Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supporting Information

Post Engineering of a Chemically Stable MOF for Selective and Sensitive Sensing of Nitric Oxide

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Section S1: Materials, General Characterization and Physical Measurements

Materials: 1,3,5 benzene tricarboxylic acid (BTC), DEA NONOate sodium salt hydrated, p-aminobenzoic acid (PABA) and NaClO were purchased from Sigma-Aldrich. $ZrOCl_2$ was purchased from Merck. All the dry solvents and other chemicals were obtained locally. These chemicals were used without further purification.

Physical Measurements: Powder X-ray diffraction patterns (PXRD) were measured on Bruker D8 Advanced X-Ray diffractometer using Cu Kα radiation (λ= 1.5406 Å) with a tube voltage of 40 kV and current of 40 mA in 5° to 40° 2θ range. Thermogravimetric analyses were recorded on Perkin-Elmer STA 6000 TGA analyzer under N_2 atmosphere with a heating rate of 10 °C min^{-1}. The Fourier transform infra-red (FT-IR) spectra were recorded on NICOLET 6700 FT-IR Spectrophotometer using KBr Pellets in 400-4000 cm^{-1} range. N_2 gas adsorption measurements were performed using BelSorp-Max instrument (Bel Japan). Prior to adsorption measurements, the activated samples were heated at 120 °C under vacuum for 12 hours using BelPrepvacII. Morphologies of the crystalline materials were recorded with Zeiss Ultra Plus field-emission scanning electron microscopy (FESEM) with integral charge compensator and embedded EsB and AsB detectors [Oxford X-max instruments 80 mm^2. (Carl Zeiss NTS, Gmbh), Imaging conditions: 2 kV, WD = 2 mm, 200 kX, Inlens detector]. Solid state UV-visible spectra were recorded on Perkin-Elmer UV visible spectrometer. UV spectra were recorded on Shimadzu UV 2600 Spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL 400 MHz or Bruker 400 MHz spectrometer. XPS studies was performed using K-Alpha+model (Thermo Fischer Scientific, UK) with Al Kα source. Raman spectra were acquired with an Xplora PLUS Raman microscope (Horiba Company) (785 nm laser and a 1200 lines/mm grating). All fluorescence measurements were done on Jobin Yvon Fluoromax-4 spectrofluorometer with stirring attachment. The time correlated single-photon counting method was used for the fluorescence lifetime measurement with the help of an Edinburgh Instrument Life-Spec II spectrometer.

Safety note: DEA NONOate sodium salt hydrated and few other chemicals used in this study are highly toxic in nature. Proper safety protocol should be followed before carefully handling these chemicals.

MOF-808 Synthesis: MOF-808 was synthesized following a reported protocol.[1] At first, 537 mg of 1,3,5-benzenetricarboxylic acid (2.5 mM) and 2.42 gm of $ZrOCl_2.8H_2O$ (7.5 mM) were dissolved in 160 ml of dimethylformamide (DMF). Then to this 160 ml of formic acid was added and the whole thing is capped in 500 ml screw capped glass jar heated at 130°C for three days. After that a white precipitate was formed. Then it was collected by several washings and centrifuged. After that it was dried in an oven at 70°C for 6 hours.

Synthesis of PABA@MOF-808: PABA@MOF-808 was synthesized following a reported protocol.[2] At first MOF-808 (200 mg) was well dispersed in DMF (10 ml) ultrasoniacally, then PABA (0.72 g, 5.2 mM) was added to the dispersed phase of MOF-808 and reacted at 60 °C for 48 hours to obtain amino functionalized MOF-808. The desired product was washed thrice a times with water and ethanol respectively, then it was placed in an oven dried at 100 °C for 12 hours.

Preparation of PABA@MOF-808 based mixed matrix membranes (MMMs): The following reported standard protocol has been adopted for the fabrication of the MOF-polymer based membrane.[3] To prepare the membrane, at first, a versatile polymer, PVDF (150 mg) was dissolved in 1.9 ml of DMF by stirring the mixture at room temperature for 24 hours. The PVDF-DMF mixture results a viscous sticky solution after one day. Then, a certain amount of fine powder of PABA@MOF-808 was added with the solution of thus prepared pure polymer to form a homogeneous mixture by stirring the whole solution for another 24 hours. After that, the mixture was casted onto aluminium foil by a regular scraper to make a flat thin-sheet membrane. Thus, fabricated system was then dried in a hot plate and further soaked in DI water, led to the fast delamination of the MMMs. Thus, obtained free-standing films were dried in air and further cut into small pieces for sensing application.

Preparation of the analytes:

DEA NONOate sodium salt hydrated (purchased from Sigma-Aldrich was used as received) was used as a source of NO. Gaseous nitric oxide was synthesized by the reaction between KI (1 M) and $NaNO_2$ (1 M) and catalyzed by acid.[4] Aqueous solutions of NO_2^- (nitrite) and NO_3^- (nitrate) were prepared from $NaNO_2$ and $NaNO_3$ respectively. Stock solution of 0.1 mM Hydrogen peroxide (H_2O_2) was prepared by diluting 30% H_2O_2 solution. Aqueous solution of NaClO was used as a source of ClO- (hypochlorite). Singlet oxygen ($^1O_2$) was generated from the reaction of hypochlorite and H_2O_2.[5]

Fluorescence Study: In typical experimental setup, 1 mg of MOF has been taken in a cuvette and 2 mL water has been added to that. Initial luminescence spectra of MOF in water has been recorded by exciting at different wavelength (spectra recorded in the range of wavelength ~300- 500 nm). Then to the dispersed MOF in water we have added the stock solution of NO in water (20 µL to 300 µL) and spectra were recorded for each addition. With each addition of NO, we found quenching in the fluorescence emission of MOF. For competing studies, we have taken NO_2^-, NO_3^-, H_2O_2, ClO^-, $^1O_2$ in water. In a typical way, for initial study we have taken 1 mg of MOF in 2 mL of water. To the dispersed MOF solution we have added 300 µL of the competing species from the stock solution and recorded the corresponding spectra to check the response of MOF. Later, in a similar way to the dispersed MOF (1 mg) in water medium (2 mL) we have added 300 µL of competing analyte and followed by the addition of 300 µL NO solution from the stock as prepared earlier. We have recorded both responses of MOF in presence of competing analytes and in presence of both competing analytes and NO. By combining these two responses we got the selectivity of MOF towards NO in presence of other competing analytes.

Quantum calculation method:

For further mechanistic insight into molecular level pathway for selective and dynamic photoluminescence quenching mediated by nitric oxide (NO) and other ROS/RNS species, we performed First-principle calculations based on density functional theory (DFT) and obtained HOMO – LUMO energy gaps for subunit of PABA@MOF-808 along with NO and other ROS/RNS species. Discovery Studio 2017 (Accelrys) program was used for DFT calculations. All the DFT calculations were performed at fine quality calculation level. The single-point energy calculations were performed using three parameters B3LYP function considering DMol3 code. In the beginning, the molecular structures of subunit of PABA@MOF-808, NO and other ROS/RNS species were fully relaxed using geometry optimization by keeping Auto mode Multiplicity factor, Double Numeric Plus Polarizing (DNP+) basis set and water as solvent. Subsequently, the structural simulation performed using simulated annealing technique on geometry relaxed subunit of PABA@MOF-808 to find possible interaction site with NO and other ROS/RNS species.

Section S2: Structural characterizations of MOF-808 & PABA@MOF-808

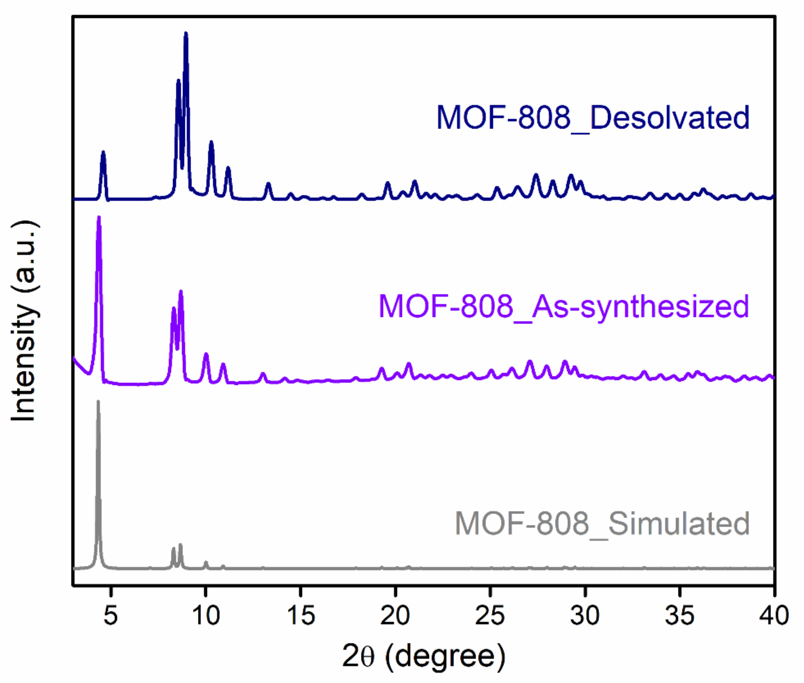


Figure S1: PXRD pattern of as-synthesized and desolvated phase of MOF-808.

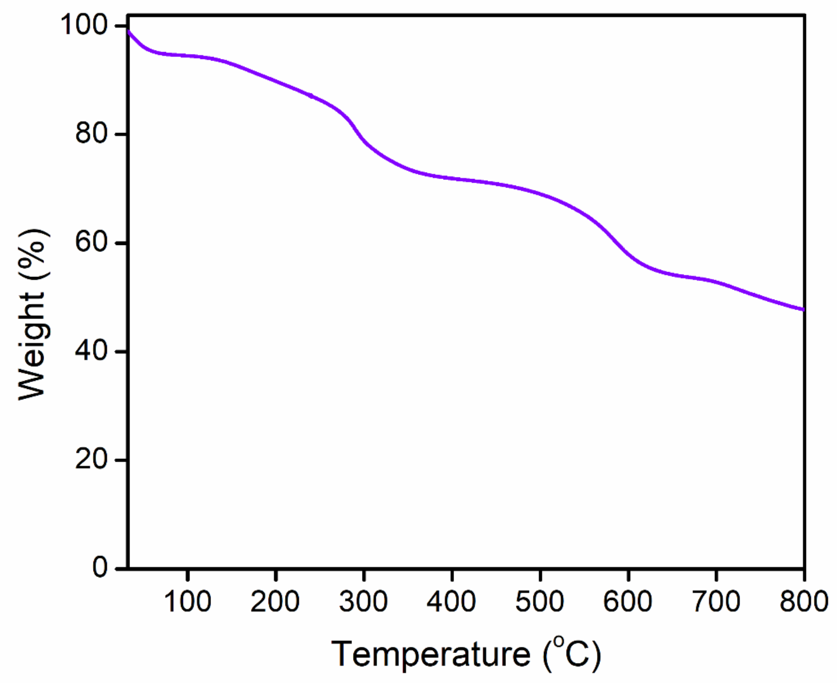


Figure S2: Thermogravimetric (TGA) profile of desolvated MOF-808.

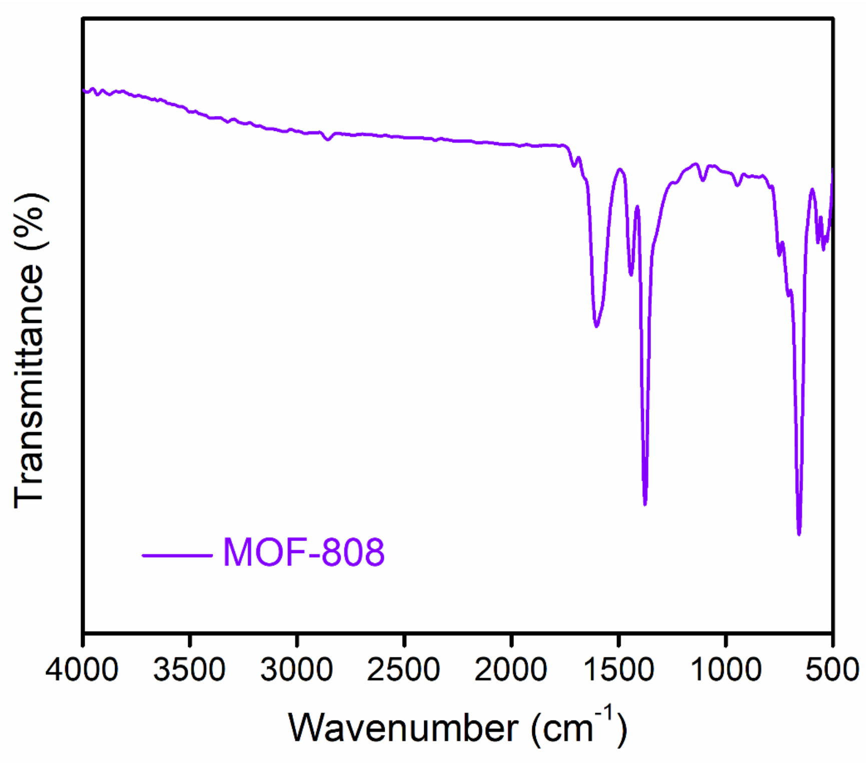


Figure S3: FTIR spectra of MOF-808.

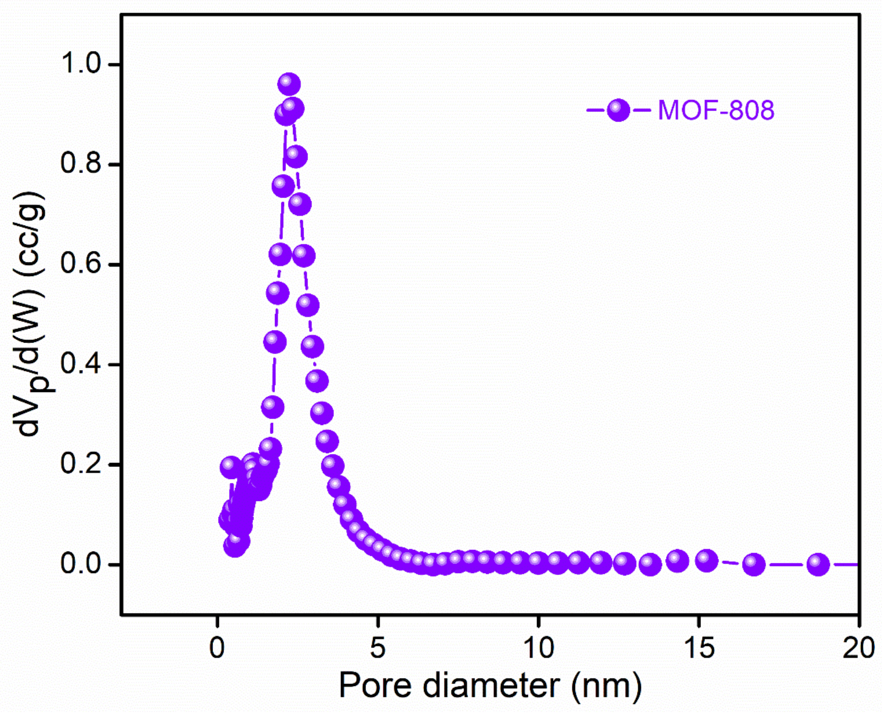


Figure S4: Pore size distribution profile of MOF-808 from N_2 sorption measurement.

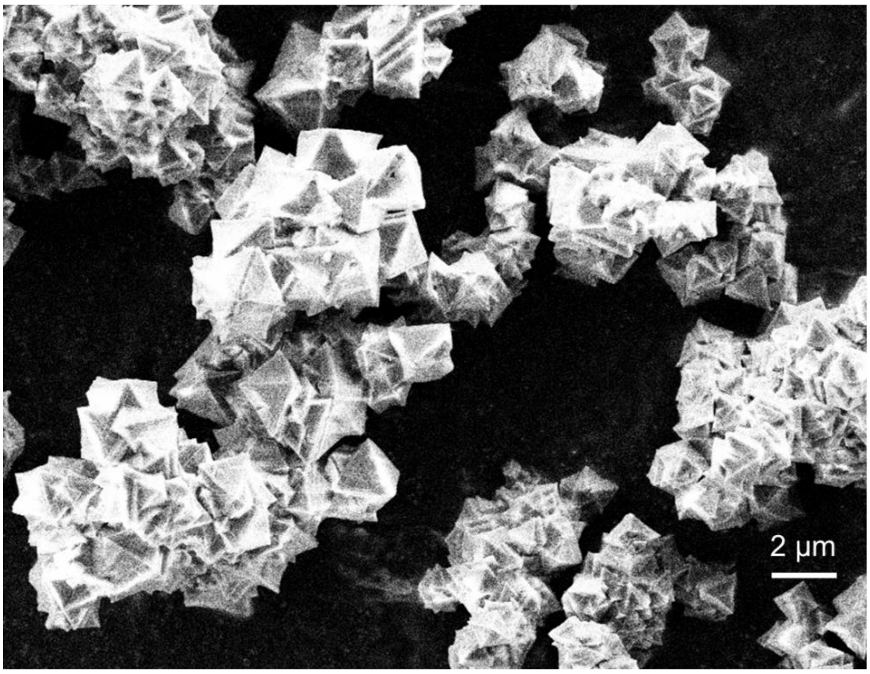
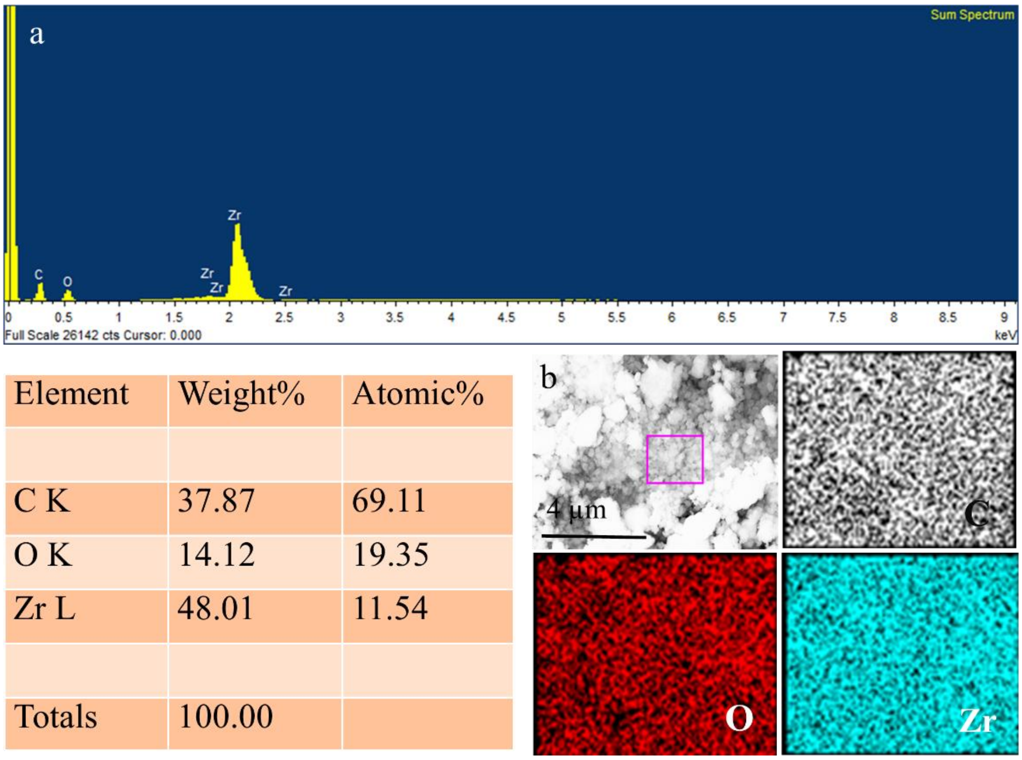


Figure S5: FESEM Image of MOF-808.



Element	Weight%	Atomic%
C K	37.87	69.11
O K	14.12	19.35
Zr L	48.01	11.54
Totals	100.00	

Figure S6: (a) EDX data and (b) Elemental mapping image of MOF-808

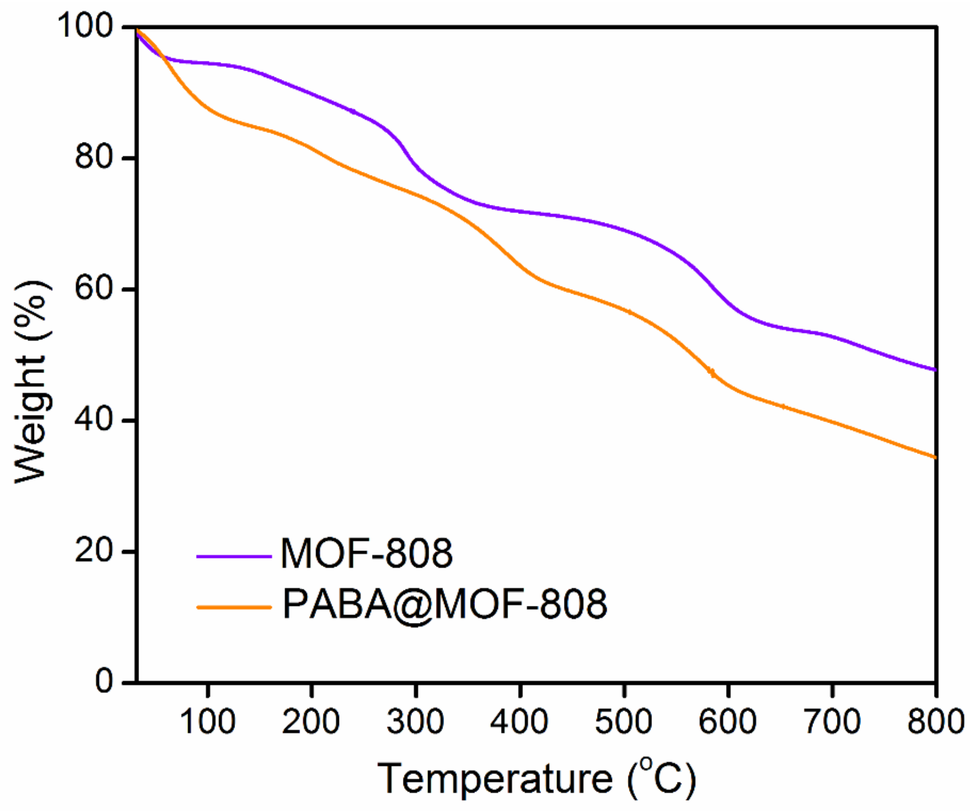


Figure S7: Thermogravimetric (TGA) profile of PABA@MOF-808 along with MOF-808.

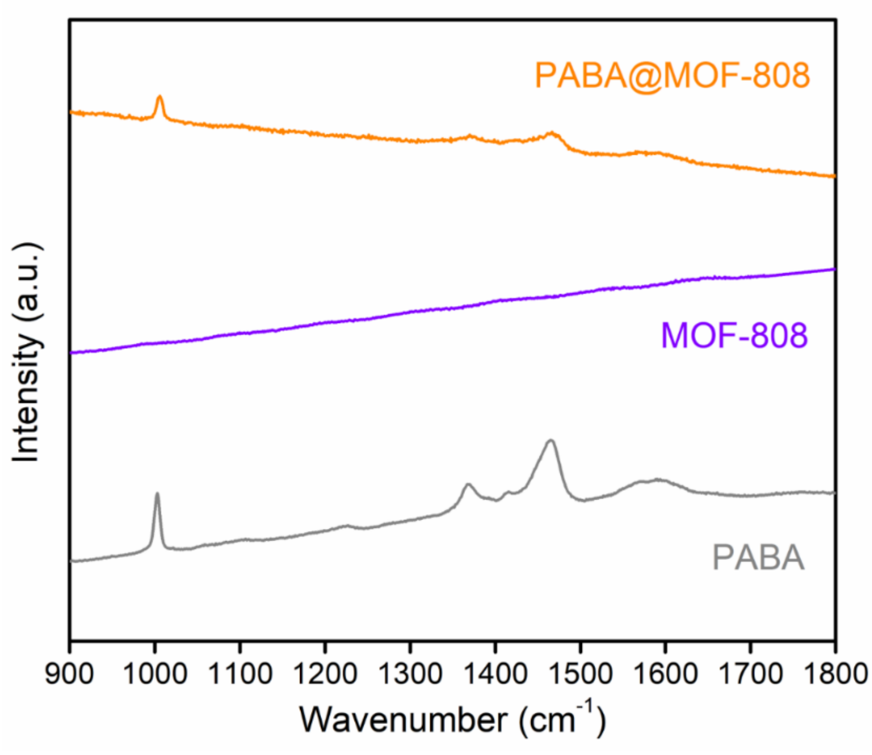


Figure S8: Raman Spectra of MOF-808 and PABA@MOF-808.

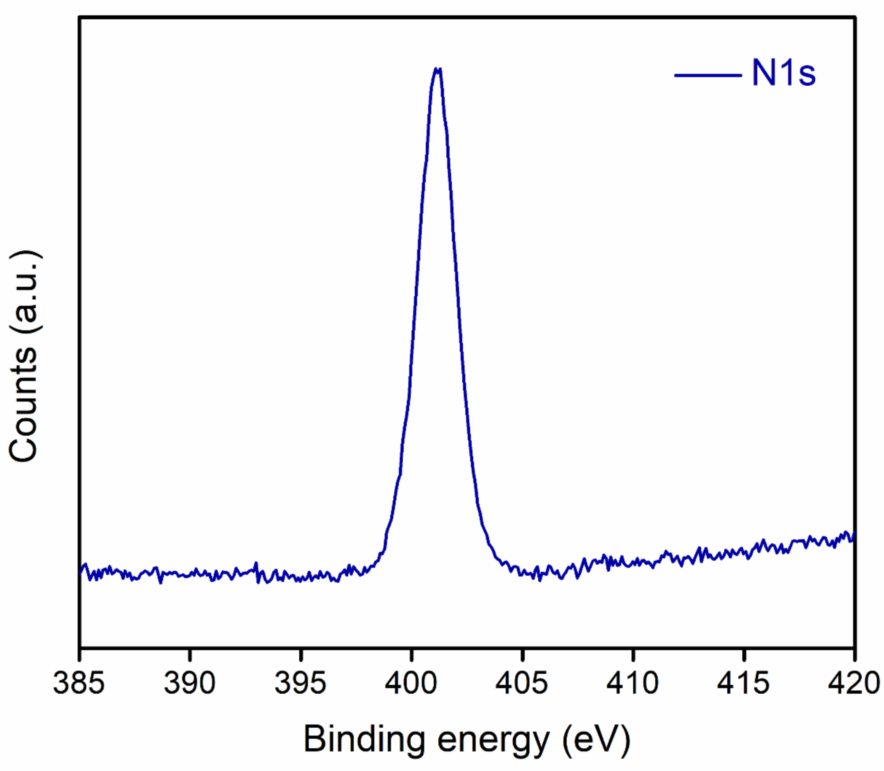


Figure S9: XPS Spectra of nitrogen (N) 1s orbital of PABA@MOF-808.

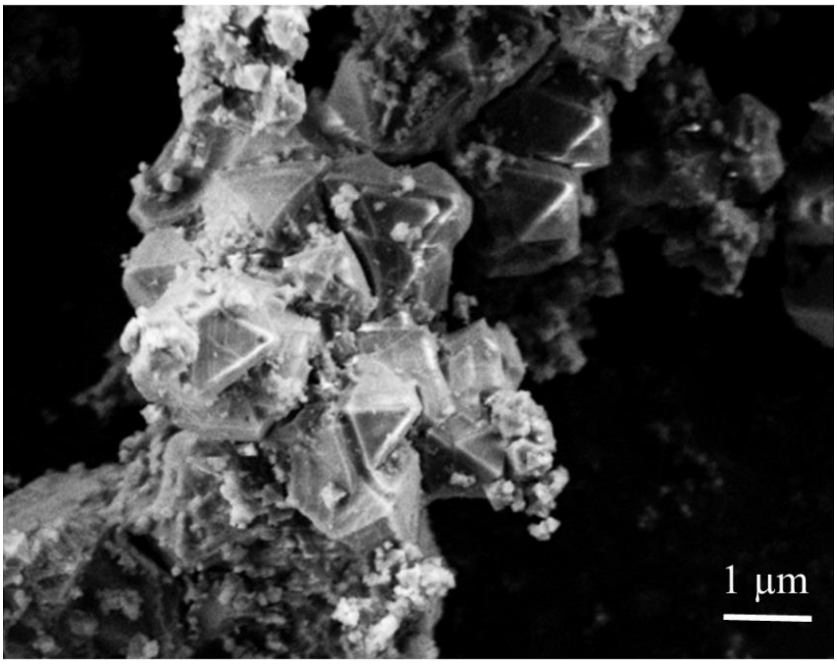
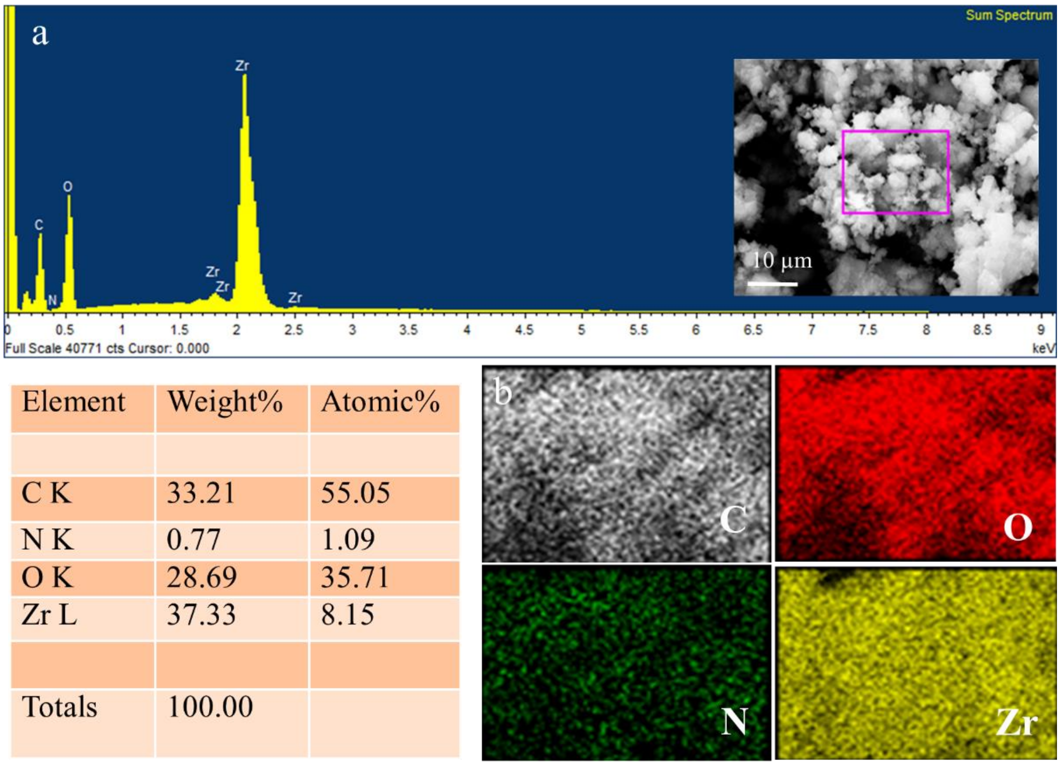


Figure S10: FESEM image of PABA@MOF-808.



Element	Weight%	Atomic%
C K	33.21	55.05
N K	0.77	1.09
O K	28.69	35.71
Zr L	37.33	8.15
Totals	100.00	

Figure S11: (a) EDX data and (b) Elemental mapping image of PABA@MOF-80

Section-S3: Hydrolytic Stability of PABA@MOF-808

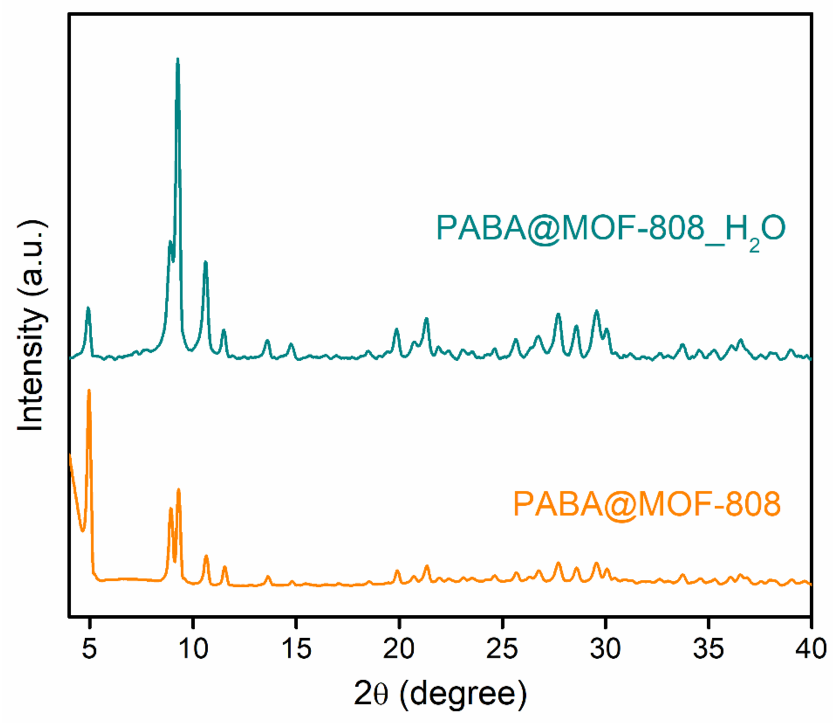


Figure S12: PXRD pattern of water treated PABA@MOF-808.

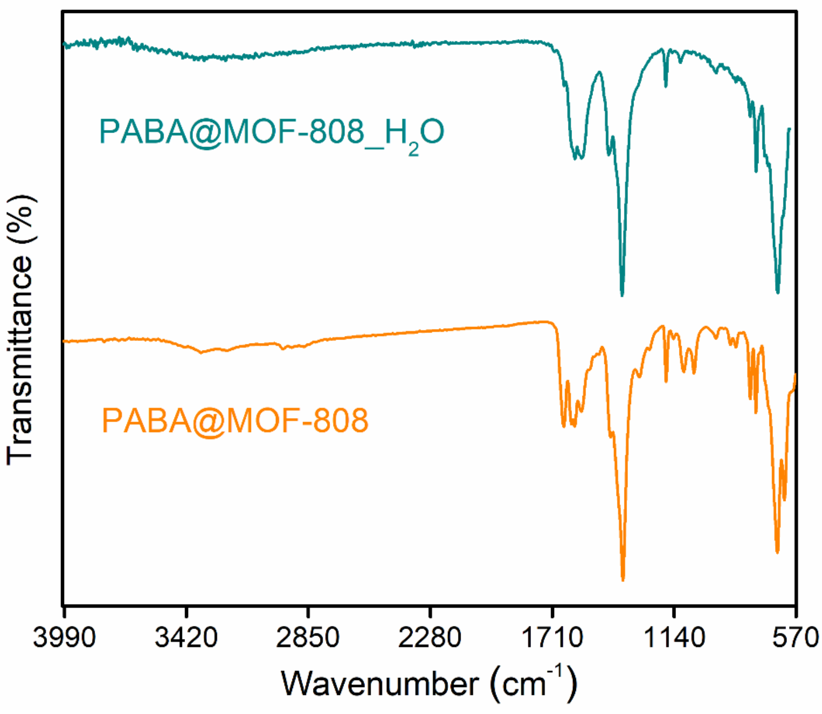


Figure S13: FTIR Spectra of water treated PABA@MOF-808.

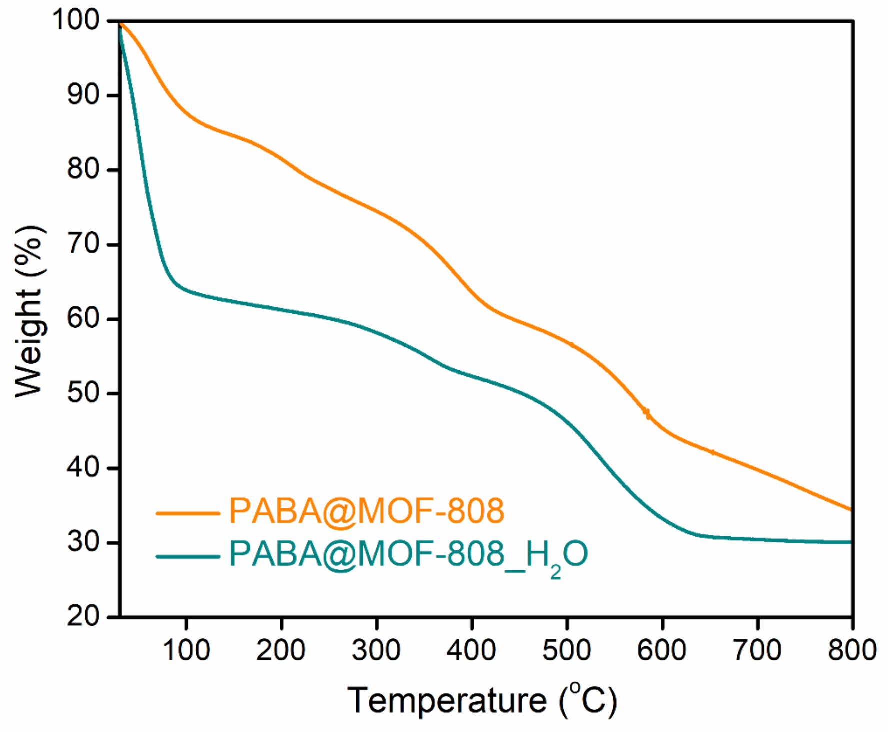


Figure S14: Thermogravimetric (TGA) profile of water treated PABA@MOF-808.

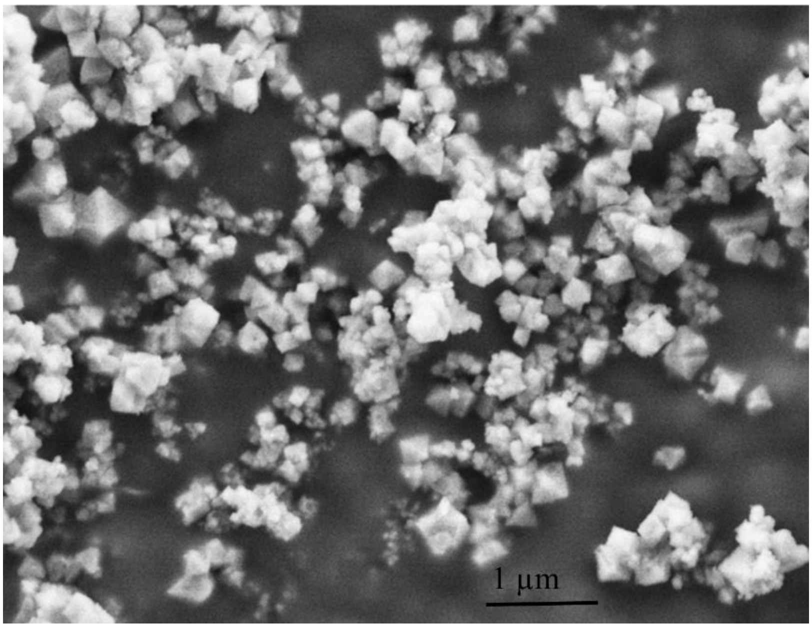
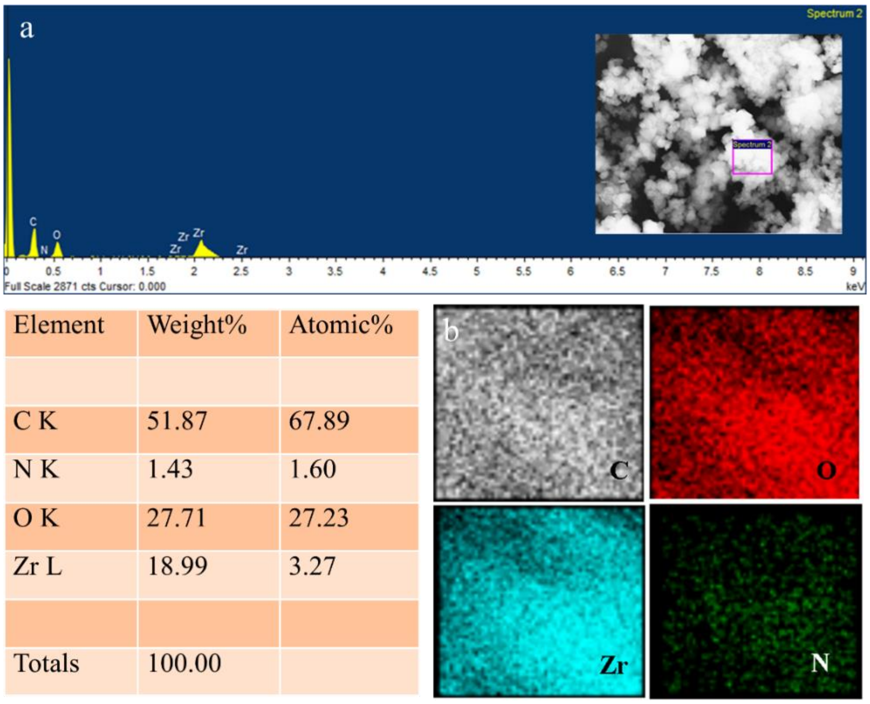


Figure S15: FESEM image of water treated PABA@MOF-808.



Element	Weight%	Atomic%
C K	51.87	67.89
N K	1.43	1.60
O K	27.71	27.23
Zr L	18.99	3.27
Totals	100.00	

Figure S16a: (a) EDX data and (b) Elemental mapping image of water treated PABA@MOF-808.

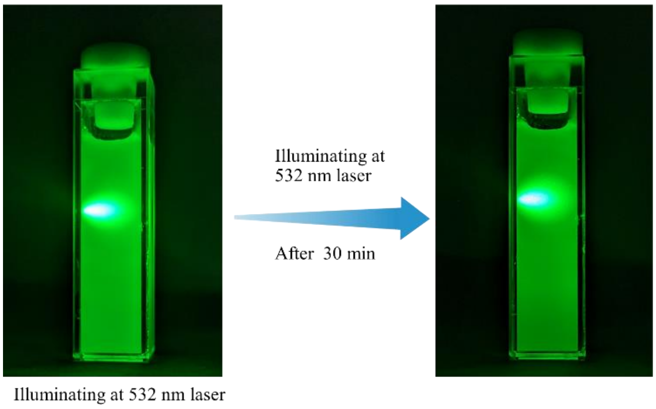


Figure S16b: Tyndall effect of PABA@MOF-808 dispersion in water (initial and after 30 min of laser exposer).

Section-S4: Optical Characterizations of PABA@MOF-808

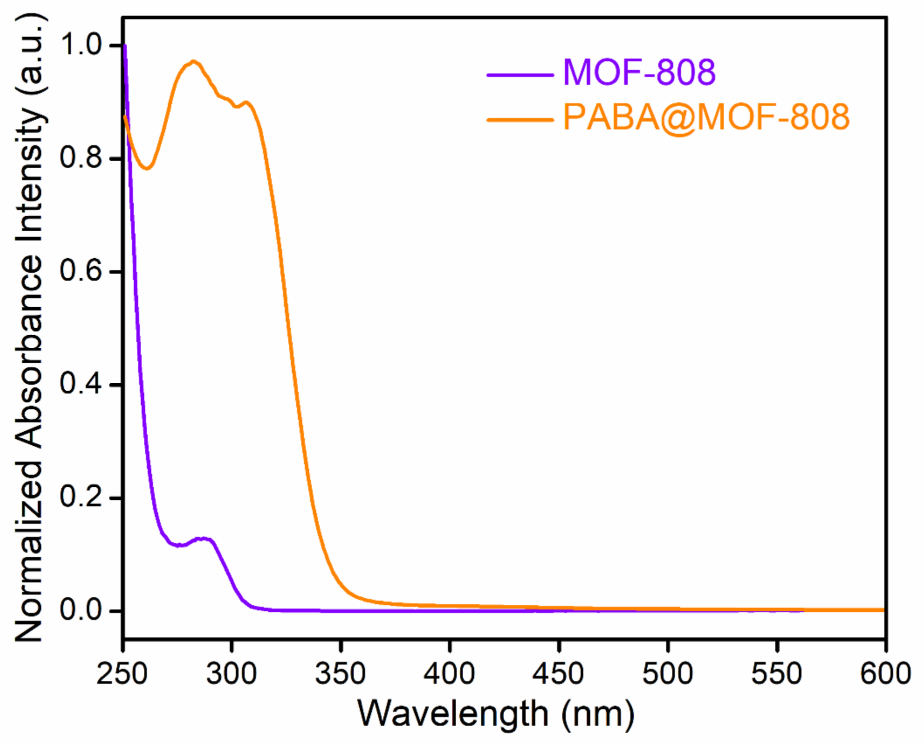


Figure S17: Diffuse reflectance UV-vis spectra of PABA@MOF-808 and MOF-808.

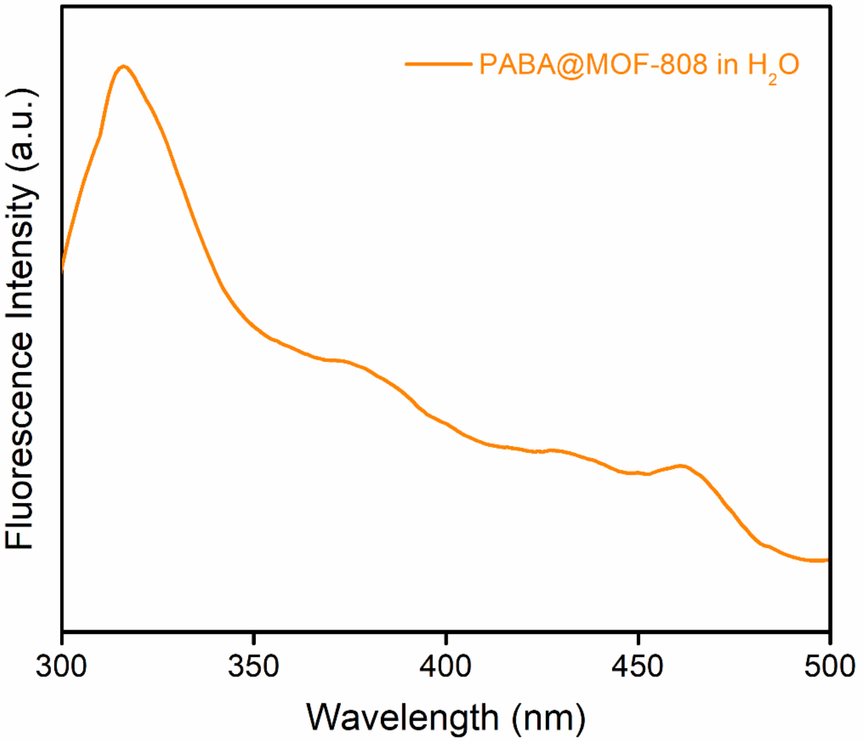


Figure S18: Photoluminescence emission spectra of water dispersed PABA@MOF-808.

Section-S5: Sensing Studies of PABA@MOF-808

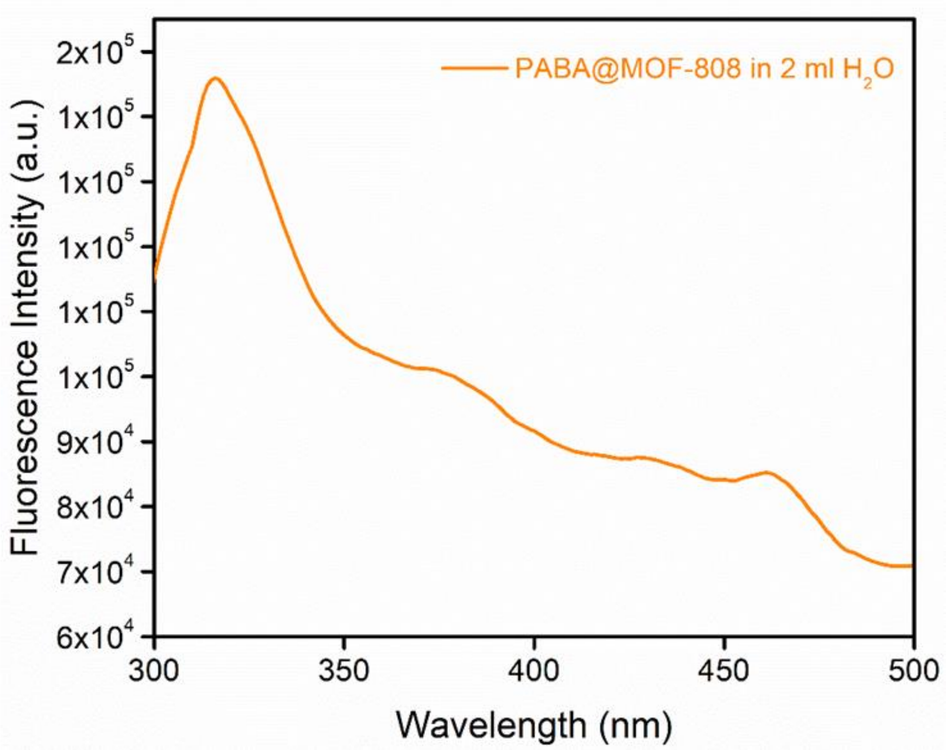


Figure S19a: Photoluminescence emission spectra of PABA@MOF-808 dispersed in 2 mL water.

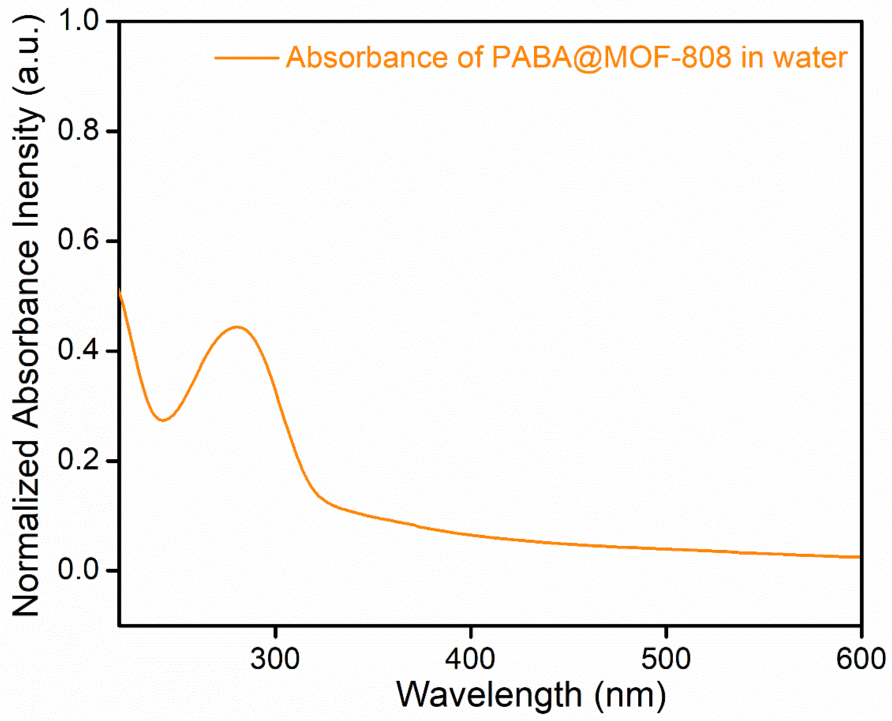


Figure S19b: Absorption spectra of PABA@MOF-808 dispersed in 2 mL water.

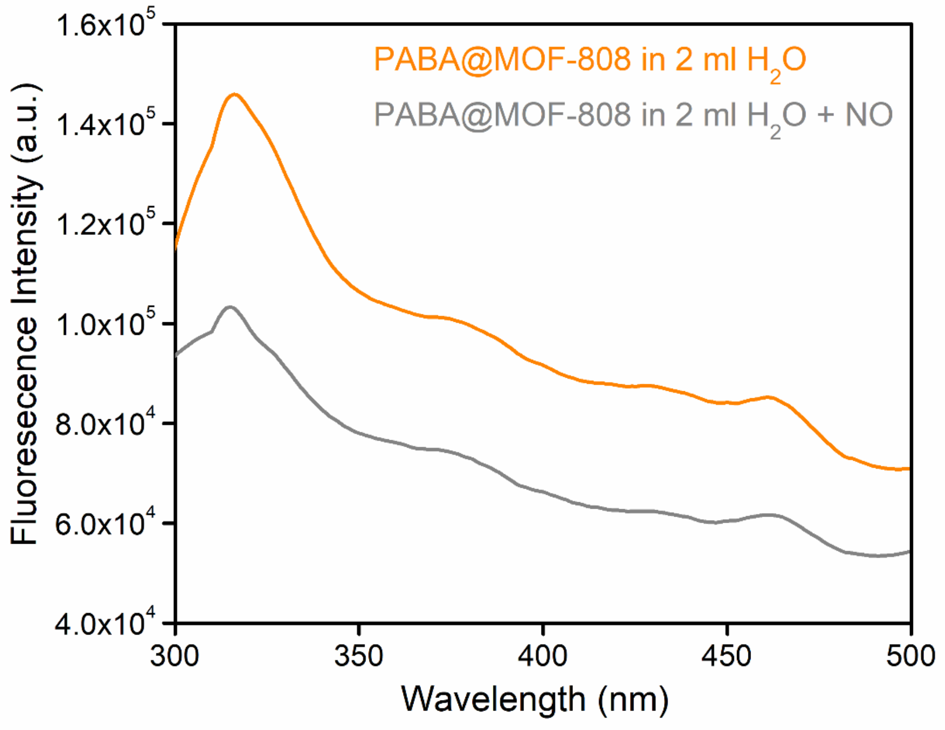


Figure S20: Change in PL intensity after addition of certain amount of NO aqueous solution.

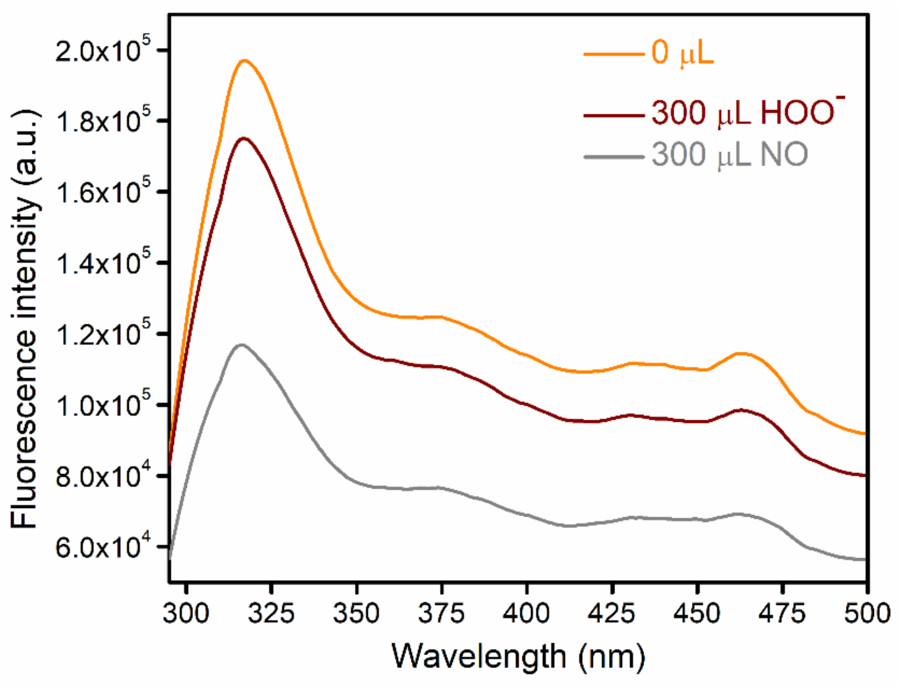


Figure S21: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous HOO^- solution, followed by the addition of 300 μL of NO aqueous solution.

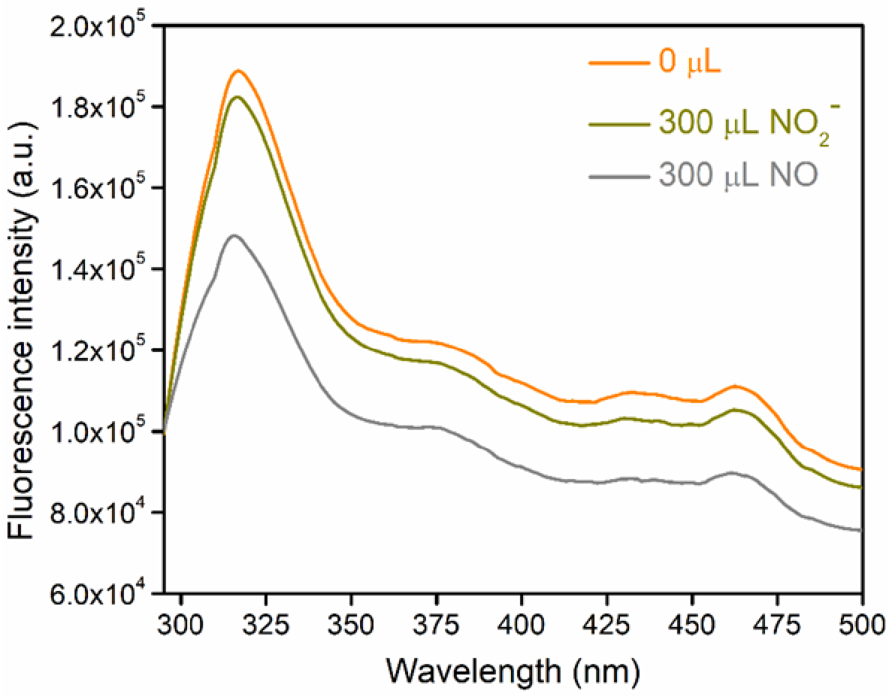


Figure S22: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 µL of aqueous NO_2^- solution, followed by the addition of 300 µL of NO aqueous solution.

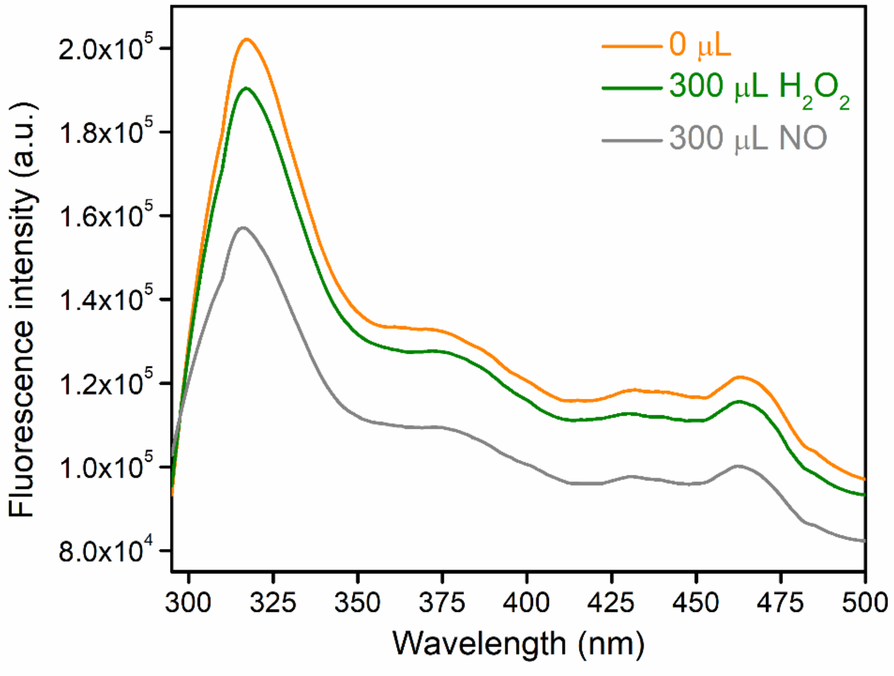


Figure S23: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 µL of aqueous H_2O_2 solution, followed by the addition of 300 µL of NO aqueous solution.

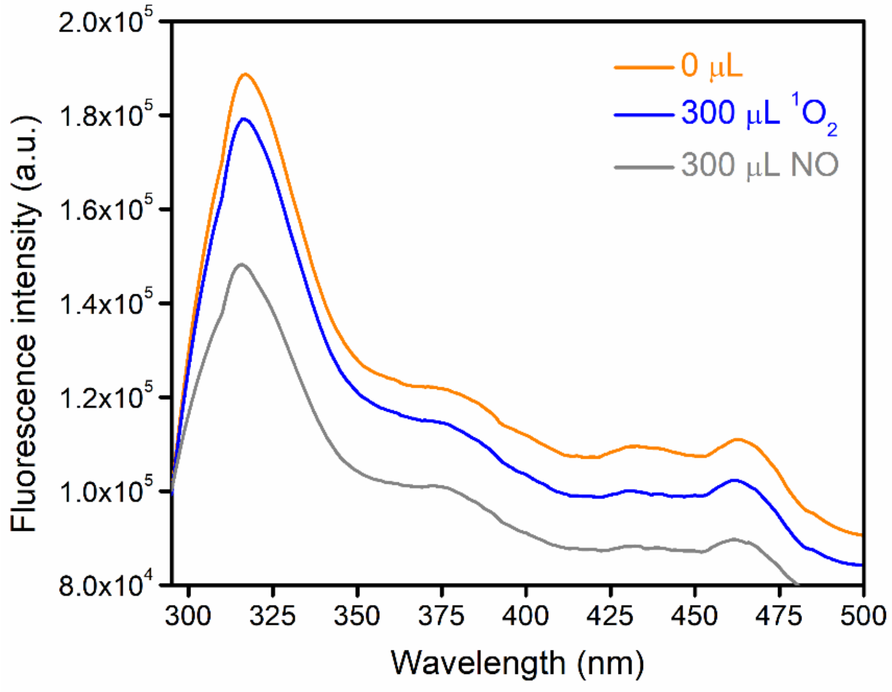


Figure S24: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous $^1O_2$ solution, followed by the addition of 300 μL of NO aqueous solution.

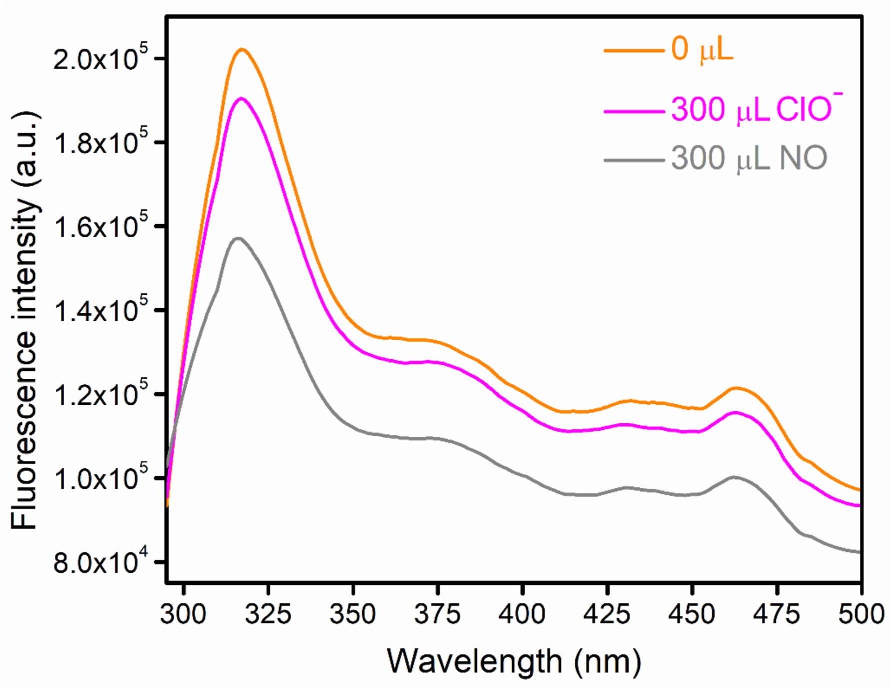


Figure S25: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous ClO^- solution, followed by the addition of 300 μL of NO aqueous solution.

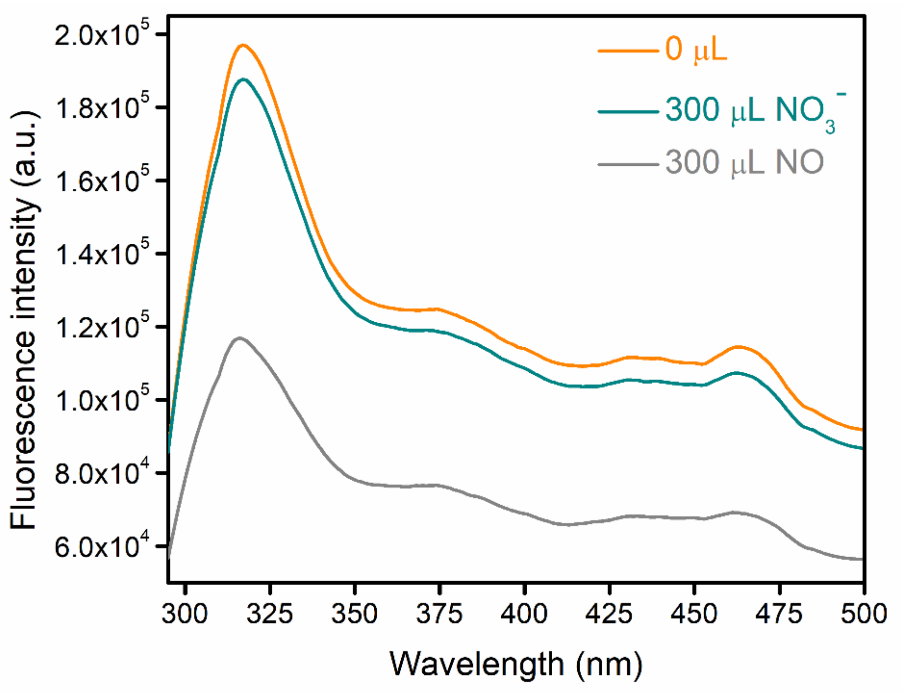


Figure S26: Fluorescence quenching response of PABA@MOF-808 upon treatment of 300 μL of aqueous NO_3^- solution, followed by the addition of 300 μL of NO aqueous solution.

Section-S6: Sensing Mechanism Studies of PABA@MOF-808

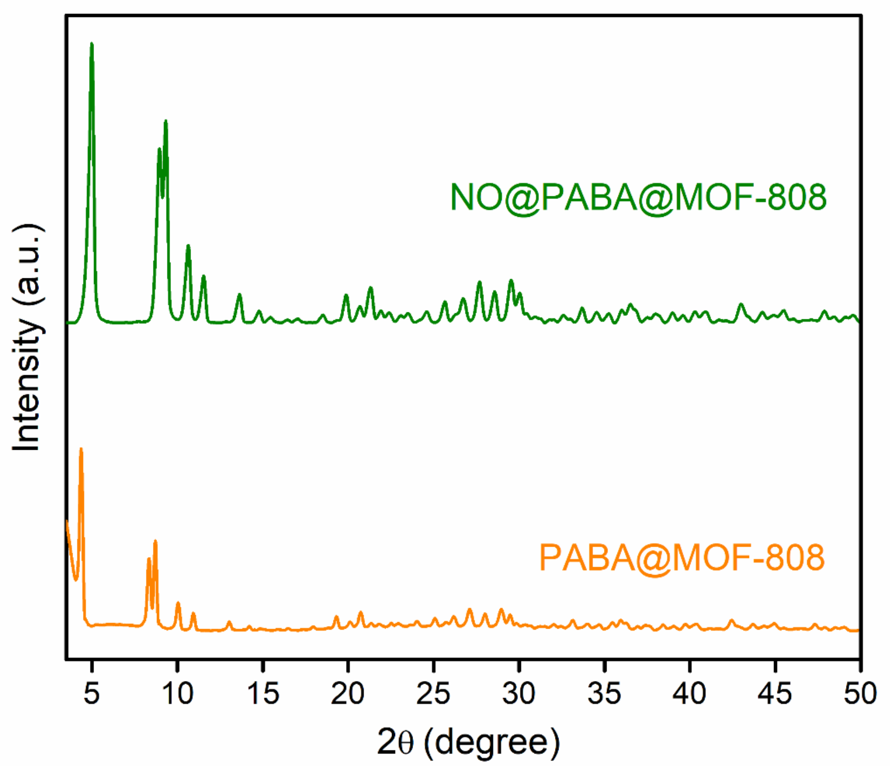


Figure S27: PXRD profile of PABA@MOF-808 before and after treatment of NO solution.

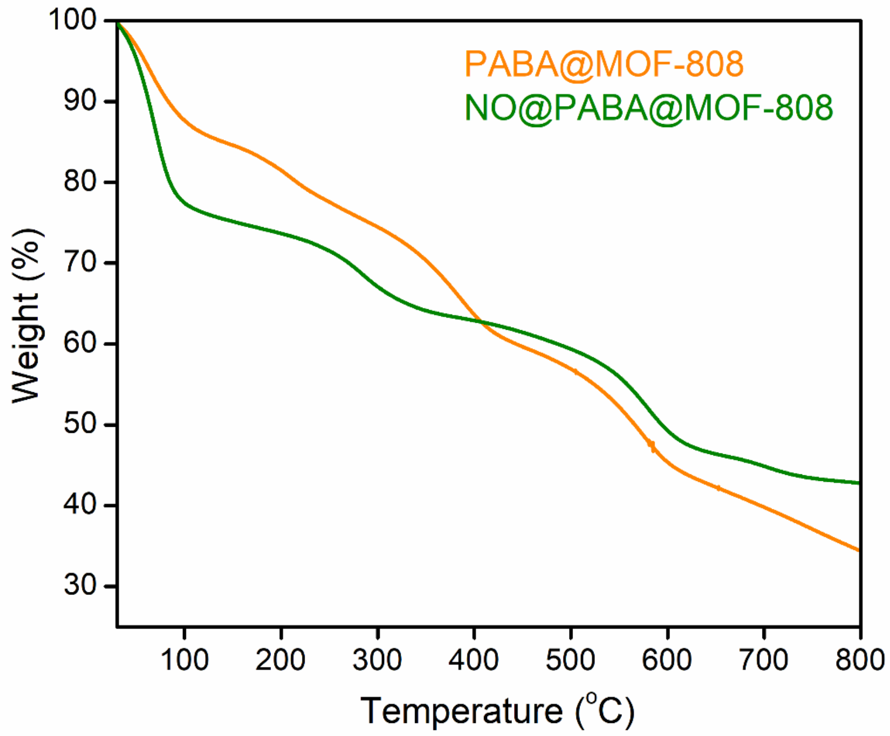


Figure S28: TGA profile of PABA@MOF-808 before and after treatment of NO solution.

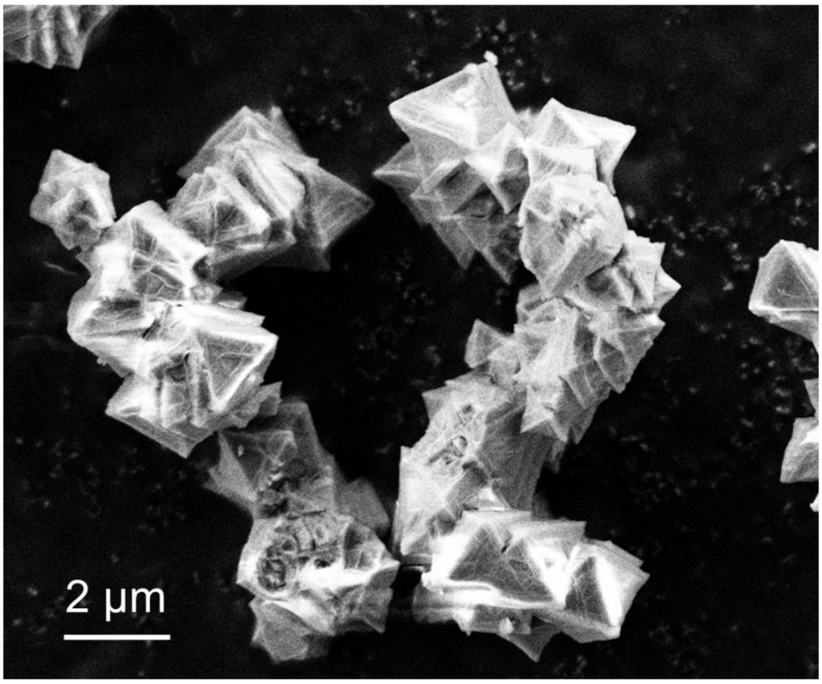


Figure S29: FESEM image of PABA@MOF-808 after treatment of NO solution.

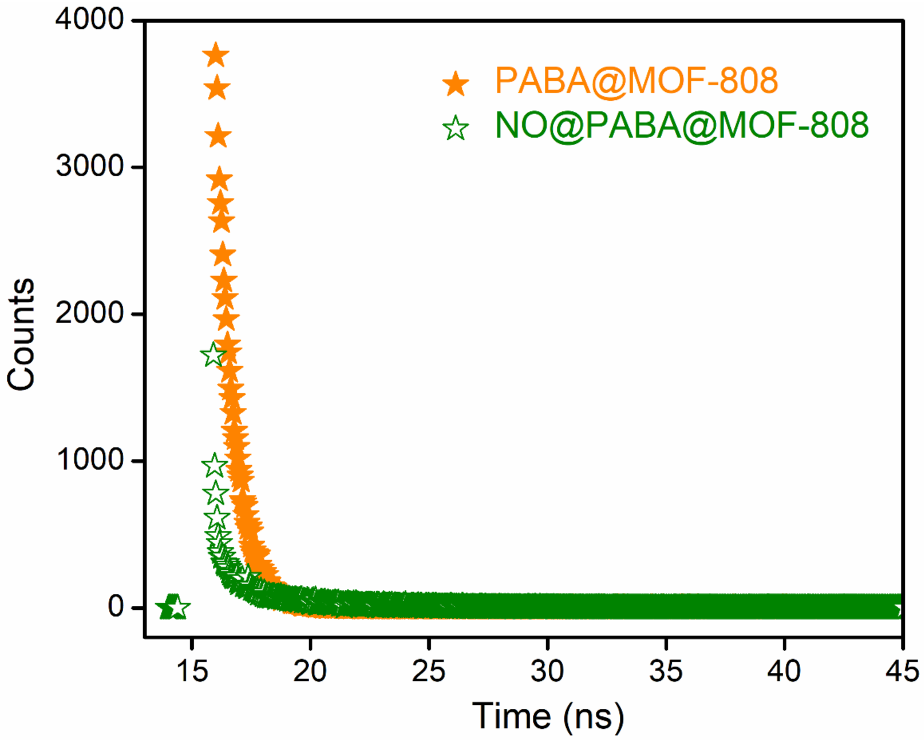


Figure S30: Time-resolved fluorescence decay profile of PABA@MOF-808 before and after NO treatment.

Table-S1: The values of different parameter for the lifetime measurements.

Compound	α_1(%)	t_1 (ns)	α_2(%)	t_2 (ns)	t_{av} (ns)	R^2
PABA@MOF-808	100	0.71	--	--	0.71	0.99
NO@PABA@MOF-808	10.7	1.18	89.3	0.04	0.93	0.99

If t_1 and t_2 are PL lifetimes for bi-exponential decay with weightage α_1 and α_2 respectively then PL decay can be fitter using- $I(t) = \sum_i \alpha_i e^{\left(t/t_i\right)}$; $i = 1,\ 2.$

And the average PL would be lifetime, $t_{av} = \frac{\alpha_1 t_1^2 + \alpha_2 t_2^2}{\alpha_1 t_1 + \alpha_2 t_2}$.

Excitation Wavelength: 285 nm; Detection wavelength: 316 nm; τ (Average lifetime) = 0.93 ns [NO treated PABA@MOF-808]; χ^2= 0.99

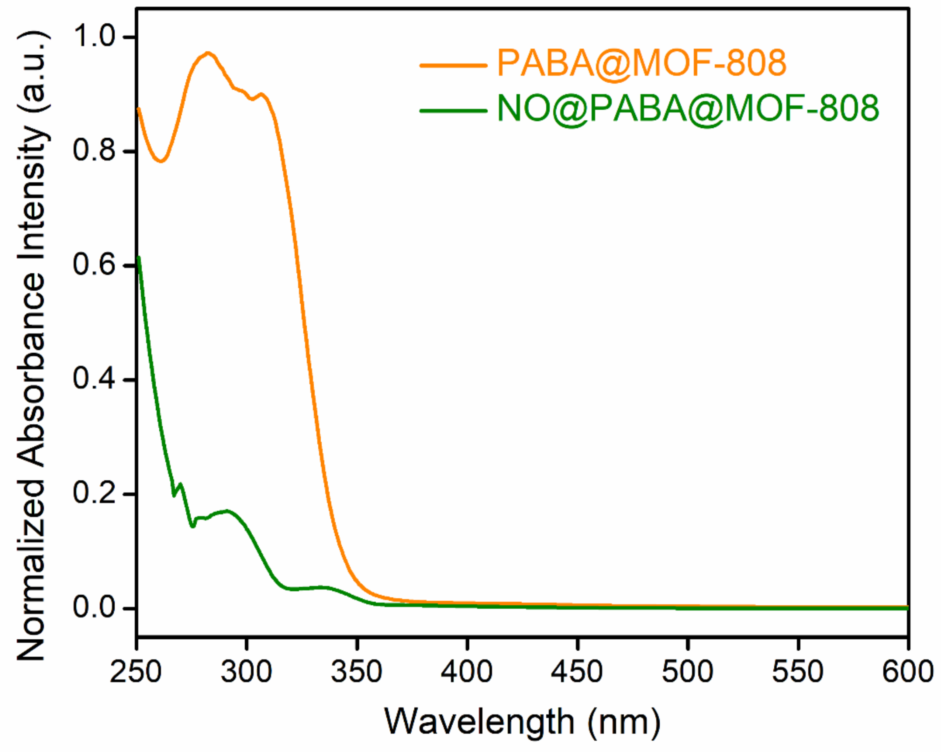


Figure S31: Diffuse reflectance UV-vis spectra of PABA@MOF-808 before and after NO treatment.

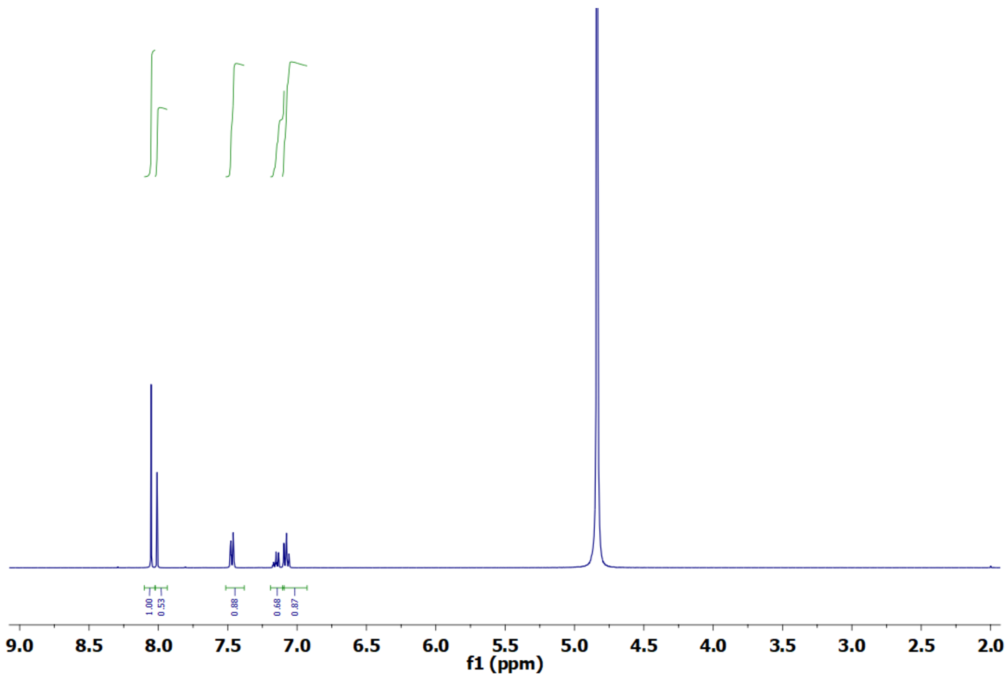


Figure S32: ^{1}H NMR spectra of PABA@MOF-808 after NO treatment.

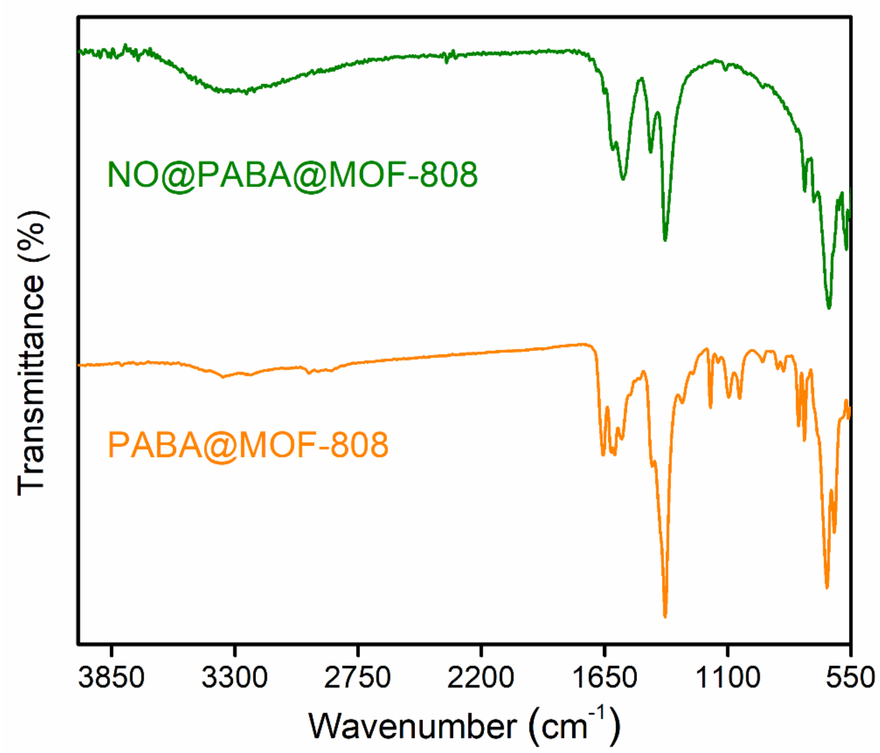


Figure S33: FT-IR spectra of PABA@MOF-808 before and after NO treatment.

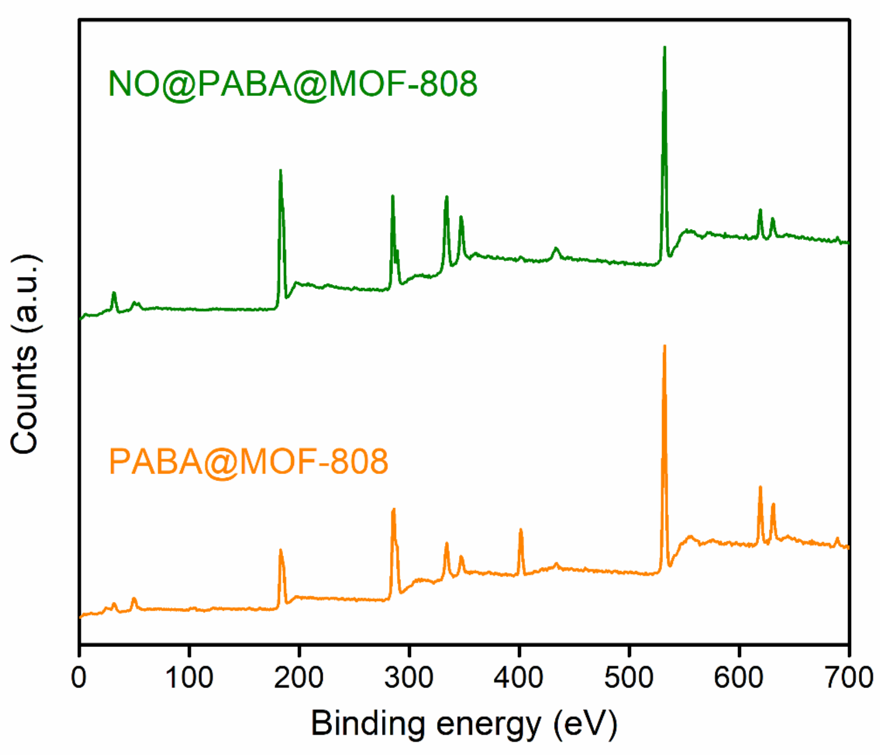


Figure S34: XPS survey spectra of PABA@MOF-808 before and after NO treatment.

Section-S7: Mixed Matrix Membrane based sensing studies.

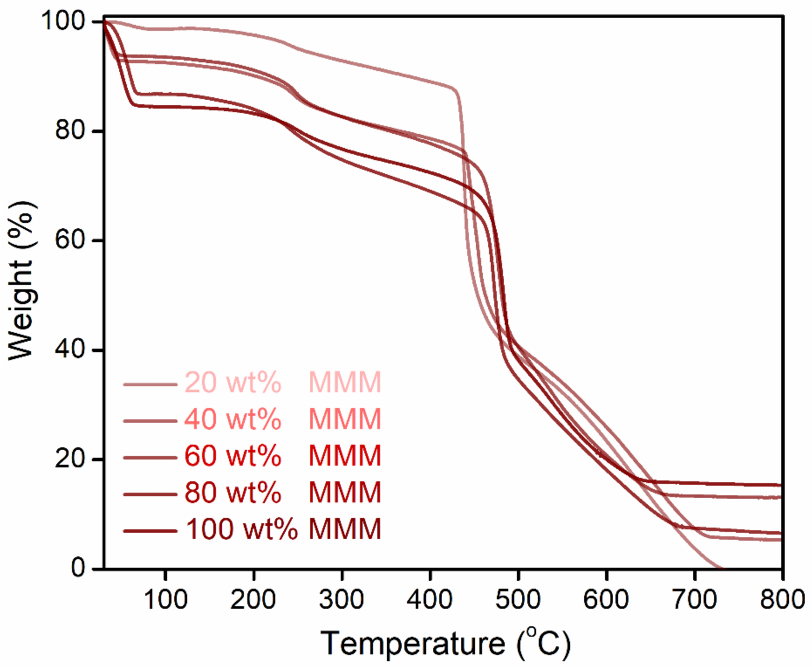


Figure S35: TGA spectra of PABA@MOF-808@PVDF MMMs with different MOF ratio.

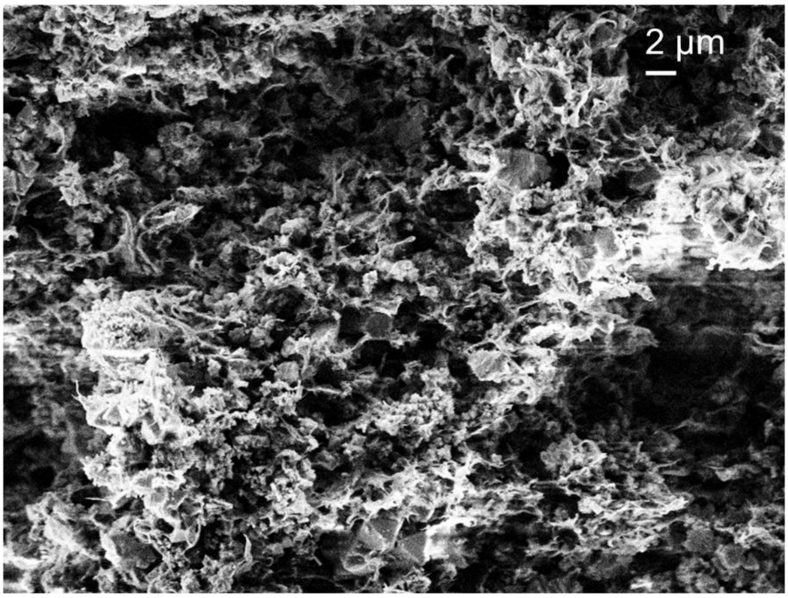


Figure S36: FESEM image of front view of PABA@MOF-808@PVDF MMMs.

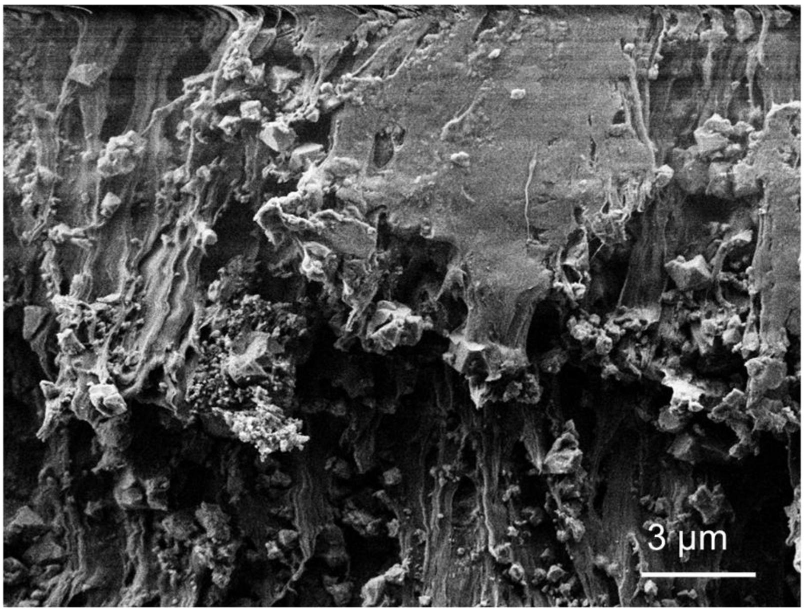


Figure S37: FESEM image of PABA@MOF-808@PVDF MMMs.

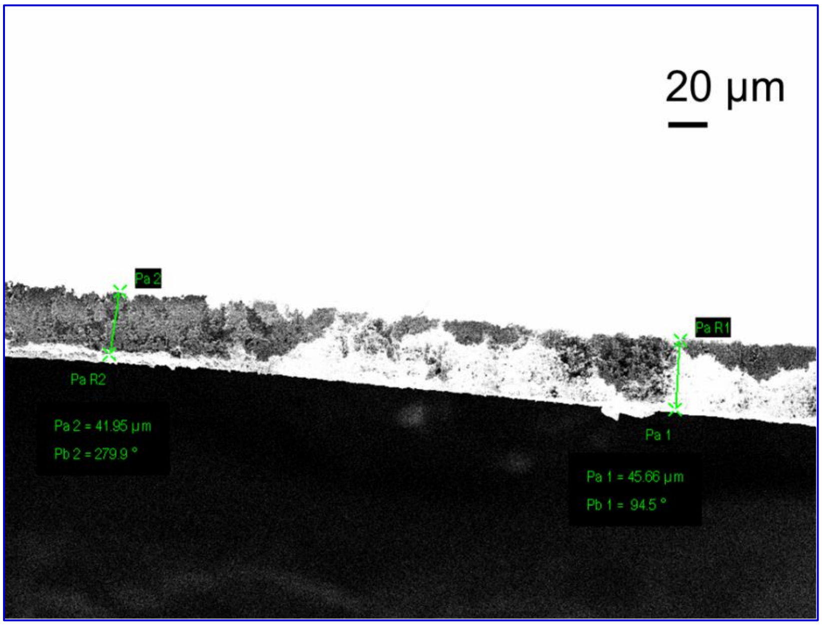
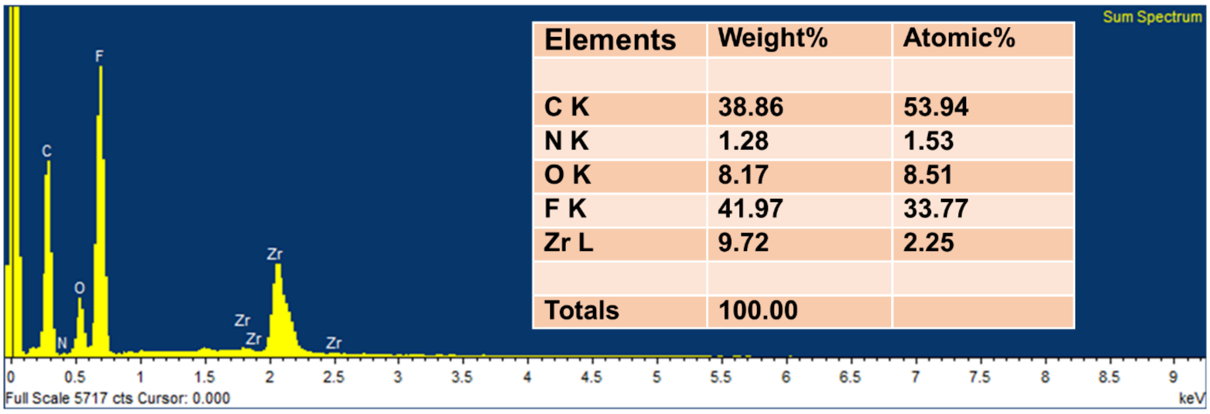


Figure S38: FESEM image of cross-section view of PABA@MOF-808@PVDF MMM.



Elements	Weight%	Atomic%
C K	38.86	53.94
N K	1.28	1.53
O K	8.17	8.51
F K	41.97	33.77
Zr L	9.72	2.25
Totals	100.00	

Figure S39: Energy dispersive X-ray spectroscopy (EDS) data of PABA@MOF-808@PVDF MMM.

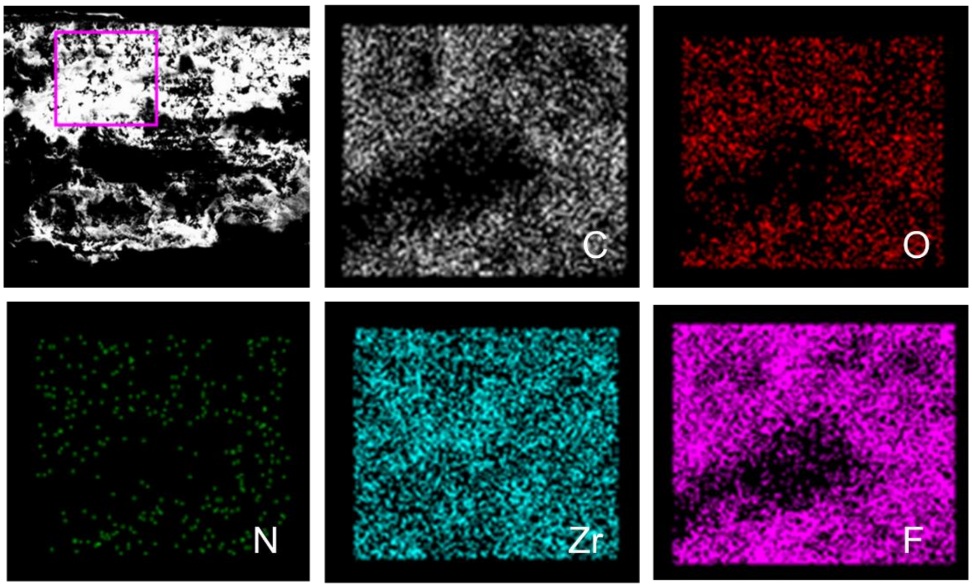


Figure S40: Elemental mapping images of PABA@MOF-808@PVDF MMM.

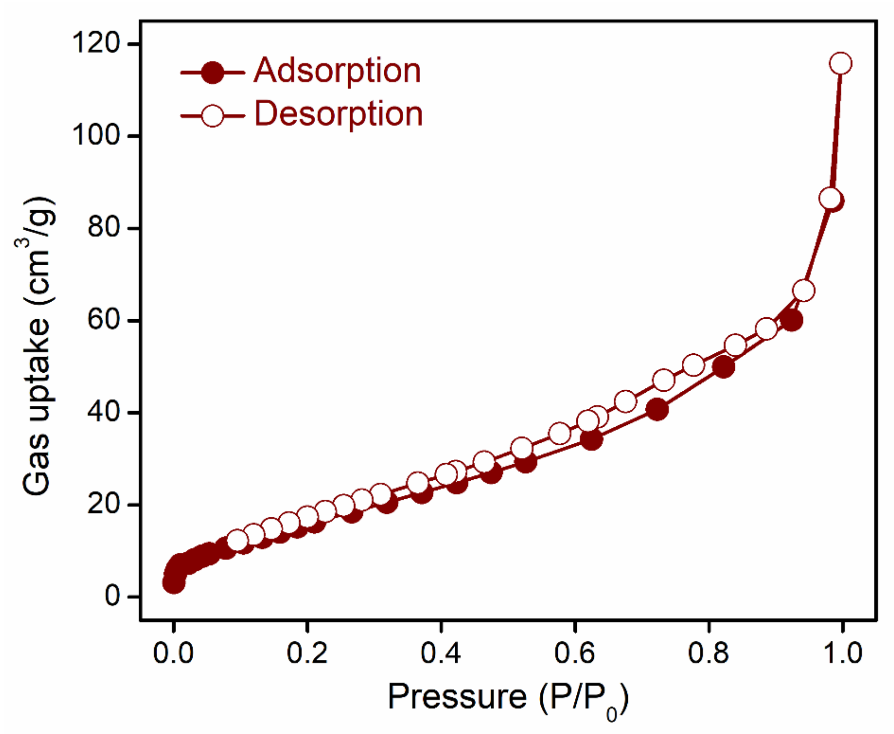


Figure S41: Nitrogen gas sorption data of PABA@MOF-808@PVDF MMM.

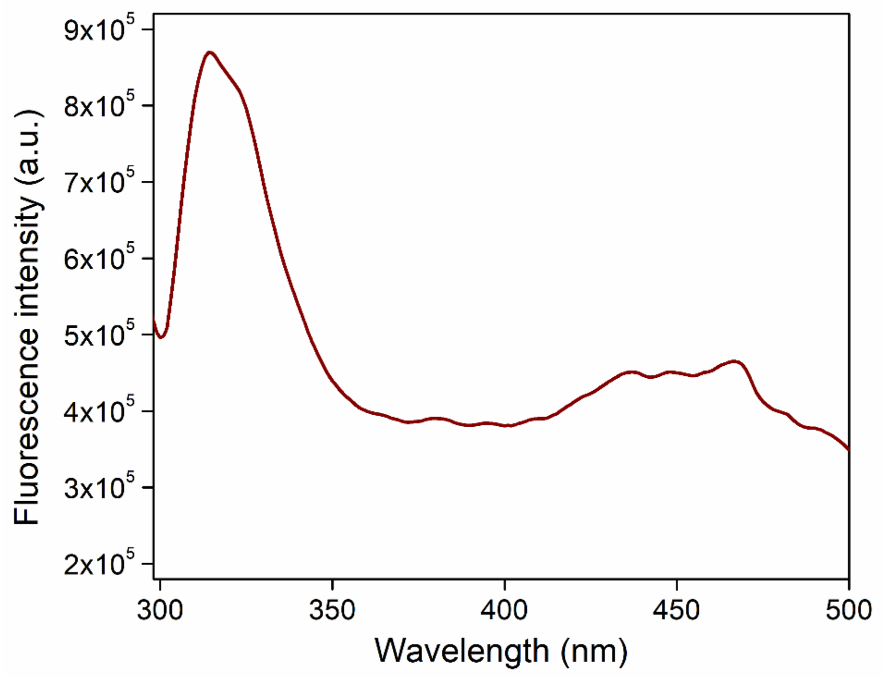


Figure S42: Photoluminescence emission spectra of PABA@MOF-808@PVDF MMM.

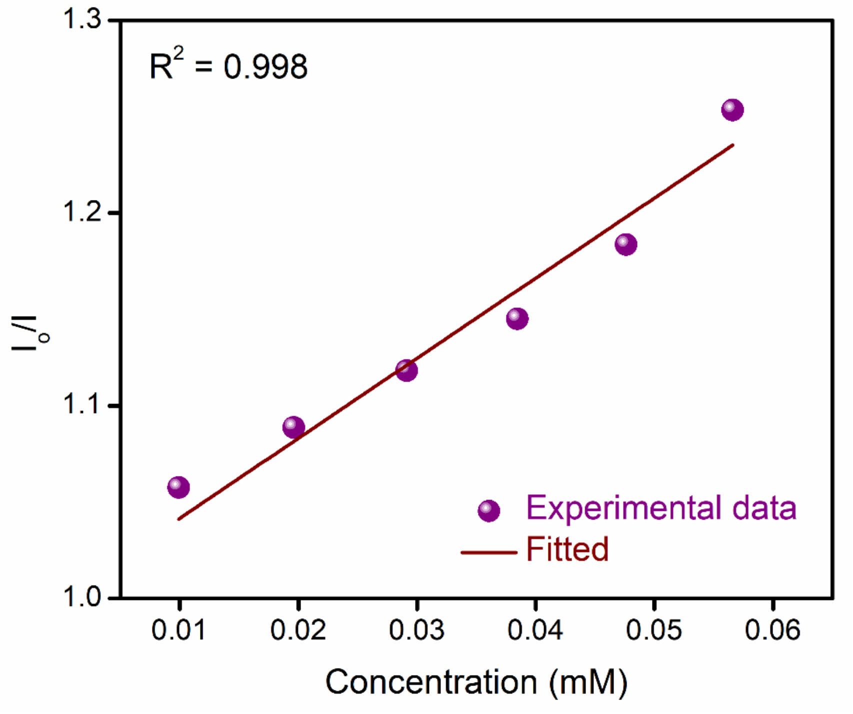


Figure S43: Stern-Volmer (SV) plots for quenching of PL intensity of PABA@MOF-808@PVDF MMM by NO.

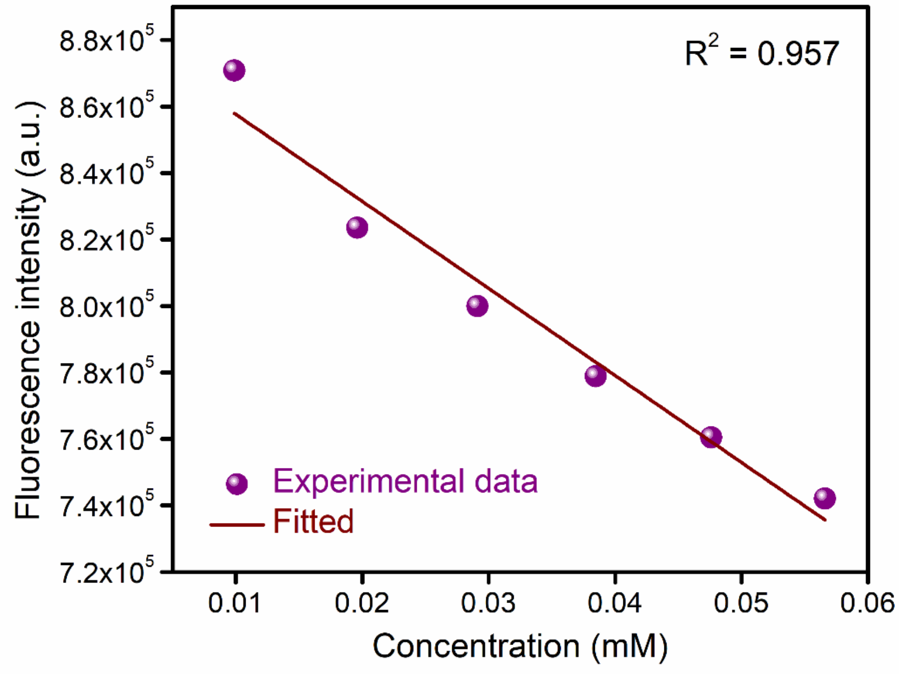


Figure S44: Plot for calculation of LOD of PABA@MOF-808@PVDF MMM towards NO detection.

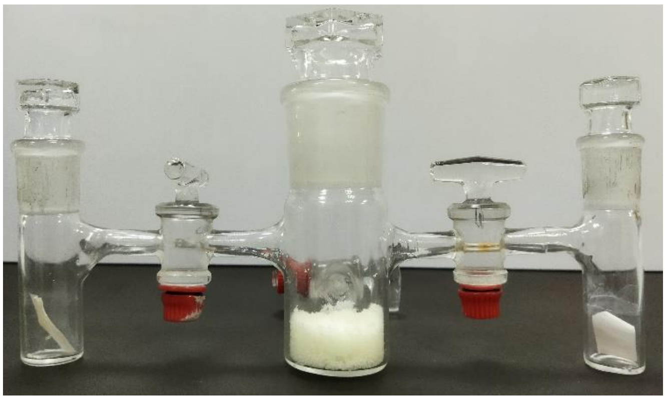


Figure S45: Digital image of set-up for demonstration of NO vapour detection by PABA@MOF-808@PVDF MMM.

Section-S8: References

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