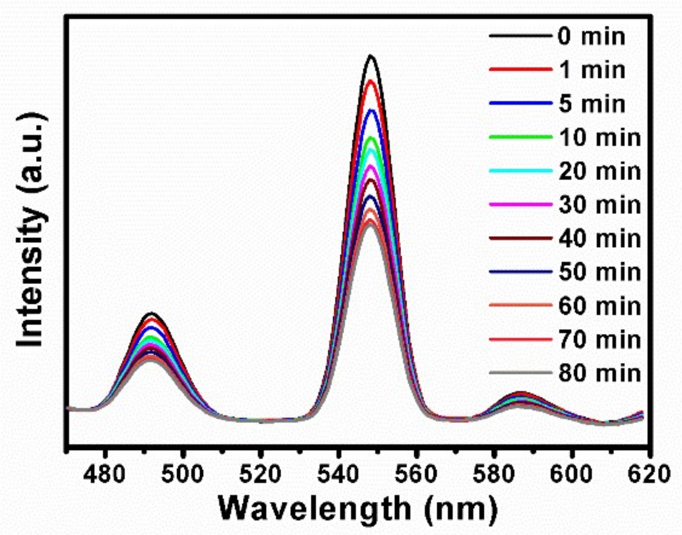

Figure S11. The FL spectrums of Tb@ZIF-2 film on exposure to formaldehyde vapor at various time intervals (λ_{ex} = 320 nm).

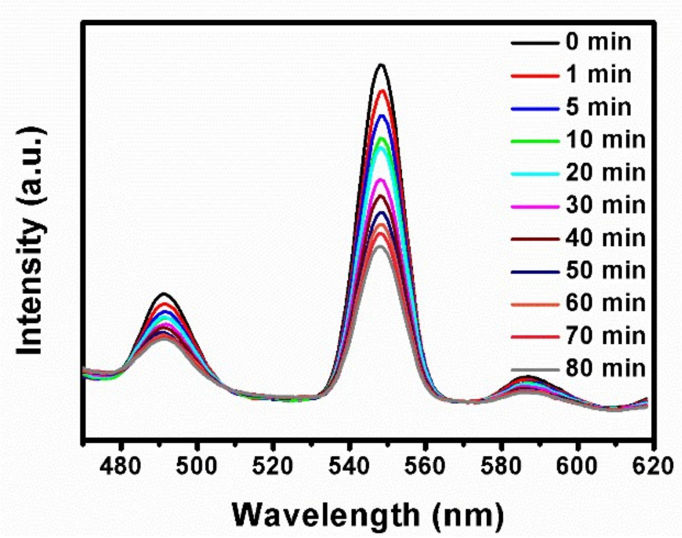

Figure S12. The FL spectrums of Tb@ZIF-3 film on exposure to formaldehyde vapor at various time intervals (λ_{ex} = 320 nm).

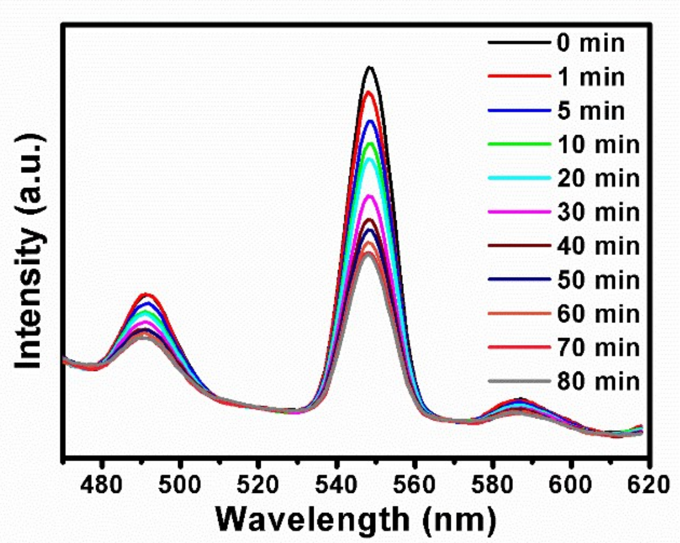

Figure S13. The FL spectrums of Tb@ZIF-4 film on exposure to formaldehyde vapor at various time intervals (λ_{ex} = 320 nm).