Synthesis and structural characterization of an amorphous and photoluminescent mixed Eu/Zr coordination compound, a potential marker for gunshot residues

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TGA analysis for the compound $[(Eu_2Zr)(btc)_3(Hbtc)_{0.5}\cdot 6H_2O)]$.

$[(Eu_2Zr)(btc)_3(Hbtc)_{0.5}\cdot 6H_2O)]$
152 x 2=304
91.2 x 1=91.2
Btc = 3 x 207=621
Hbtc = (0.5) x 208=104
6 H_2O = 108
Total = 1228

H_2O molecules
6 x 18 = 108
108/1228 = 8.8%
(found 9%, calculated 8.8%)

To confirm the ratio of Zr/Eu
R 36%
$Eu_2O3 + ZrO_2$ = 352 + 127 = 479
479/1228 = 39%

Elemental Analysis

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Fisons - EA1108

Data de análise: 14/10/2022

Cód_CA	Massa (mg)	%C	%H	%N	%S
Ayla sample	2,244	30.75	1.86	0	0

Micro balança: Sartorius Micro (XM-1000 P)
Calibrada em: 22/03/2022 (Evagon - Jundiaí/SP)

2S

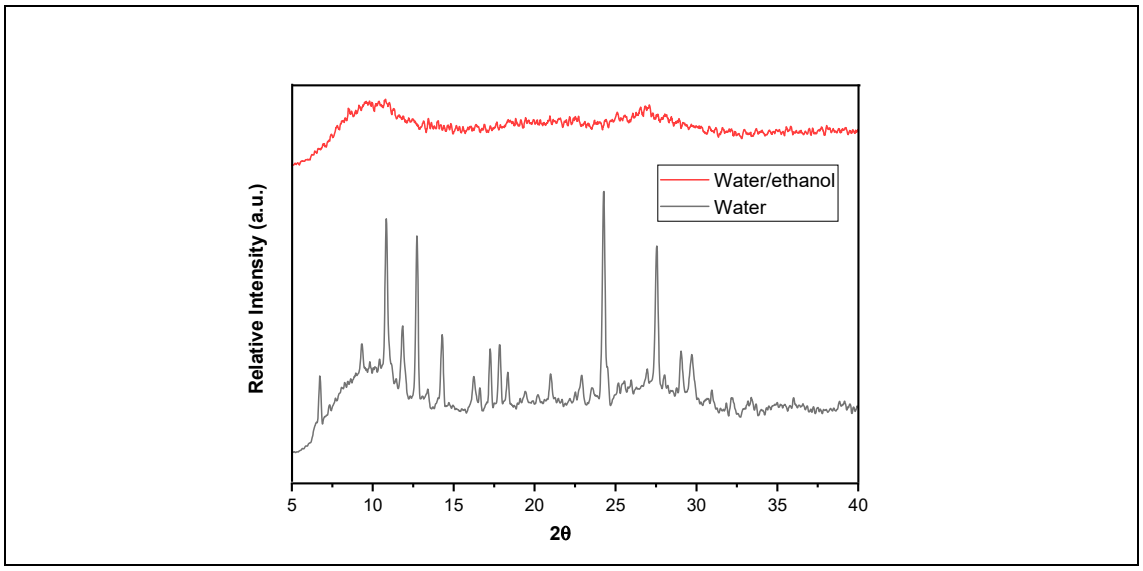

Figure S1. XRD pattern of luminescent compound $[(Eu_2Zr)(btc)_3(Hbtc)_{0.5}\cdot 6H_2O)]$ synthesized in water/ethanol and in water.

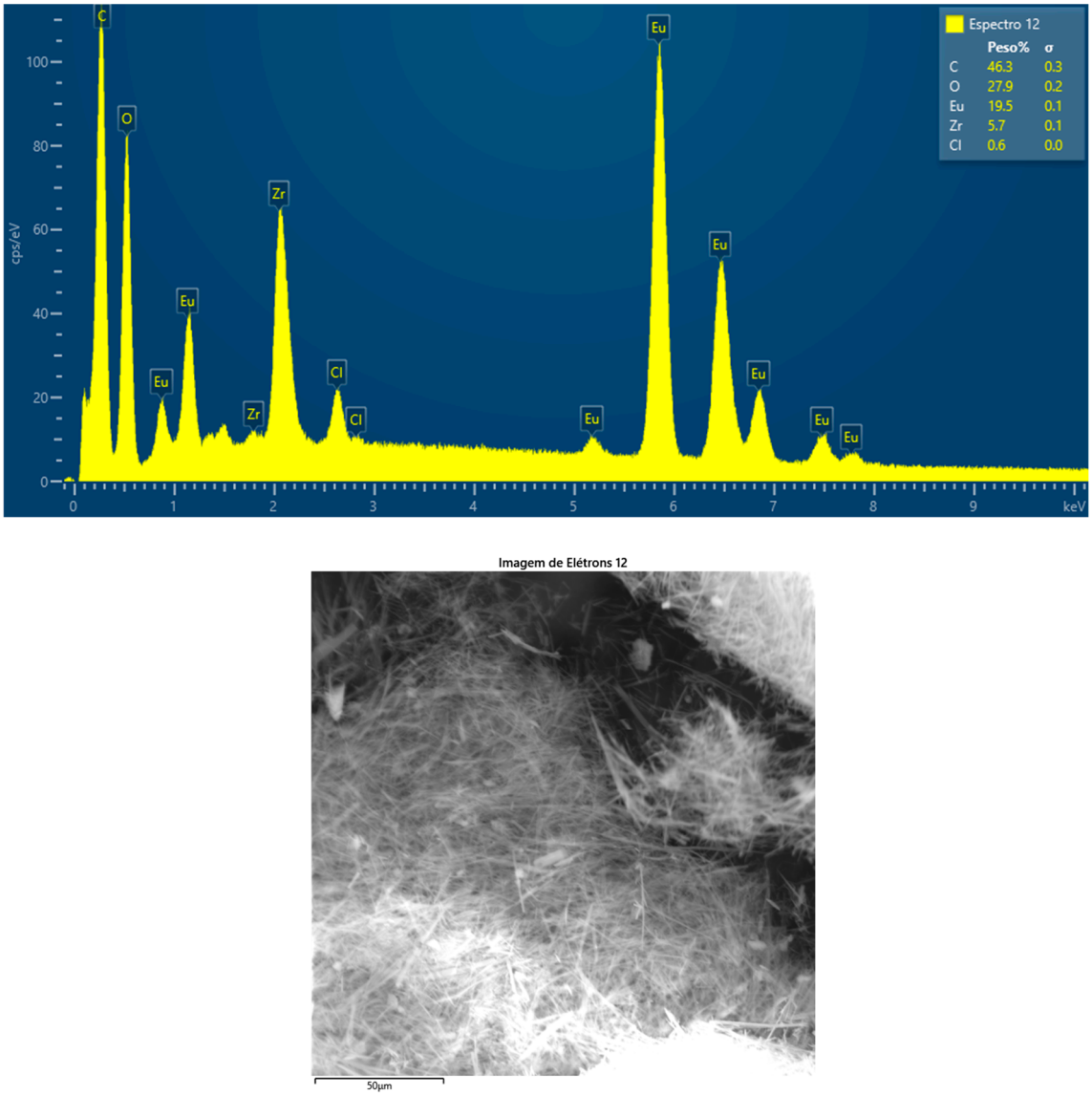

Figure S2. Chemical composition (EDS) analysis of $[(Eu_2Zr)(btc)_3(Hbtc)_{0.5}\cdot 6H_2O)]$.

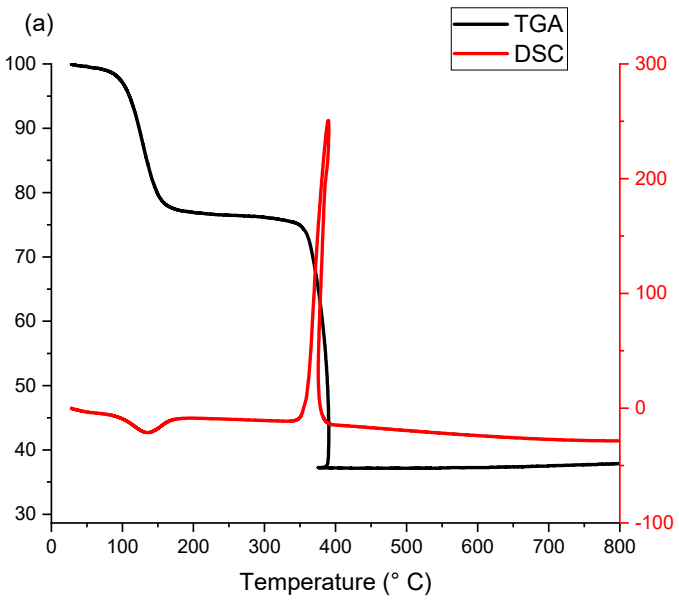

Figure S3. TGA/DSC analysis of Eu-BTC.

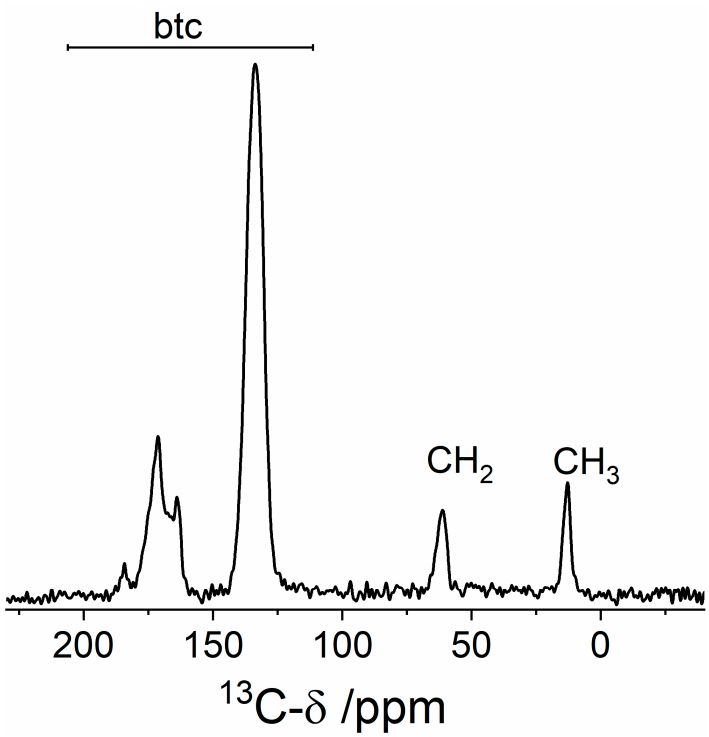

Figure S4. $^{13}C\{^{1}H\}$ CPMAS spectrum of the compound $[(Eu_2Zr)(btc)_3(Hbtc)_{0.5}\cdot 6H_2O)]$.

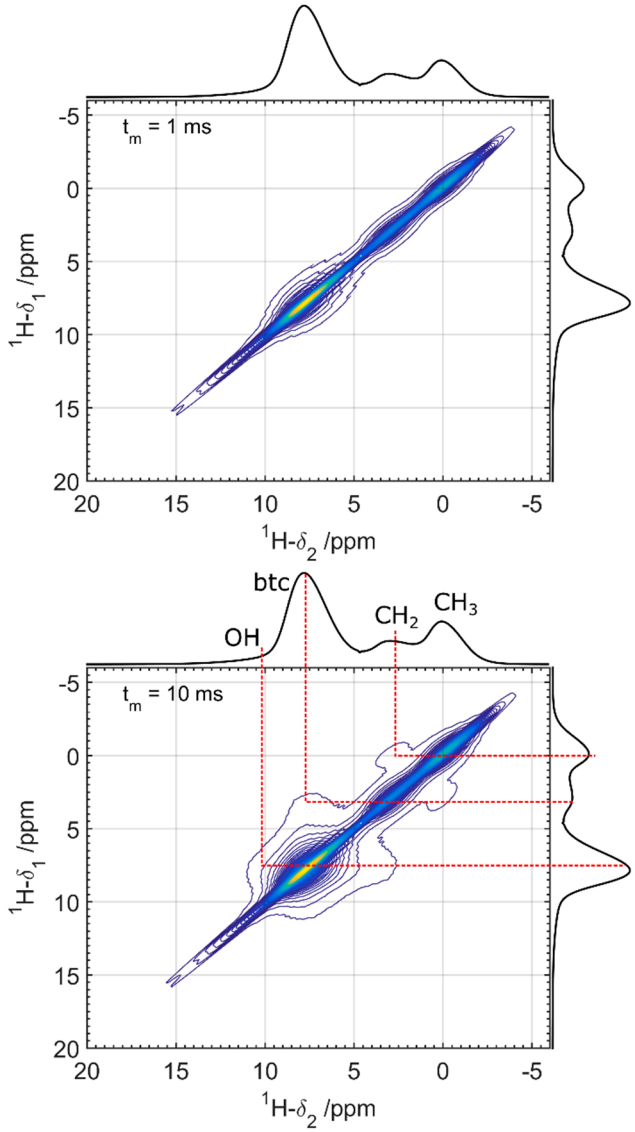

Figure S5. 2D ^{1}H-^{1}H EXSY spectra for [$(Eu_2Zr)(btc)_3(Hbtc)_{0.5}\cdot 6H_2O$)] measured at two mixing times, 1 ms and 10 ms, under 60 kHz MAS. The dashed lines indicate the presence of ^{1}H-^{1}H correlations for the longer mixing time. For short mixing times (1 ms), the spectrum reveals no exchange between distinct ^{1}H species. For longer mixing times cross-peaks revealing exchange between ^{1}H in CH_2 and CH_3 groups in ethanol become visible, while the same is true for the correlation between btc protons with CH_2 and OH groups from the metal oxide cluster, revealing spatial proximity between these groups. Most probably, ethanol OH groups coordinate with btc COO^- ones by being hydrogen bound. The interaction of ethanol with btc species prevents the coordination with the metallic species, blocking the growth of the structure. Experimental details: experiments were performed at 60 kHz using a 1.4 s recycle delay and mixing times of 1 and 10 ms. A total of 512 points were collected in the indirect dimension with a time increment of 16.67 μs, corresponding to a spectral width of 60 kHz.

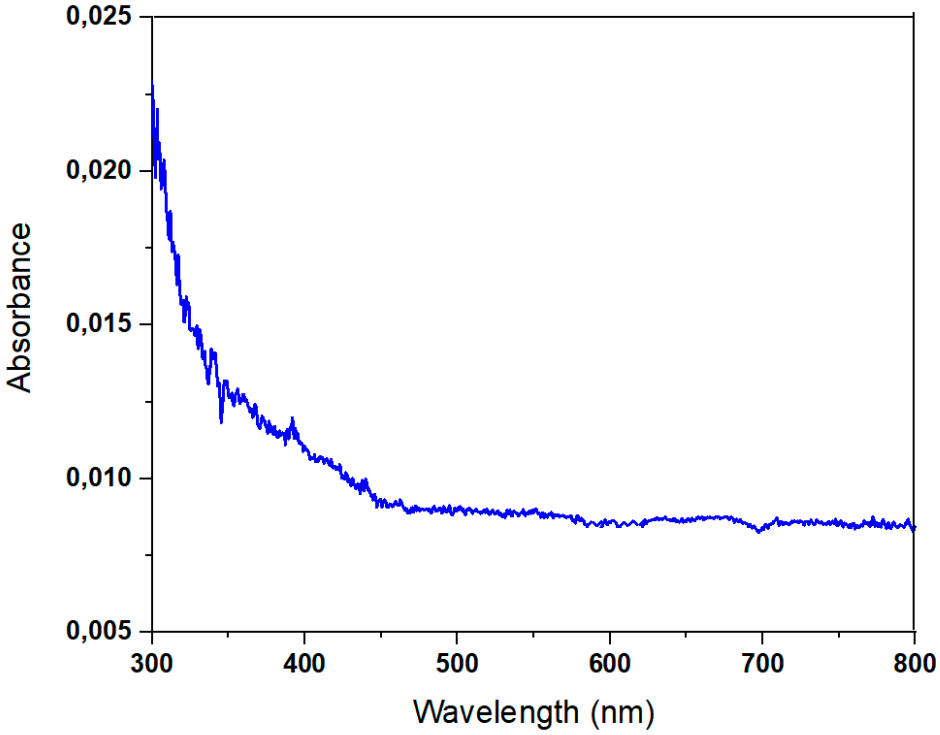

Figure S6. UV–VIS spectra of the luminescent compound [$(Eu_2Zr)(btc)_3(Hbtc)_{0.5}\cdot 6H_2O$)].

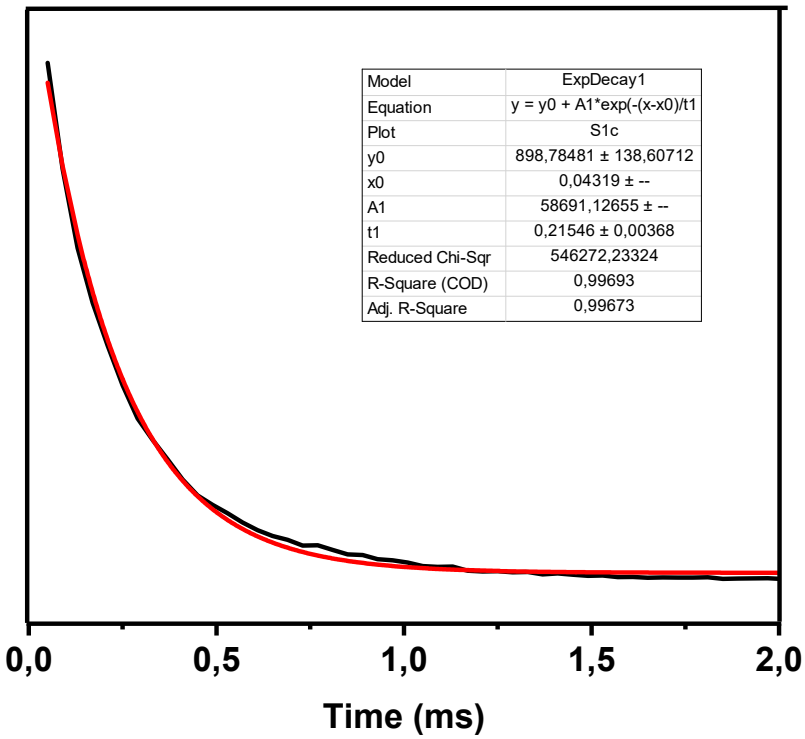

Figure S7. Exponential fitting of the decay curve of luminescent compound [$(Eu_2Zr)(btc)_3(Hbtc)_{0.5}\cdot 6H_2O$)].