**Electronic Supplementary Information** 

# Luminescent terbium-containing metal-organic framework films: new approaches for the electrochemical synthesis and application as detectors for explosives

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# Experimental

All the electrodeposition experiments were controlled by an EG&G potentiostat/galvanostat (model 273), and run in a small electrochemical cell (10 mL). A platinum foil (*circa* 5 cm<sup>2</sup>) was used as counter electrode and a home-made Ag/AgCl (3 M KCl) electrode served as reference. For the synthesis of MOF layers the working electrode was a material containing the same Ln element needed for the formation of the desired MOF: Terbium metal to prepare Tb-BTC, and gadolinium metal to prepare Gd-BTC. In these cases, being the electrodeposition of MOF we use an anodic process, the working electrode is the anode and the current and voltage applied positive.

On the other hand, in the synthesis of oxide layers the working electrode is the cathode, therefore the current and voltage applied are negative. Aluminium or zinc plates were used as working electrode-substrates on top of which the oxides were electro-deposited.

# Tb-BTC

Tb-BTC was synthesised electrochemically starting from a solution composed by 10 g/L methyltributylammonium methyl sulphate (MTBS,  $\geq$ 95%), 10 g/L 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC), in 50–50 vol% demineralised water–absolute ethanol mixture. The syntheses were run at 60 °C for 15 min applying a constant current of 1 mA/cm<sup>2</sup>.

# Gd-BTC and Gd(Tb)-BTC

Gd-BTC was synthesised in the same conditions reported for Tb-BTC, except that a gadolinium foil was used as anode instead of a terbium foil.

Gd-BTC doped with Tb (Gd(Tb)-BTC) was synthesised in a similar fashion but adding also a Tb(NO<sub>3</sub>)<sub>3</sub> solution to the electrolyte, in three concentrations: 0.002 M, 0.004 M and 0.01 M. The electrochemical synthesis must start immediately after the addition of the Tb(III) solution to the solution containing the linker and the conductive salt since the conditions used cause spontaneous precipitation of the MOF in solution,<sup>1</sup> especially when the Tb(NO<sub>3</sub>)<sub>3</sub> concentration is high.

# ZnO-Tb on Zn

ZnO doped with Tb (ZnO-Tb) was synthesised following the cathodic process proposed by Li et al.<sup>2</sup> A 0.02 M Tb(NO<sub>3</sub>)<sub>3</sub> solution was prepared by adding Tb<sub>4</sub>O<sub>7</sub> to demineralised water acidified with nitric acid, in the right stoichiometric proportions.  $H_2O_2$  was added dropwise in order to reduce Tb<sup>4+</sup> to Tb<sup>3+</sup>. To this Tb(III) solution were added Zn(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O (0.01 M) and CH<sub>3</sub>COONH<sub>4</sub> (0.05 M). A zinc plate partially covered with lacquer to leave *circa* 1 cm<sup>2</sup> exposed to the solution was used as cathode/working electrode. The synthesis was performed at 70 °C for 2.5 h, applying a current of -2 mA/cm<sup>2</sup> (-20 A/m<sup>2</sup>).

# TbO<sub>x</sub> on Al

 $TbO_x$  layers have been electrodeposited on an aluminium substrate via a synthesis method similar to the one described above for ZnO-Tb.  $CH_3COONH_4$  (0.01 M) was added to a 0.02 M Tb(NO<sub>3</sub>)<sub>3</sub> solution synthesised as above. A similar electrolytic bath was studied by Lu et al.<sup>3</sup>, who obtained

 $TbO_{2-x}$  in flower-like structures, but we adapted the synthesis conditions to have thicker layers by increasing the current to -5 mA/cm<sup>2</sup> and applying it for 30 min at 70 °C.

The layers surfaces were then transformed into MOF using the same set-up and solution used for Tb-BTC, at 60 °C for 15 min, with a positive current of 1 mA/cm<sup>2</sup>. 200  $\mu$ L of 0.02 M Tb(NO<sub>3</sub>)<sub>3</sub> solution was added just after starting the electrochemical process.

### DNT detection

In order to investigate the detection properties of our samples we tested them in the presence of 2,4-dinitrotoluene (DNT) both in ethanol solution and in air. For the detection in ethanol, the cuvette with the sample was filled with 1 mL of absolute ethanol (99.9%), and DNT (0.01 M solution in absolute ethanol) was added step by step with a micropipette.

For the detection in the gas phase, the lifetime of the samples was recorded after having left them for 24 h in a vacuum oven at 70 °C. DNT crystals were then introduced in the cuvettes and close inside them to build up the characteristic partial pressure (2.7 ppm at 25 °C). The second lifetime measurements were taken after two days of exposure.

#### Instruments

Scanning electron microscope (SEM) pictures and Energy Dispersive X-ray Spectroscopy (EDX) have been taken with a FEI XL30 and a FEI-Nova NanoSEM 450. Being non-conductive, the SEM samples have been sputter-coated with a layer of Au or Pt/Pd in order to increase the electrical conductivity and have better imaging. X-ray diffraction patterns (XRD) were recorded with a Seifert 3003 T X-ray powder diffractometer.

The photoluminescence spectra and the decay curves were recorded with an Edinburgh Instruments FS900 spectrofluorimeter. An ozone-free xenon lamp of 450 W was used as a radiation source for the steady state measurements. The spectra were recorded in a 90° detection geometry. The excitation spectra were between 240 and 580 nm in 0.1 nm steps, using 0.1 to 0.5 mm excitation slits and 10 mm emission slits, by monitoring the maximum emission intensity observed in the respective emission spectrum. The excitation spectra were corrected in real time according to the lamp intensity and the optical system of the excitation monochromator using a silicon diode as a reference. The emission spectra measured from 500 to 720 nm in 0.1 nm steps, using 10 mm excitation slits and 0.05 mm emission slits, exciting in the maximum of the respective excitation spectrum. All the emission spectra were corrected according to the optical system of the emission decay curves were obtained with a pulsed 60 W xenon microsecond flash lamp in the range from 0 to 40 ms and with 10 mm excitation slits and 0.10 mm emission slits. All the samples were excited at 300 nm and the detection was at 544 nm.

# Chemicals

1,3,5-benzenetricarboxylic acid (trimesic acid, H<sub>3</sub>BTC 98% pure) was purchased from ABCR, Germany; and Methyltributylammonium methyl sulphate (MTBS,  $\geq$ 95% purity), Tb<sub>4</sub>O<sub>7</sub> (99.95%), and dinitrotoluene (DNT, 97% purity) from Sigma-Aldrich, Germany. Absolute ethanol (99.9%) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%) were produced respectively by VWR France and UCB Belgium. The supplier of CH<sub>3</sub>COONH<sub>4</sub> (ammonium acetate, 99%) was Riedel-de Haën, Sigma-Aldrich, Germany, while terbium and gadolinium metal foils (99.9% pure) were purchased from Chempur, Germany.



Figure 1: XRD patterns of Gd-BTC, Gd(Tb)-BTC, and Tb-BTC layers (on Tb and on Al), and simulated pattern from Wen et al.<sup>4</sup>



Figure 2: (a) Lifetime measurements of Tb-BTC, Gd-BTC and three Gd(Tb)-BTC with different Tb content. (b) Tb content in the Gd(Tb)-BTC layers measured with EDX. (c) Gd-BTC (left), Gd(Tb)-BTC (4 mM, 22 % Tb/Gd) (middle) and Tb-BTC (right) under visible light and under UV irradiation (circa 254 nm).



*Figure 3:* ZnO-Tb, excitation and two emission spectra, one for each excitation band: 300 nm and 400 nm.



*Figure 4: Left: an SEM picture of a layer of ZnO doped with Tb(III). Right: the correspondent EDX spectrum.* 



Figure 5: XRD patterns of ZnO, ZnO-Tb (ZnO doped with Tb), ZnO-Tb transformed in X-BTC, Tb-BTC, and the patterns of LaBTC( $H_2O$ )<sub>6</sub><sup>4</sup> and  $Zn_6(OH)_3(BTC)_3(H_2O)_3$ ]·7 $H_2O^5$ 



Figure 6: SEM pictures of Tb-BTC layers synthesised from TbO<sub>x</sub> deposited on Al.



*Figure 7: Lifetime measurements in (a) ethanol and (b) air of Tb-BTC samples exposed or not to DNT. The samples were excited at 300 nm and the detection was at 544 nm.* 

### References

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