# A lanthanide MOF immobilized in PMMA transparent films as a selective fluorescence sensor for nitroaromatic explosive vapours.

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#### 1. Experimental Section

#### 1.2 Materials and methods

1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC), Terbium (III) nitrate hexahydrate, triethylamine (TEA), dimethylformamide (DMF), poly(methyl-methacrylate) (PMMA), 2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene, 2,4,6-trinitrophenol and 2,3-dimethyl-2,3-dinitrobutane were purchased from Sigma-Aldrich. 2,4,6-trinitrotoluene was synthetized following the procedure proposed by M. G. Guillén et al.<sup>1</sup> Other chemical reagents and solvents were of analytical grade and without further purification.



**Figure S1**: Structure of (a) 1,3-dinitrobenzene, (b) 2,4-dinitrotouene, (c) 2,3-dimethyl-2,3-dinitro-butane, (d) 2,4,6-trinitrotoluene, (e) 2,4,6-trinitrophenol.

The powder X-ray diffraction (PXRD) pattern of Tb(BTC) was collected using a D8I-90 diffractometer (Bruker) with Cu target (40 kV, 30 mA) from 5° to 50°. Scanning electron microscope (SEM) images were obtained at 5 kV using a FEI Teneo microscope. For Fourier transform infrared spectroscopy measurements (FTIR), the compounds were dispersed in ethanol and a drop of this dispersion was deposited onto a Si substrate in order to obtain the transmittance infrared spectra, with a IFS-66s spectrometer (Bruker) using a scanner velocity of 2.2 KHz and with resolution of 4 cm<sup>-1</sup>. Fluorescence spectra were obtained with a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

#### 1.3 Tb(BTC) synthesis

The preparation of Tb(BTC) (BTC=1,3,5-benzenetricarboxylate) was performed by the adaptation of the method proposed by Xiao et. al<sup>2</sup> Briefly, a solution of 126.6 mg of Tb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 20 mg of trimesic acid dissolved in a mixture of 4 mL of DMF, 4 mL of ethanol and 3.2 mL of distilled water in a 50 mL beaker, was stirred for 3 hours. After this time, a 13.5 mL flask containing a mixture of 0.2 mL of triethylamine (TEA) and 0.3 mL of distilled water was placed in the previous beaker, which was sealed with several pieces of parafilm. The beaker was then fixed to the bath of an ultrasonic generator at 60 °C, 37 kHz of frequency and 100% power, for 2 minutes. It was immediately observed the formation of a white precipitate. The resulting suspension was centrifuged at 3500 rpm, the DMF solution was discarded and the solid was washed 3 times with ethanol. Afterwards the washed material was dried overnight at 70 °C.

#### 1.4 PMMA based films preparation

For the fabrication of PMMA mixed matrix membranes (MMMs), a solution of 1% wt PMMA (Mw = 120000) in chloroform was prepared. Then, Tb(BTC) powder was added into the PMMA/CHCl<sub>3</sub> solution to obtain a MOF concentration of 10 mg cm<sup>-3</sup> and the suspension was well-dispersed under magnetic stirring for 10 minutes. Afterwards, 50  $\mu$ l of this mixture was spin-coated at 3000 rpm during 10 seconds on clean glass substrates. The films were dried in air and subsequently, annealed in an oven at 100 °C for 1 hour in order to remove the possible solvent occluded into the MOF cavities.

#### 1.5 Sensing assays

In the sensing assays, the Tb(BTC)@PMMA films were introduced in a glass vial previously saturated with a certain quantity of TNT and TNP (approximately 10 mg), and were hermetically closed. Given the low vapour pressure of the nitroaromatic explosives, saturation of the headspace was ensured by awaiting one week before measuring. Saturation of the sensor response was also ensured by a 20 hours reaction time after introduction of the sensors in the vials. In the kinetics experiments, different exposure times were used. After the exposure time, the films where directly interrogated by fluorescence spectroscopy in all cases.

#### 2. Characterization

The material isolated as a crystalline white powder was characterized by PXRD as shown in Figure S2. The synthesized material shows virtually the same diffraction pattern as the simulated one with Mercury 3.10 software (Cambridge Crystallographic Data Centre). The difference in the relative intensity of some peaks is likely to be produced by the specific morphology of the analysed particles where some atomic planes can be more exposed than others.

The coordination between the Tb(III) centres and the carboxylate groups of the ligand was confirmed by FTIR as shown in Figure S3. As can be seen, the H<sub>3</sub>BTC reagent exhibits two intense bands characteristic of the C=O stretching (1695 cm<sup>-1</sup>) and C-O stretching (1270 cm<sup>-1</sup>) modes of its carboxylic acid groups. Upon coordination of the BTC ligand to the metal centres, these bands completely disappear in the Tb(BTC) IR spectrum. Moreover, new bands appear in this spectrum peaking at 1385 cm<sup>-1</sup> and 1540 cm<sup>-1</sup>, that are assigned to the symmetric v<sub>s</sub>(CO<sup>2-</sup>) and asymmetric v<sub>as</sub>(CO<sup>2-</sup>) stretches, respectively. Further confirmation of the BTC salt and that of the Tb(BTC). On the other hand, the absence of carbonyl bands in Tb(BTC) spectrum shows there are not solvent (DMF) molecules occluded into the MOF cavities.



**Figure S2**: (a) PXRD patterns of the as-synthesized Tb(BTC) and simulated from the Tb(BTC) crystal structure data; (b) the coordination environment of the Tb(III) centre; (c) the extended packing arrangement revealing channels along the *c*-axis of the unit cell. H-atoms were omitted for clarity. The images b and c were prepared from the original CIF file deposited as supporting materials in ref. 2.



**Figure S3**: Transmittance FTIR spectra of H<sub>3</sub>BTC ligand (black line), BTC salt (BTC<sup>3-</sup>) (red line) and Tb(BTC) MOF (green line).



**Figure S4**: Photoluminescence spectra ( $\lambda_{ex}$ =350 nm) of the Tb(BTC) powder. Each band is labelled with its corresponding electronic transition.



**Figure S5**: Cross-section of Tb(BTC)@PMMA film. The polymer layer has a thickness of 1 µm along all the surface of the substrate.

## 3. Aditional sensing results



**Figure S6**: Photoluminescence spectra ( $\lambda_{ex}$ =305 nm) of Tb(BTC)@PMMA films before and after exposure to (a) DNT, (b) DNB and (c) DMNB.



**Figure S7**: Photoluminescence spectra ( $\lambda_{ex}$ =305 nm) of Tb(BTC)@PMMA films before and after exposure to (a) acetic acid, (b) toluene and (c) chloro-benzene.



**Figure S8**: Photoluminescence spectra ( $\lambda_{ex}$ =305 nm) of Tb(BTC)@PMMA films before and after 10 second and 20 hours exposure to saturated 2,4-DNT vapours.

### 4. References

 Guillén, María G., Gámez, Francisco; Roales, Javier; Lopes-Costa, Tânia; Pinto, Sara; M.A., Calvete; Mário J.F., Pereira; Mariette M.; Pedrosa, José M. Sensors and Actuators B: Chemical, 2018, 260.

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