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Supporting Information

Electrochemical Preparation of Metal-organic Framework Films for Fast Detection of Nitro Explosives

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1. General methods: Voltage supply was performed by *Epsilon* electrochemical workstation. Scanning electron microscopy (SEM) images were acquired on a *Phenom G2* instrument. Powder X-ray diffraction (PXRD) of MOF films were carried out on a *Mini Flex II* diffractometer using CuKα radiation (λ = 0.154 nm). Roughness and thickness of MOF films were determined by a *Dektak XT* Profiler. Optical photos were taken using a *Canon Digital IXUS 9901S* camera. The fluorescence spectra were acquired on a *Cray Eclipse* instrument. The original emission spectra of MOF thin film in air was acquired on *FLS980 fluorescence spectrophotometer*.

2. Preparation of $Zn_3(BTC)_2$ films: two zinc plates (4 cm × 1.3 cm × 0.2 mm) were partially immersed in a solution of H_3BTC (1g) and ammonium fluoride (NH_4F, 1g) in 100 mL of deionized water, in which ammonium fluoride plays a role of supporting electrolyte, as well as balancing pH of the solution. The solution was kept at 65 °C for one hour with continuous N_2 bubbling to remove oxygen. By applying a voltage, $Zn_3(BTC)_2$ film was able to be grown on the anode Zn plate. As-prepared MOF films were washed thoroughly with EtOH and water, respectively, which remained unchanged before and after washing. MOF films with different morphology were able to be prepared by applying different voltages and reacting for different period of time.

3. Nitro explosive detection: taking nitrobenzene detection as an example, a slide of MOF film was placed in 10 mm quartz cuvette and corresponding fluorescence emission spectra were recorded upon excitation at 327 nm after injecting nitrobenzene solutions of ethanol, acetonitrile, cyclohexane, N,N-Dimethylformamide (DMF) and isopropanol, respectively, with various concentrations (200.0, 100.0, 50.0, 25.0, 10.0, 5.0, 1.0, and 0.5 ppm etc.). Detection of other nitro explosives in ethanol (as an optimized solvent system) was carried out following a similar procedure described above. MOF films were recovered by washing with ethanol and drying at room temperature.

4. Supporting figures

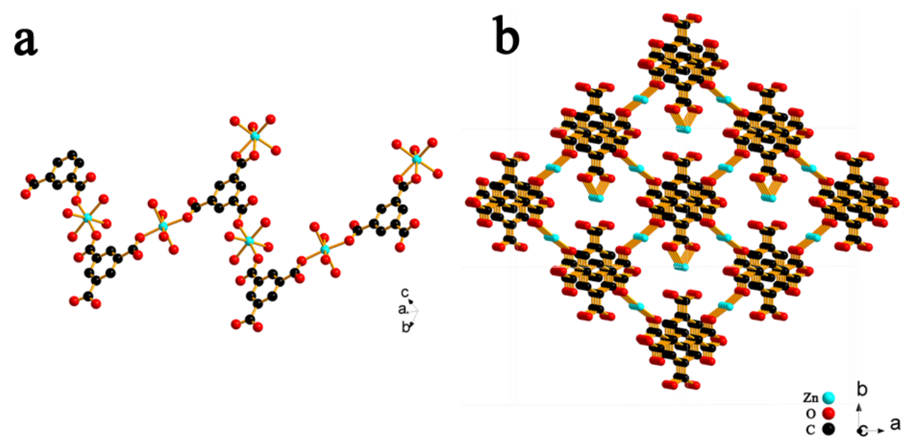


Fig. S1 a) The Zn-BTC chain, including the asymmetric unit b) Molecular-packing diagram of $Zn_3(BTC)_2$ viewed along the c-axis, showing open metal sites in 1-D channels created in 3-supramolecular metal-organic framework.

Fig. S2 A photograph of the as-prepared $Zn_3(BTC)_2$ film.

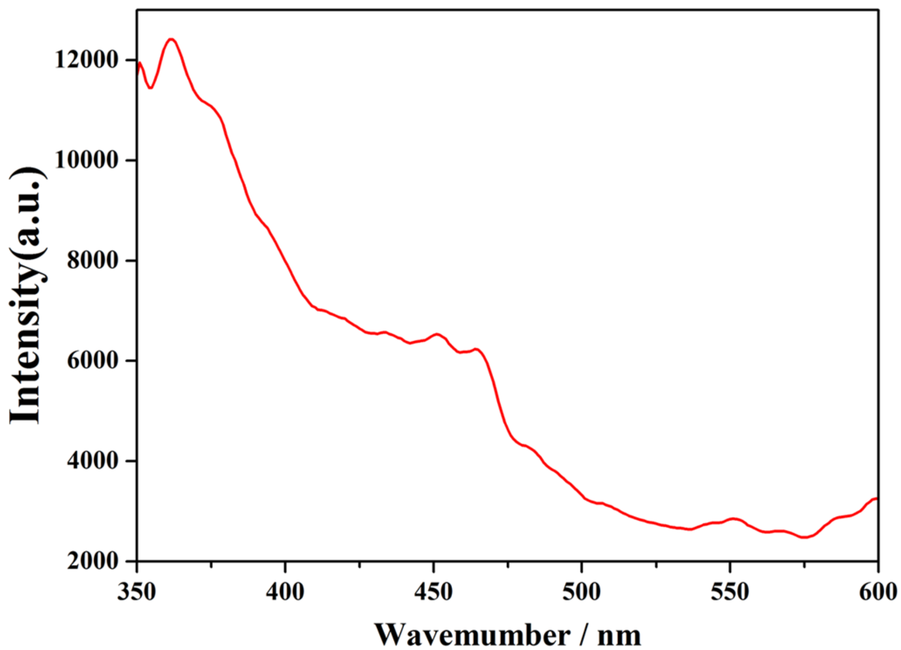
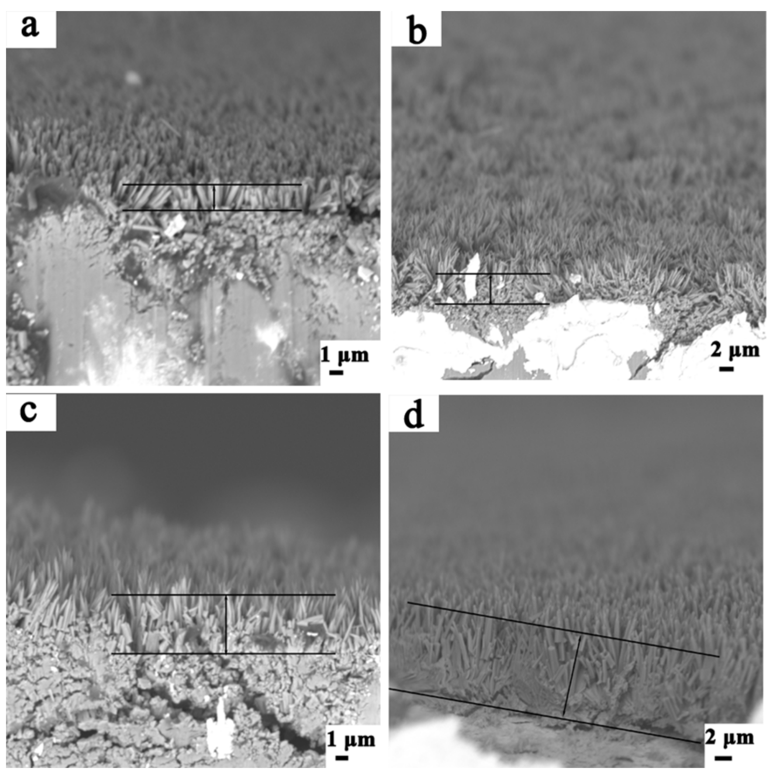


Fig. S3 The emission spectra of $Zn_3(BTC)_2$ film in air using an excitation wavelength of 327 nm.



Fi. S4 SEM images of MOF films (cross-section view) prepared at (a) 0.5 V, (b) 1.0 V, (c) 1.5 V, (d) 2.0 V for 60 seconds, respectively.

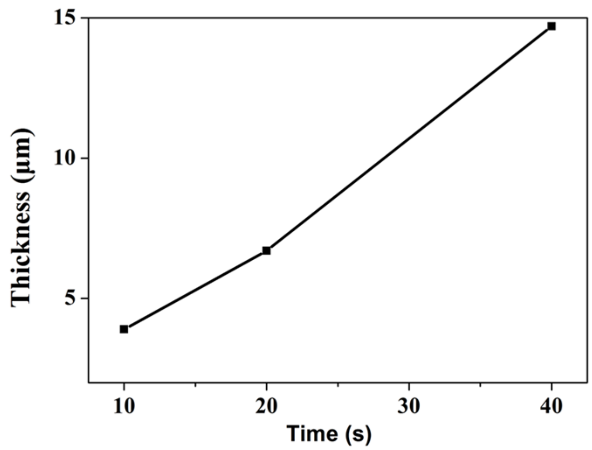


Fig. S5 The thickness of MOF thin film with reaction time increasing.

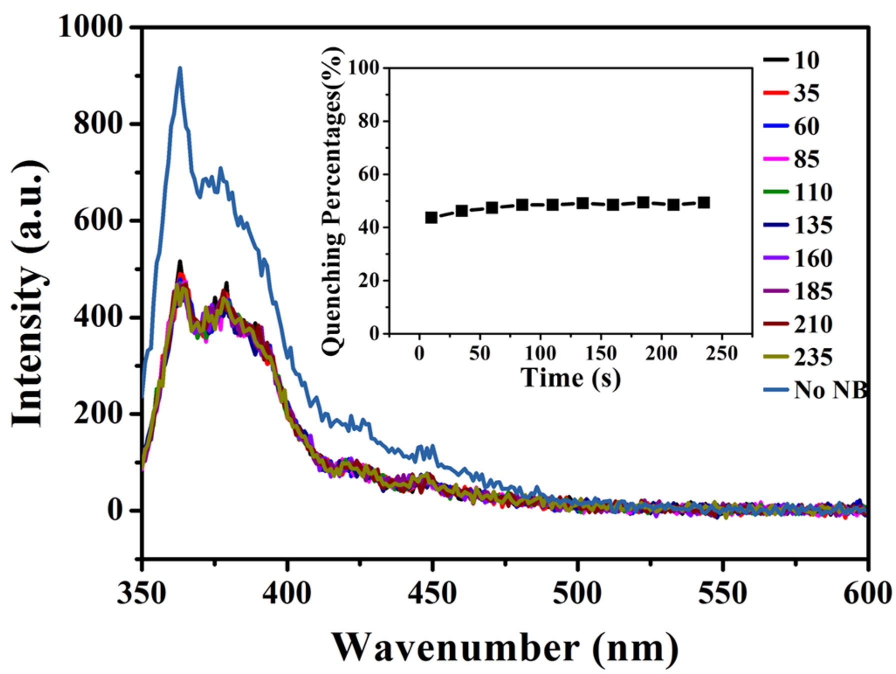


Fig. S6 Time-dependent emission spectra after dipped MOF film into 100 ppm NB solution (in ethanol). Inset is the Time-dependent quenching percentage of MOF films calculated from 362 nm.

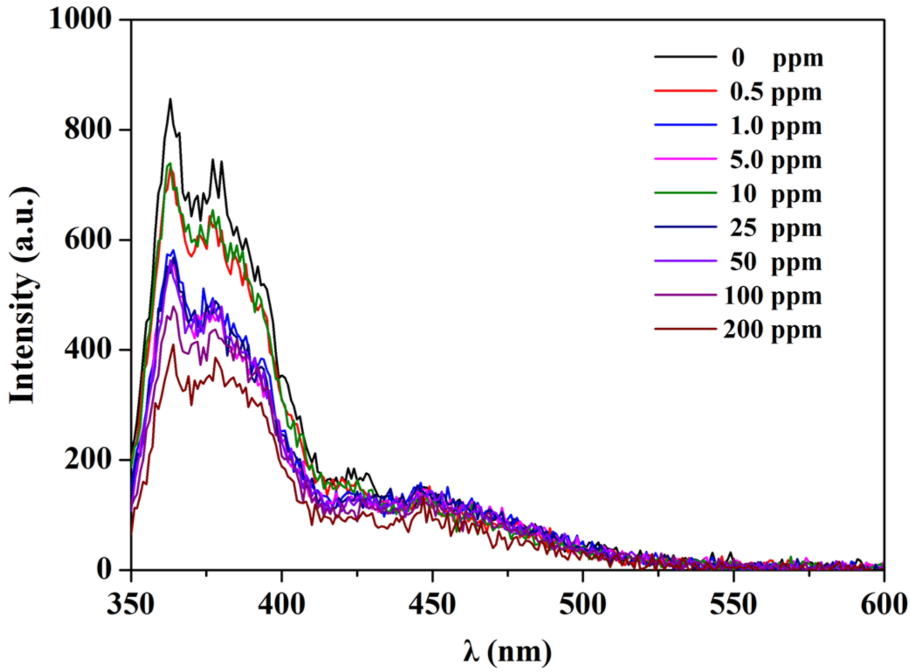


Fig. S7 The emission spectra of $Zn_3(BTC)_2$ film in cyclohexane using an excitation wavelength of 327 nm.

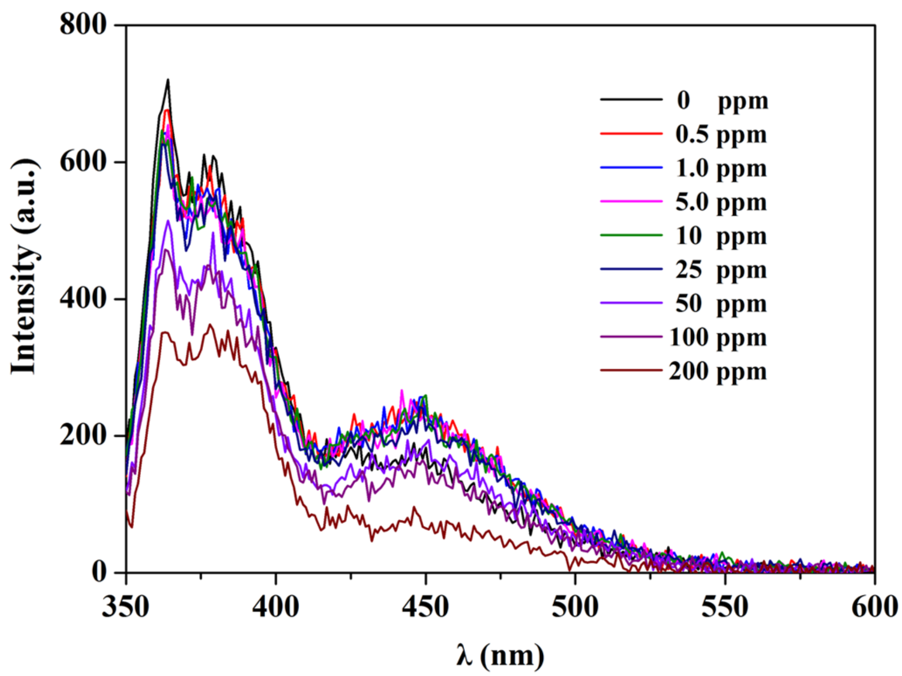


Fig. S8 The emission spectra of $Zn_3(BTC)_2$ film in DMF using an excitation wavelength of 327 nm.

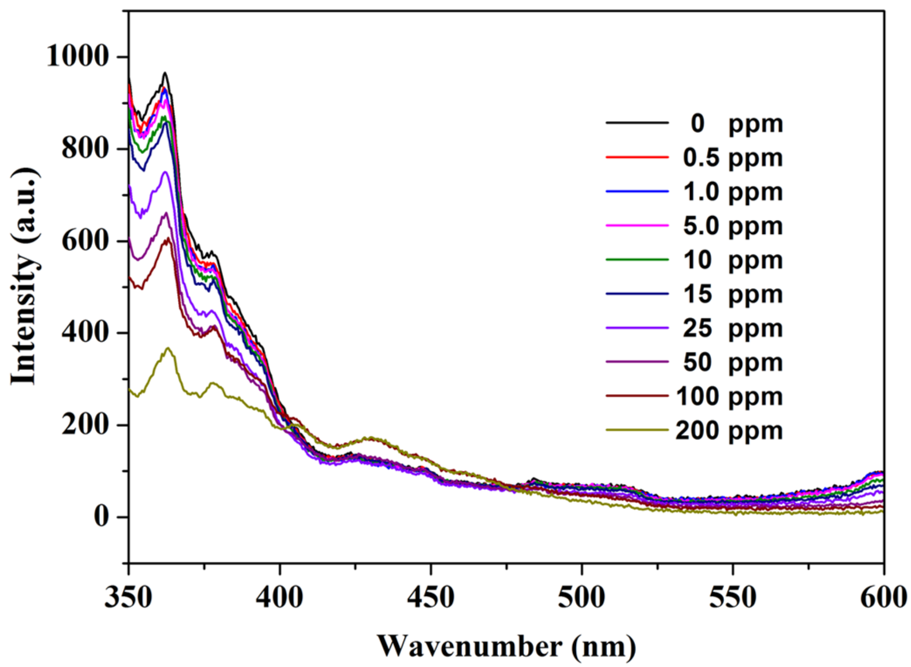


Fig. S9 The emission spectra of $Zn_3(BTC)_2$ film in ethanol using an excitation wavelength of 327 nm.

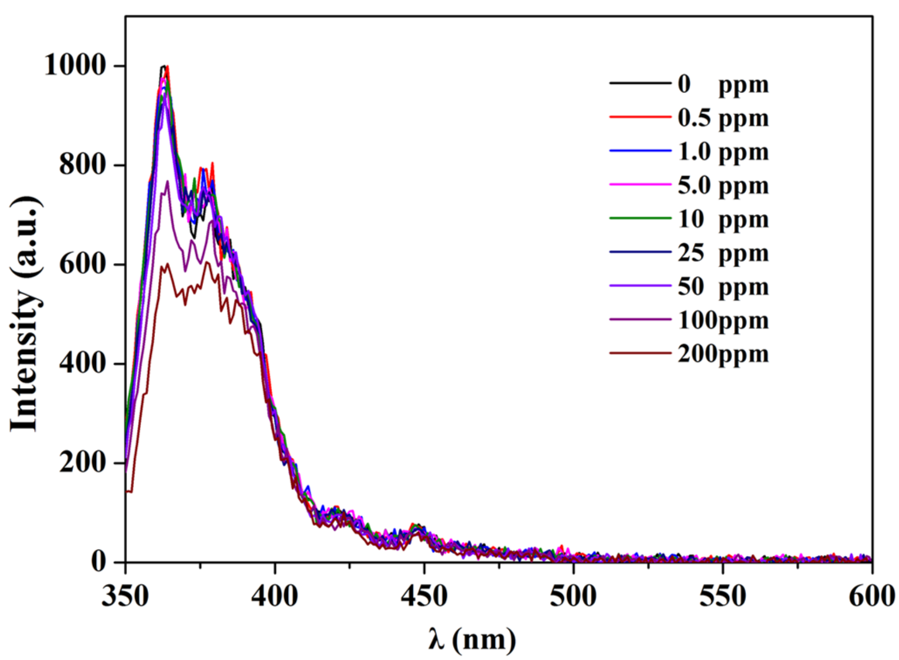


Fig. S10 The emission spectra of $Zn_3(BTC)_2$ film in acetonitrile using an excitation wavelength of 327 nm.

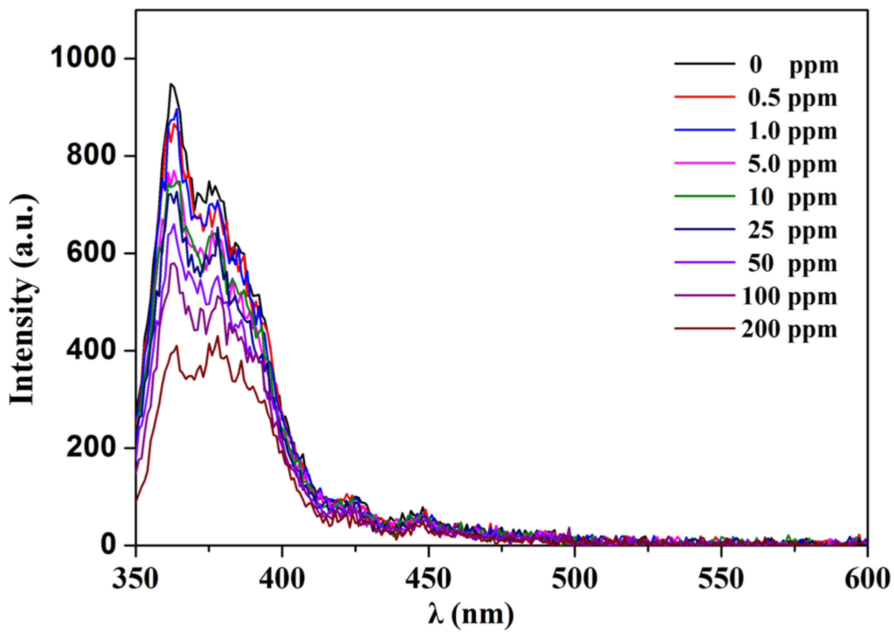


Fig. S11 The emission spectra of $Zn_3(BTC)_2$ film in isopropanol using an excitation wavelength of 327 nm.

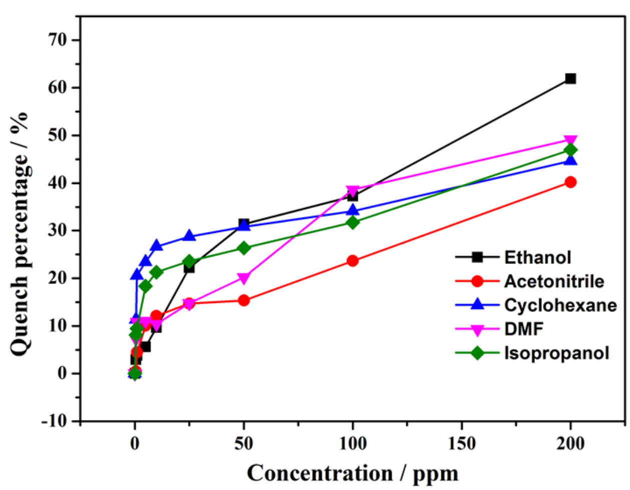


Fig. S12 The concentration-dependent quenching percentage of NB in different solvents. (Excited and monitored at 327 nm and 362 nm, respectively).

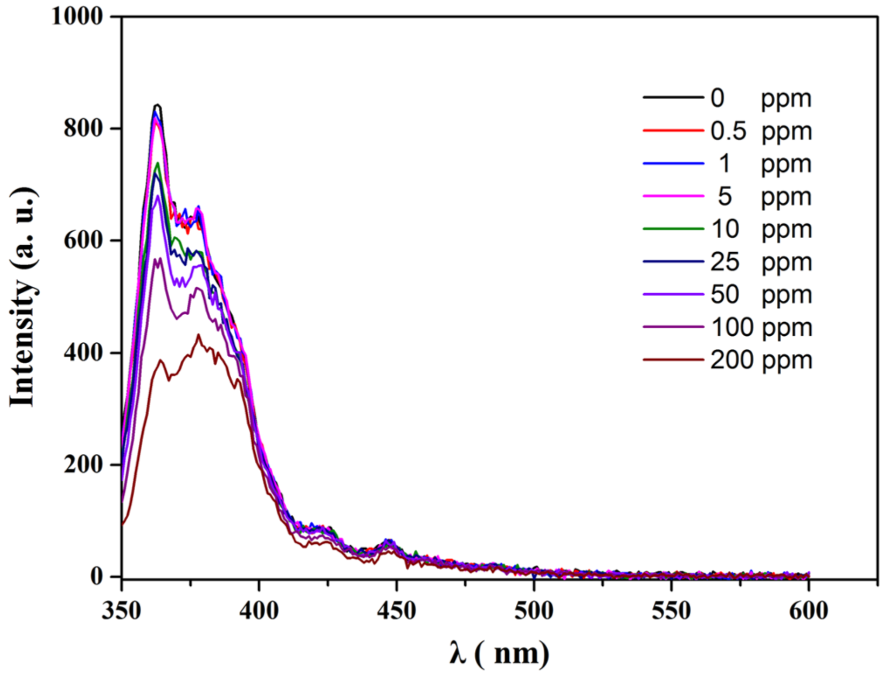


Fig. S13 Emission spectra $Zn_3(BTC)_2$ film with different concentration of 4-NT in ethanol solutions excited at 327 nm.

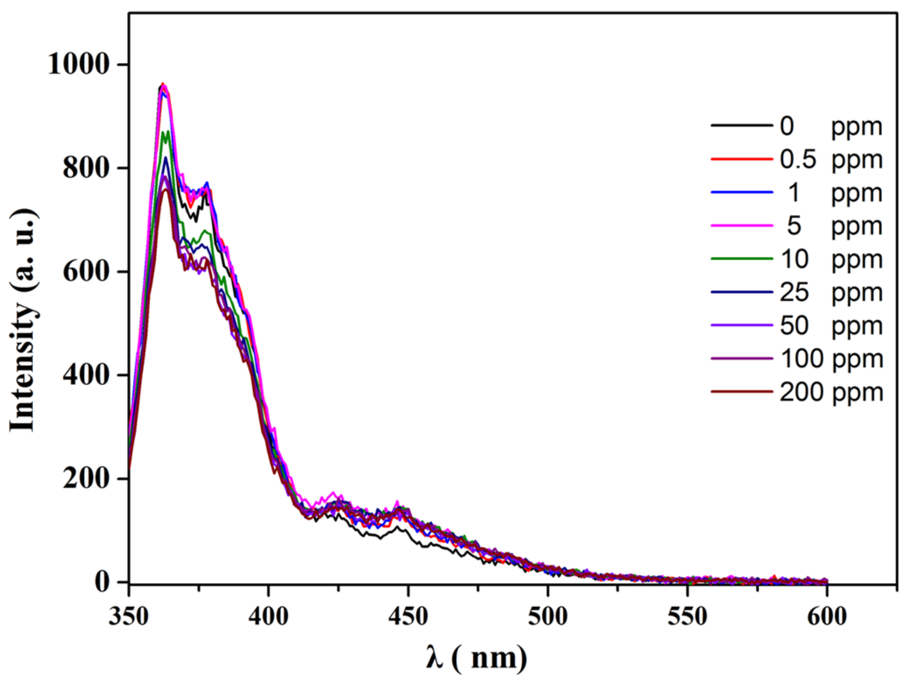


Fig. S14 Emission spectra of $Zn_3(BTC)_2$ film with different concentration of DMNB in ethanol solutions excited at 327 nm.

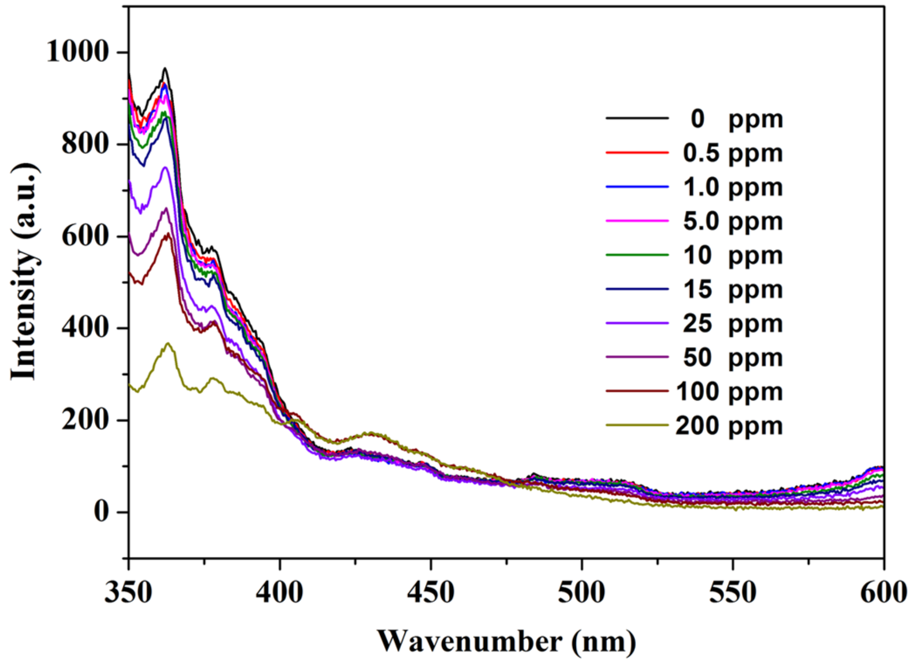


Fig. S15 Emission spectra of $Zn_3(BTC)_2$ film with different concentration of NB in ethanol solutions excited at 327 nm.

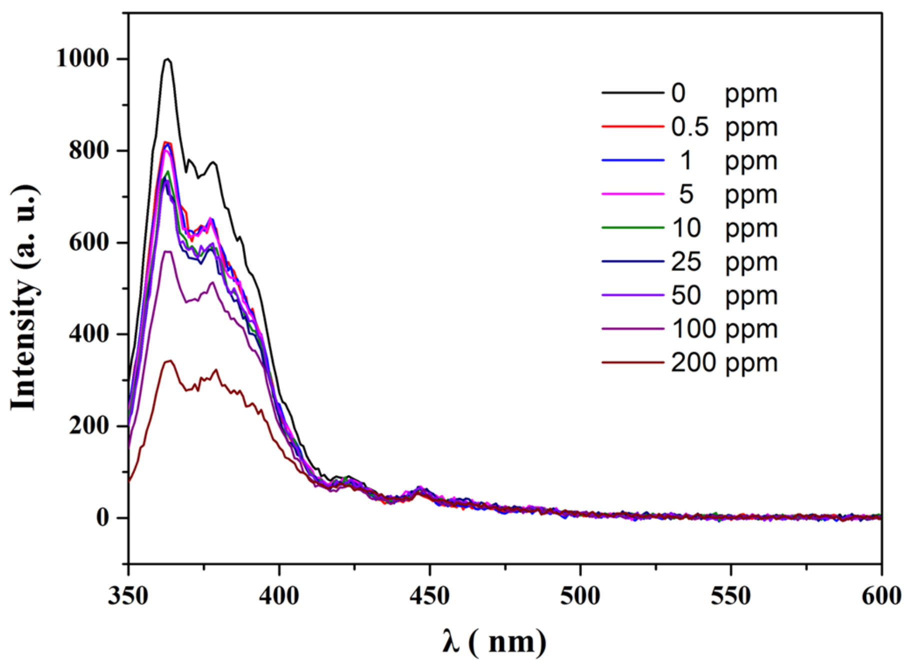


Fig. S16 Emission spectra of $Zn_3(BTC)_2$ film with different concentration of 1,3-DNB in ethanol solutions excited at 327 nm.

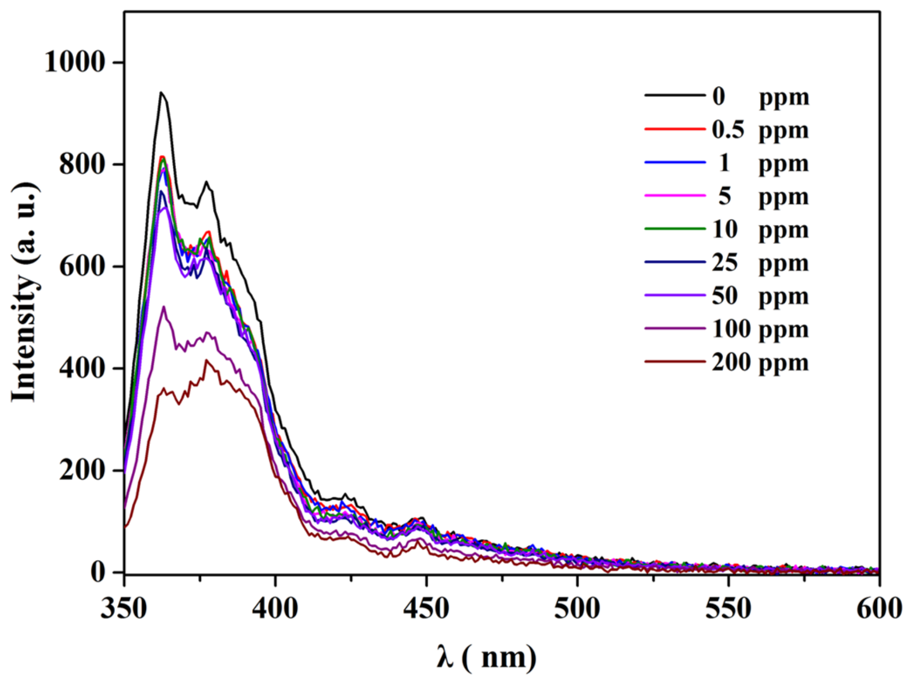


Fig. S17 Emission spectra of $Zn_3(BTC)_2$ film with different concentration of TNT in ethanol solutions excited at 327 nm.

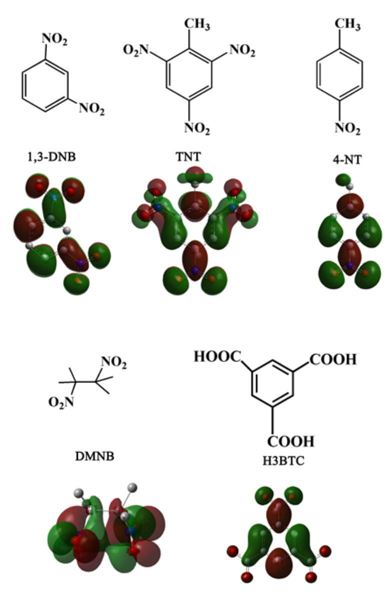


Fig. S18 Structures of model nitro explosives and their LUMO.

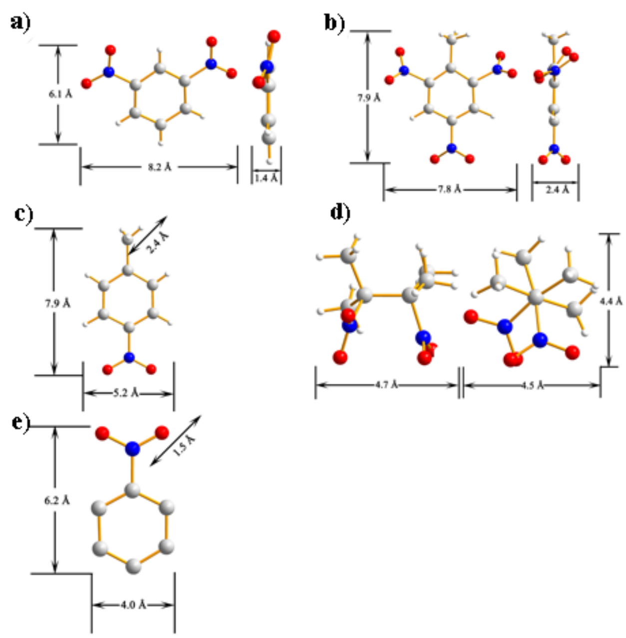


Fig. S19 Molecule sizes of various nitro explosives.

Type of detection	Nitro explosive	Limit of detection (ppm)	Reference
Dipersed powder in solution	NB	50	*Chem. Asian J.* **2013**, *8*, 982 – 989
Dipersed powder in solution	NB	50	*J. Mater. Chem.*, **2012**, *22*, 15939
Dipersed powder in solution	TNT	227.13 (1mM)	*Angew.chem.Int.Ed.***2013**,*52*,2881
Dipersed powder in solution	NB	5910 (0.048M)	*Inorg. Chem.* **2013**, *52*, 589−595
Dipersed powder	TNT	10	*Chem. Eur. J.* **2014**, *20*, 3589 – 3594

in solution			
Dipersed powder in solution	4-NT, 1,3-DNB	100	*J. Mater. Chem. A*, **2014**, *2*,1465
Dipersed powder in solution	NB, 4-NT, TNT	36,41.19,68.13 (0.3mM)	*Dalton Trans.*, **2013**, *42*, 5718
Dipersed powder in water	TNT, DMNB, 1,3-DNB,NB	500	*Chem.Commun.* DOI:10.1039/c4cc03053b
Spin-coating on substrates	TNT	15 (6.7 uM)	*Chem. Commun.*, **2011**, *47*, 12137 – 12139
Spin-coating on substrates	DMNB	2.7	*Angew. Chem. Int. Ed.* **2009**, *48*, 2334 – 2338
MOFs films	DMNB, TNT, 1,3 DNB, NB, 4-NT	0.5	Our work

Fig. S20 Limit of detection comparation of MOFs in various test pattern.

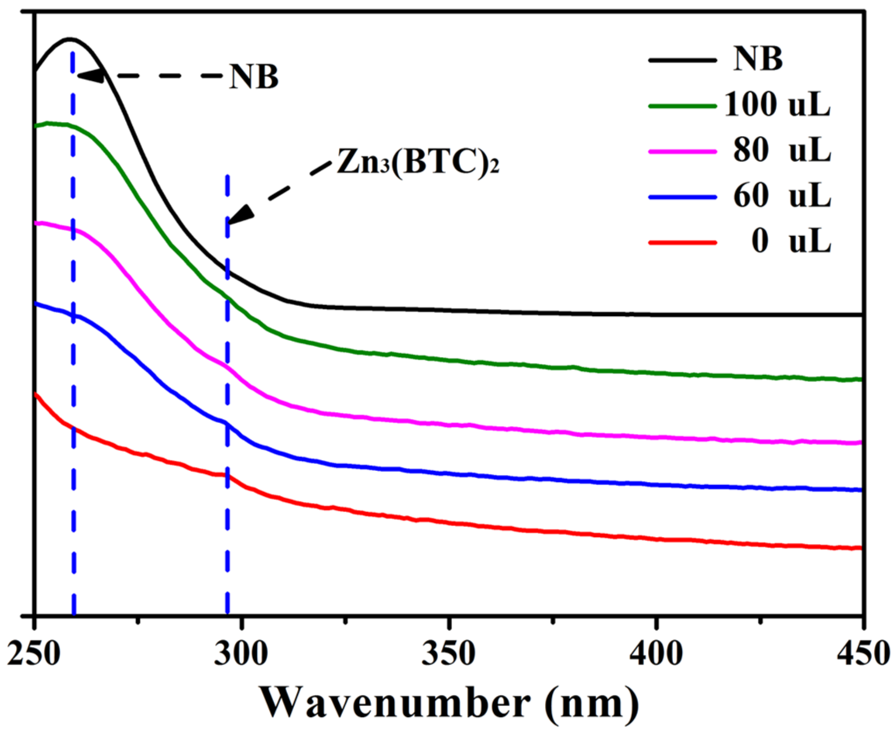


Fig. S21 Absorbance spectra of nitrobenzene and $Zn_3(BTC)_2$ with addition of NB in ethanol.

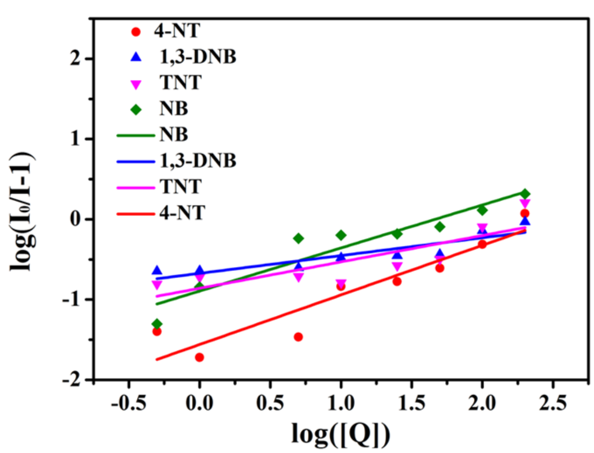


Fig. S22 The modified Stern-Volmer plots of different nitro explosives. (Excited and monitored at 327 nm and 362 nm, respectively)

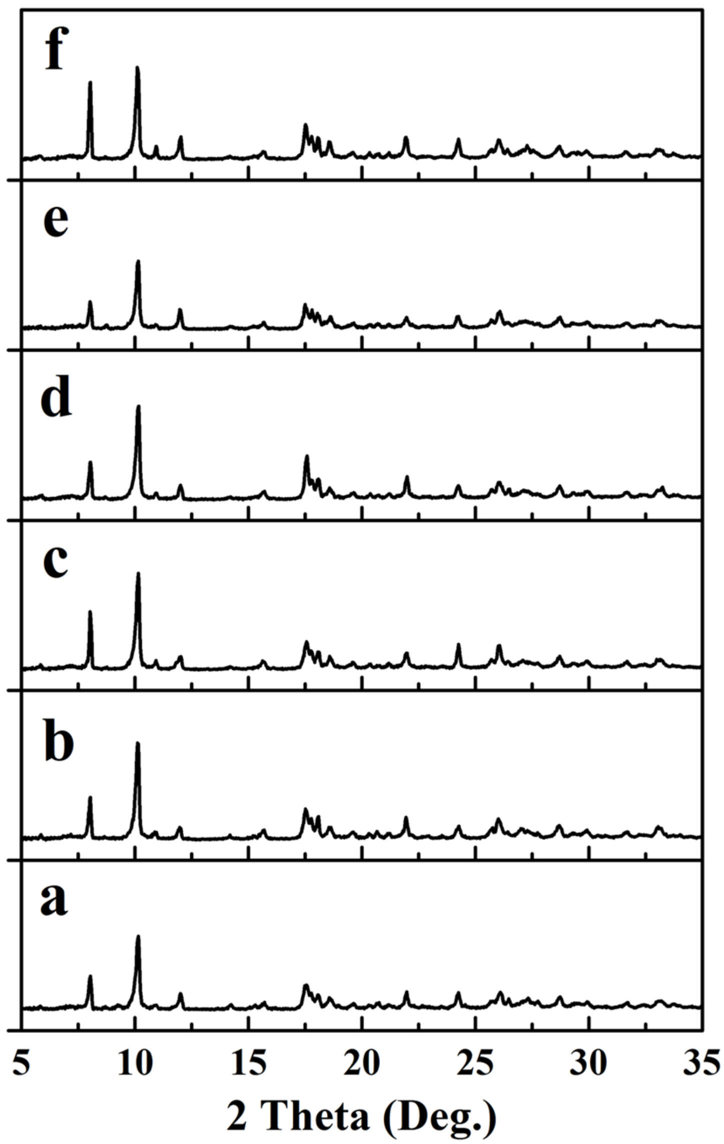


Fig. S23 PXRD of the MOF films: before (a) and after nitro explosive detection of 4-NT (b), DMNB (c), 1,3-DNB (d), NB (e), TNT (f).

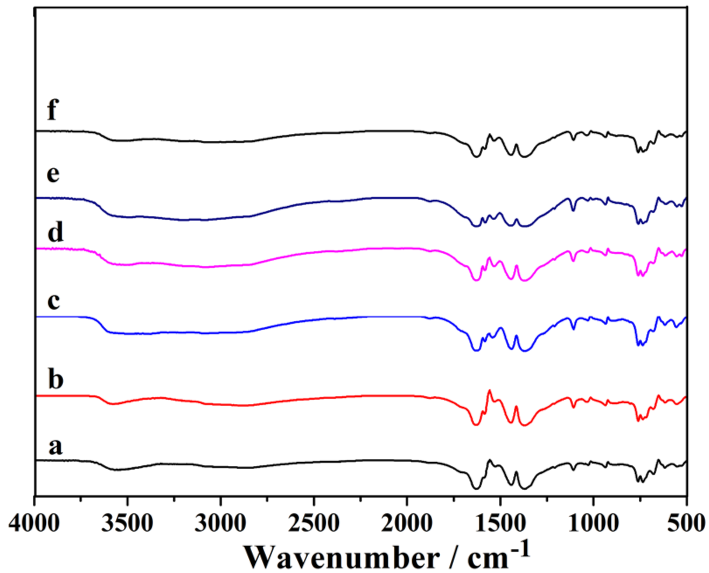


Fig. S24 IR spectra of the MOF films: before (a) and after nitro explosive detection of DMNB (b), 4-NT (c), 1,3-DNB (d), TNT (e), NB (f).

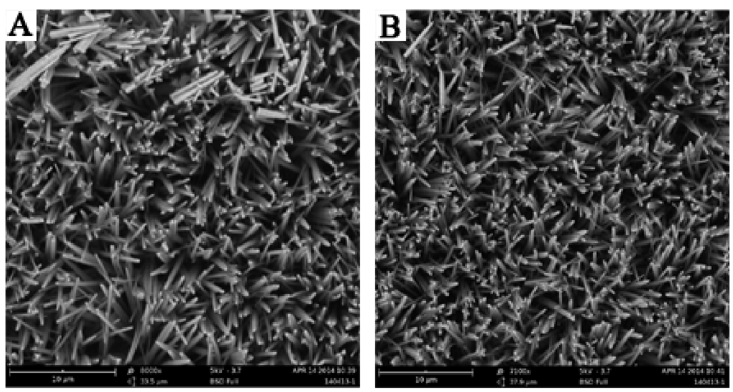


Fig. S25 Morphology of the MOF film A) before; B) after the detetion reaction of 1,3-DNB.

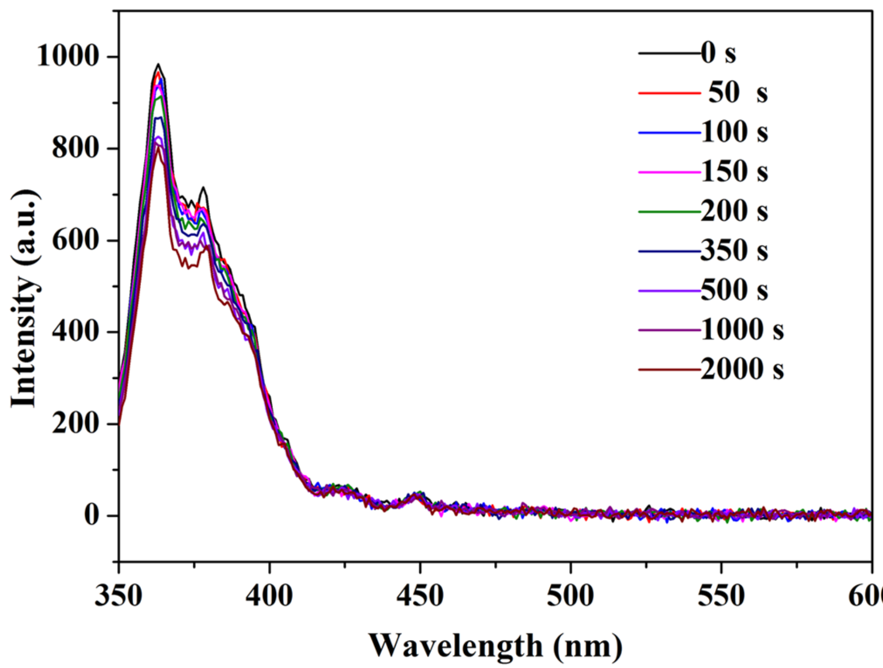


Fig. S26 Time-dependent emission spectra after exposure of MOF film to the NB vapour.

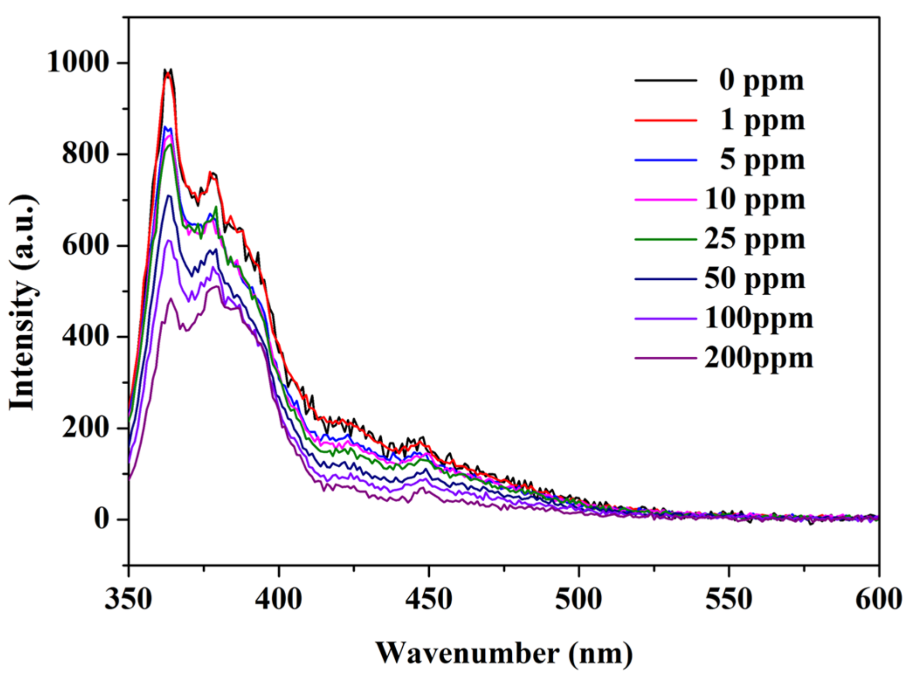


Fig. S27 The change in the fluorescence intensity of MOF film in water upon incremental addition of aqueous 200 ppm NB solution.