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COMMUNICATION

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

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Nicolo` Campagnol^a, Ernesto Rezende Souza^b, Dirk E. De Vos^c, Koen Binnemans^b and Jan Fransaer^{a*}

The flexibility of the electrochemical synthesis of MOFs films is illustrated by the preparation of well-adhering layers of luminescent MOFs on electrically conductive solid substrates. The luminescent layers have been successfully tested for the detection of 2,4-dinitrotoluene (DNT).

Metal-Organic Frameworks (MOFs) are a new family of materials with high surface areas and with unique properties due to their porous character. MOFs are formed by organic linkers and metal centres and, among the many metals used for their synthesis, rare earths show particularly promising features for potential applications.¹ The electrochemical synthesis is an effective technique for the preparation of well-closed MOF layers with a good adhesion on a solid surface.² This method consists in anodically generating the ions needed for the formation of the MOF framework in a solution containing the organic linker. Even if this method allows the synthesis of different MOFs, a limitation of it is that only MOFs with the same metal as the substrate can be prepared (e.g. a Cu-MOF on a copper substrate).

In this paper we present new routes for the electrochemical synthesis of MOFs films. By acting on the electrolyte, it is shown how it is possible to synthesise layers of MOFs with mixed cations. For example, a Gd-BTC layer (BTC = 1,3,5-benzenetricarboxylic acid) which normally is poorly luminescent, can be deposited in a highly luminescent version thanks to the partial substitution of Gd(III) ions by Tb(III) ions. On the other hand, by acting on the substrate, we show how it is possible to avoid the use of expensive and reactive metals (e.g. metallic terbium and gadolinium) to synthesise MOF layers containing ions of these elements. In

^aDepartment of Materials Engineering (MTM), KU Leuven, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium. E-mail: Jan.Fransaer@mtm.kuleuven.be

^bDepartment of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

^cCentre for Surface Chemistry and Catalysis (COK), KU Leuven, Kasteelpark Arenberg 23, B-3001 Leuven, Belgium.

Electronic Supplementary Information (ESI) available: experimental details, XRD of all samples, spectra of ZnO(Tb), lifetime and EDX data of Gd(Tb)-BTC samples. SEM picture of Tb-BTC on Al. Lifetimes in presence of DNT. See DOI: 10.1039/c000000x/

principle, this can be applied to deposit MOFs on any conductive surface. To demonstrate this, we synthesised Tb-BTC on aluminium and Zn-BTC doped with Tb(III) on zinc. Moreover, since Tb-BTC (Tb(1,3,5-btc)·(H₂O)₆) is reported to be a promising material for sensing of small molecules,³ the synthesised layers were used as sensors for 2,4-dinitrotoluene (DNT), an unavoidable by-product of TNT, both in air and dissolved in ethanol.

As a first step, Tb-BTC and Gd-BTC layers were synthesised electrochemically on terbium and gadolinium metal foils by immersing the foil in a water-ethanol solution containing the linker (the electrolyte), and applying a potential. The synthesised layers were crystalline and their XRD patterns showed the characteristic peaks of the monoclinic phase reported previously for these Ln-BTC MOFs.^{3a,4} Several experimental conditions were tested (different experiment durations, current densities, and electrolyte compositions), and while the crystallinity was not constant for all the conditions used, all the layers obtained had the fibrous-needle morphology expected for these MOFs. The crystals were well intergrown and completely covered the surface of the metal substrate (Figure 1).

Tb-BTC samples featured a main UV excitation band with a maximum at 300 nm, while this band shifted to longer wavelength (320 nm) for pure Gd-BTC samples. When excited at a wavelength of 300 nm, the samples containing Tb(III) ions exhibited green photoluminescence with the characteristic narrow emission lines arising from the ⁵D₄→⁷F_J (J = 6, 5, 4, 3) transitions of Tb(III).

Gd-BTC doped with Tb(III) (Gd(Tb)-BTC) was synthesised in a similar way as Gd-BTC, but with the addition of Tb(NO₃)₃ in the electrolyte. The electrochemical synthesis must start just after the injection of the Tb(III) dopant to the electrolyte containing the linker and the conductive salt, since the conditions used cause spontaneous precipitation of the MOF in solution.⁵ All the Gd(Tb)-BTC samples showed the same needle morphology as the pure Gd-MOFs and Tb-MOFs, and similar XRD patterns. The Tb-to-Gd ratio in the MOF could be tuned by varying the Tb(III) concentration in solution. As expected,⁶ even with low amounts of Tb(III) in the matrix, the excitation and emission spectra of Gd(Tb)-BTC are similar to those of pure Tb-BTC.

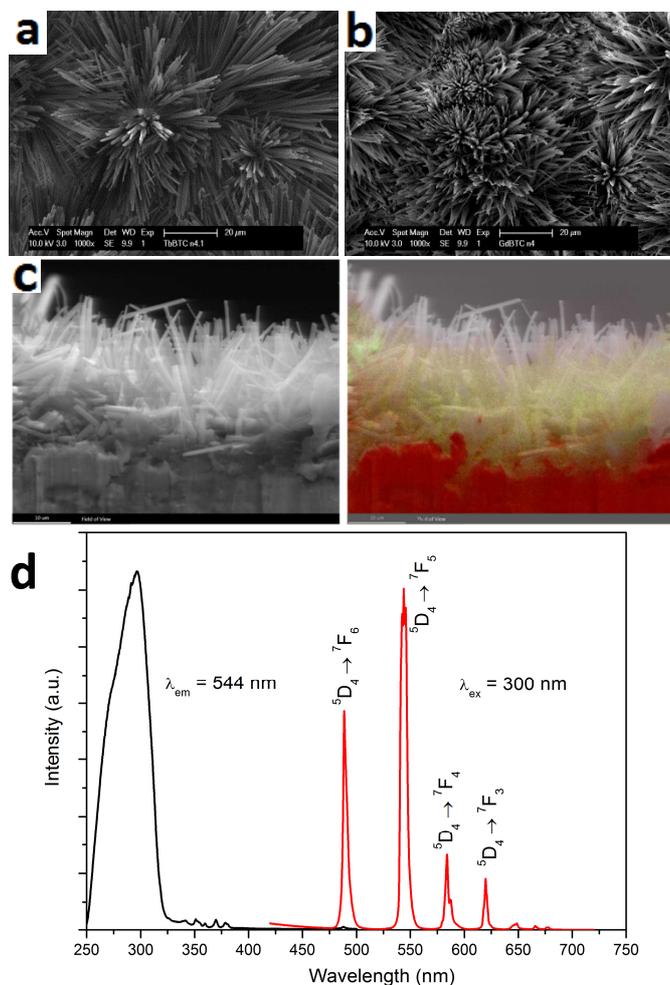


Figure 1: SEM pictures of a Tb-BTC (a) and Gd-BTC(b) samples. Cross section with and without elemental contrast of a Gd(Tb)-BTC layer: Gd (red) can be found both in the MOF layer and in the substrate, while Tb (green) only in the MOF layer (c). Emission and excitation spectra of a Tb-BTC layer (d).

In fact, all the samples have a white colour, but, when exposed to an UV lamp, all Tb(III)-containing samples show a typical green emission colour, while pure Gd-BTC samples show only a pale blue fluorescence due to ligand emission.⁵ Nevertheless, differences could be observed for the luminescence lifetimes of the samples: samples with high Tb(III) concentrations exhibited shorter lifetimes, similar to those of Tb-BTC. By tuning the Tb-to-Gd ratio in the matrix, it is possible to synthesise layers with emission intensities higher than pure Tb-BTC layers.⁶ By diluting Tb(III) in the Gd-BTC lattice, the concentration quenching effect typical of pure Tb(III) compounds can be avoided, resulting in samples with a higher photoluminescence efficiency.⁶

The electrodeposition of the isostructural Tb-BTC and Gd-BTC MOFs is *per se* an interesting outcome, but the possibility of depositing a MOF with partially substituted metal centres in a controlled way, is a more general result that can lead to several applications also in other fields and with different systems.⁷

We already demonstrated the possibility of depositing metallic iron on copper to be then transformed into MOF,^{2c} but unfortunately it very difficult if not impossible to electrochemically deposit some metals, including the rare earths. We therefore decided to synthesise ZnO doped with Tb(III) (ZnO(Tb)) to be used as substrate, following a literature method.⁸ As can be observed in Figure 2, the obtained layers consist of hexagonal crystals more

packed than those described in the literature, but both the EDX spectra and the XRD are consistent with what was expected: in the layers are present Zn, O and Tb, and the phase recorded is the one reported by Li *et al.*⁸ The conversion of a ZnO(Tb) layer into MOF was done electrochemically using the same experimental parameters as those for the synthesis of Tb-BTC, with the difference that the substrate was ZnO(Tb) on top of Zn metal instead of Tb metal. After conversion, the obtained films had completely lost the hexagonal structure (Figure 2) and a layer of intergrown needles similar to those observed in Tb-BTC samples covered the surface (Figure 1).

The luminescence spectra confirm the successful incorporation of Tb(III) ions in the ZnO layer. An undoped ZnO layer has a broad excitation band at 360 nm and a broad emission band with a maximum at 450 nm. When Tb(III) ions are present in the ZnO lattice a new excitation band appears at circa 300 nm. This band, when excited, emits a pale green light typical of Tb(III). The spectra of ZnO(Tb) excited at 300 nm and 400 nm, showing which emission is due to which excitation band, can be found in the ESI. The ZnO(Tb)-BTC layers showed spectra very similar to those of Tb-BTC. In the excitation spectrum the broad band at 400 nm is still visible, but it is much weaker than that at 300 nm. In the emission spectrum, the main contribution is given by the four narrow lines characteristic of Tb(III). This demonstrates that the surface is covered by an emitting Tb(III) compound similar to Tb-BTC. While SEM and luminescence observations suggested that the synthesised MOF is a Tb-containing compound such as Tb-BTC, EDX and XRD analyses showed that the needles phase synthesised is actually a Zn-BTC MOF, doped with Tb(III). The phase detected, $Zn_2(BTC)(OH)(H_2O) \cdot 1.67H_2O$, has never been synthesised electrochemically and its luminescence properties are unknown, but it has been reported that its 3D structure shows surprisingly high hydrothermal stability for a Zn-based MOFs, and it is not significantly affected by 40 cycles of water adsorption and

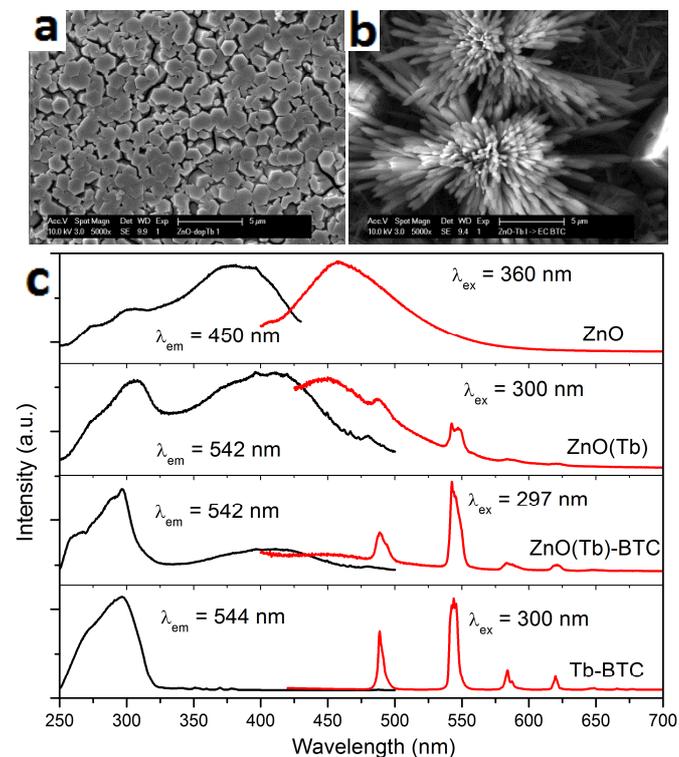


Figure 2: (a) SEM picture of a layer of ZnO doped with Tb(III). (b) the surface transformed into MOF. c): excitation and emission spectra of: ZnO, ZnO(Tb) (ZnO doped with Tb(III)), ZnO(Tb)-BTC (ZnO(Tb) transformed in Zn-BTC), and Tb-BTC.

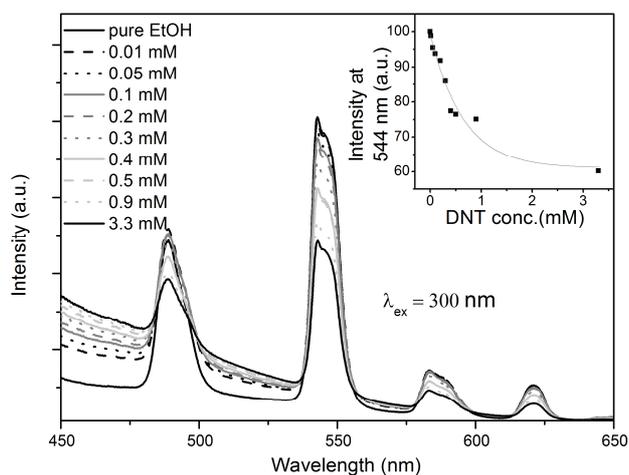


Figure 3: Emission spectra of Tb-BTC supported on an aluminium plate, immersed in ethanol solution, and the change in the signal after addition of different DNT concentration.

desorption.⁹ Layers of $Zn_2(BTC)(OH)(H_2O) \cdot 1.67H_2O$ might therefore be synthesised on any conductive surface and, thanks to the added luminescence properties, the status of these coatings can be rapidly checked even if the layers are placed in difficult visible conditions like in narrow conduits.

As stated previously, one of the most promising applications for Tb-MOFs is their potential use as sensors. The formation of a layer is often essential to make sensing devices,^{1e} but the use of a lanthanide metal as substrate is prohibitive due to high cost and reactivity. For this reason, we propose a method similar to the one used to synthesise luminescent layers of Zn-BTC. A layer of TbO_x was synthesised similarly to $ZnO(Tb)$, avoiding the use of Zn(II) ions in solution, and changing also the substrate to aluminium. The obtained layers were amorphous and relatively rough, but have a good adhesion. The oxide layers were transformed into Tb-BTC using the same electrolyte as the one used with the terbium metal foils with one difference: the addition of a 0.4 mM $Tb(NO_3)_3$ aqueous solution just after the synthesis starts. The obtained layer consisted of very small crystals, and this addition is essential to increase the overall crystal dimensions, leading to layers with a higher crystallinity. In Figure 3 are reported the emission spectra of Tb-BTC layers (supported on Al) in ethanol with various concentrations of DNT. The MOF is able to detect DNT in concentrations < 0.1 mM (corresponding to *circa* 23 ppm) independently to the substrate used for the synthesis (Tb metal or TbO_x). At this concentration, the Tb(III) luminescence intensity (measured as the intensity of emission at 544 nm) is quenched to *circa* 90 % of its initial value. The quenching is also reflected in the luminescence lifetime of the samples: The lifetime of a sample in ethanol solution increased from 0.49 ms to 0.57 ms when the sample was exposed to DNT (3.3 mM) and decreased to 0.53 ms after rinsing it with ethanol and re-immersing it in a clean ethanol solution (see ESI). The detection of DNT in the gas phase is more difficult than in ethanol, especially if the concentration given by the actual DNT vapour pressure at room temperature is used (2.7 ppm at 25 °C).^{1e} With our luminescence set-up, it was not possible to run a similar experiment like those run in ethanol solution and therefore we used the lifetime changes to verify the detection.

The resulting lifetime measurements, just after degassing in a vacuum oven and after exposure to DNT vapour are reported in the ESI. The lifetime of the sample changed from 0.48 ms to 0.58 ms when the layer was exposed to a DNT atmosphere, showing that the material is sensitive to the presence of DNT, not only in the liquid,

but also in the gas phase. The gas phase detection properties of the chosen MOF must still be improved, but the synthesis method proposed is flexible, and the synthesis of layers of other MOFs can be attempted if they appear to be more promising than $Tb(1,3,5\text{-}btc) \cdot (H_2O)_6$.

In conclusion, the high flexibility of the electrochemical synthesis of MOFs has been demonstrated by depositing a series of luminescent porous layers from and on different substrates. Thanks to this method it is possible to grow well covering crystalline layers of Ln-MOFs on top of lanthanide metal substrates, like terbium or gadolinium. Moreover, this method can be used to deposit MOF layers with different metal centres in tuneable ratios, leading, for example, to Tb(III)-doped Gd-BTC layers showing the typical emission bands of the Tb(III). Acting on the substrate, we were able to synthesise a doped version of a non-emitting Zn-based MOF (Zn-BTC) and Tb-BTC on oxide layers previously deposited on a substrate *e.g.* a zinc or an aluminium plate, opening a wide array of possibilities for the electrochemical synthesis of MOF layers, that has been so far limited to the use of the specific metal used as metal centre in the MOF framework. Tb-BTC layers have been successfully tested as sensors, showing to be promising for luminescence sensing of explosives.

Notes and references

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