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# A multifunctional dual-luminescent polyoxometalate@metal-organic framework EuW<sub>10</sub>@UiO-67 composite as chemical probe and temperature sensor

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12 **Keywords: Polyoxometalate, Metal-Organic Framework, Sensor, Ratiometric Luminescent**  
13 **Thermometer, Europium.**

## 14 Abstract

15 The luminescent [EuW<sub>10</sub>O<sub>36</sub>]<sup>9-</sup> polyoxometalate has been introduced into the cavities of the highly  
16 porous zirconium luminescent metal-organic framework UiO-67 via a direct synthesis approach,  
17 affording the EuW<sub>10</sub>@UiO-67 hybrid. Using a combination of techniques (TGA, BET, Elemental  
18 analysis, EDX mapping,...) this new material has been fully characterized, evidencing that it contains  
19 only 0.25% in europium and that the polyoxometalate units are located inside the octahedral cavities  
20 and not at the surface of the UiO-67 crystallites. Despite the low amount of europium, it is shown  
21 that EuW<sub>10</sub>@UiO-67 acts as a solid-state luminescent sensor for the detection of amino-acids, the  
22 growth of the emission intensity globally following the growth of the amino-acid pKa. In addition,  
23 EuW<sub>10</sub>@UiO-67 acts as a sensor for the detection of metallic cations, with a high selectivity for Fe<sup>3+</sup>.

24 Noticeably, the recyclability of the reported material has been established. Finally, it is shown that  
25 the dual-luminescent EuW<sub>10</sub>@UiO-67 material behave as a self-calibrated-ratiometric thermometer  
26 in the physiological range.

27

## 28 1 Introduction

29 Polyoxometalate (POM)-based photosystems are currently undergoing a remarkable development  
30 due to their high relevance in photocatalysis or their ability to act as efficient photoswitches or  
31 fluorescent probes (Han et al., 2015; Natali et al., 2015; Saad et al., 2015; Chen et al., 2017; Holmes-  
32 Smith et al., 2016). Focusing on this last topic, both materials based on purely inorganic POMs  
33 incorporating luminescent metallic centers and hybrid organic-inorganic entities bearing grafted  
34 organic optically active moieties have been elaborated. For example, fluorescent microspheres  
35 prepared from a Lindqvist POM covalently connected to pyrene groups have been used for the  
36 detection of foodborne pathogens (Ju et al., 2016). Inorganic tungsten and/or molybdenum POMs  
37 incorporating rare earth (RE) centers have also been shown to act as efficient luminescent probes. For  
38 instance, cryogenic optical thermal probes made of polyoxomolybdate building blocks incorporating  
39 Eu<sup>III</sup> and Tb<sup>III</sup> ions have been recently reported (Kaczmarek et al., 2017). The luminescence of such  
40 RE-incorporating POMs is also very sensitive to the chemical environment. This can be illustrated  
41 considering the works devoted to the interaction between proteins and the seminal [EuW<sub>10</sub>O<sub>36</sub>]<sup>9-</sup>  
42 (EuW<sub>10</sub>) europium decatungstate characterized by narrow emission bands, a large Stokes shift and a  
43 long lifetime (Sugeta and Yamase, 1993). The characteristic emission of the europium decatungstate  
44 located at ca. 620 nm is strongly enhanced in presence of bovine or human serum albumin without  
45 any alteration of the secondary structure of the protein, showing that such simple molecular oxides  
46 could act as biological optical labelling agents (Hungerford et al., 2008; Zheng et al., 2010).  
47 Accordingly, Wu et al. showed that hybrid nanospheres made of arginine/lysine-rich peptides and  
48 EuW<sub>10</sub> are characterized by a large Eu<sup>III</sup> luminescence enhancement. Using a combination of  
49 techniques, it was evidenced that the observed phenomenon was due to the exclusion of the hydration  
50 water molecules from the secondary coordination sphere of EuW<sub>10</sub> caused by the strong electrostatic  
51 and hydrogen bond interactions between POMs and basic amino-acids (AAs) (Zhang et al., 2015).  
52 Inversely, it was found that acidic AAs quench the luminescence while nonpolar AAs do not  
53 significantly influence the optical properties of the POM (Zhang et al., 2016). The processing of  
54 EuW<sub>10</sub> by incorporation into films has been achieved, allowing the fabrication of moisture-

55 responsive systems (Clemente-León et al., 2010; Xu et al., 2011; Qiu et al. 2015). Based on all these  
56 results, we have undertaken to elaborate a multi-functional hybrid system where the  $\text{EuW}_{10}$  POM is  
57 incorporated in the cavities of a metal-organic framework (MOF). This class of 3D coordination  
58 networks represents a unique platform for the development of solid-state luminescent materials due  
59 to their crystalline nature, permanent porosity, chemical tunability and robustness (Hu et al., 2014;  
60 Lustig et al., 2017; Fernando-Soria et al., 2012). To date, POM@MOF materials have been mainly  
61 synthesized for catalytic purposes. Two main synthetic strategies have been considered: (i) a one-pot  
62 strategy, where the precursors allowing the formation of the MOF and the POM are mixed altogether,  
63 the MOF being built around the POM (direct synthesis) and (ii) the POM is impregnated into the  
64 preformed MOF (two-step strategy). Such materials have shown their efficiency for catalytic  
65 reactions ranging from the oxidation of alkylbenzene (Sun et al., 2016) to the C-H activation of  
66 nitrile (Shi et al., 2016) and water oxidation (Mukhopadhyay et al., 2018; Paille et al., 2018).  
67 Interestingly, it has also been shown that a single-molecule magnet iron POM isolated in the cavities  
68 of a diamagnetic MOF preserves its magnetic properties (Salomon et al., 2016). Besides, while Ln-  
69 MOFs and Ln-doped MOFs have been largely studied, the encapsulation of a well-defined inorganic  
70 luminescent compound in MOFs for sensing and detection has been rarely described (Wu et al.,  
71 2017; Cui et al., 2015). The white water-stable and highly porous zirconium MOF UiO-67 has been  
72 selected (Cavka et al., 2009), and the ability of the  $\text{EuW}_{10}$ @UiO-67 composite to act as sensor for  
73 metallic cations and AAs was investigated. Considering the dual-luminescent properties of  
74  $\text{EuW}_{10}$ @UiO-67 – arising from both the inserted POMs and the 3D host network – its aptitude to act  
75 as a self-calibrated temperature sensor has also been explored.

76

## 77 2 Experimental section

### 78 2.1 Physical methods

79

80 Infrared (IR) spectra were recorded on a Nicolet 30 ATR 6700 FT spectrometer. Powder X-Ray  
81 diffraction data were obtained on a Bruker D5000 diffractometer using Cu radiation (1.54059 Å). C,  
82 H, N elemental analyses were performed by the Service de microanalyse of CNRS, 91198 Gif-sur-  
83 Yvette Cedex France. EDX measurements were performed on a JEOL JSM 5800LV apparatus.  
84 Thermogravimetry analyses (TGA) were performed on a Mettler Toledo TGA/DSC 1, STARE

85 System apparatus under oxygen flow (50 mL min<sup>-1</sup>) at a heating rate of 5°C min<sup>-1</sup> up to 800°C. N<sub>2</sub>  
86 adsorption isotherms were obtained at 77 K using a BELsorp Mini (Bel, Japan). Prior to the analysis,  
87 approximately 30 mg of sample were evacuated at 90°C under primary vacuum overnight. Room-  
88 temperature and temperature-dependant photoluminescence spectra were recorded on a Jobin-Yvon  
89 Fluorolog 3 fluorometer equipped with a CCD camera (excitation source: 450 W Xe arc lamp). The  
90 temperature was controlled by a nitrogen-closed cycle cryostat with vacuum system  
91 measuring and an Oxford Instrument ITC503S auto-tuning temperature controller with a  
92 resistance heater. The temperature can be adjusted from ca. 77 to 300 K with a maximum  
93 accuracy of 0.1 K. The sample temperature was fixed to a particular value using the  
94 auto-tuning temperature controller; after waiting 5 min to thermalize the sample, five  
95 consecutive steady-state emission spectra were measured for each temperature. The  
96 luminescence sensing experiments were carried out by introducing EuW<sub>10</sub>@UiO-67 powder (1.5 mg)  
97 into aqueous solution (3 mL, 10<sup>-2</sup> mol L<sup>-1</sup>) of MCl<sub>x</sub> (M<sup>n+</sup> = Na<sup>+</sup>, K<sup>+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>, Mn<sup>2+</sup> and  
98 Fe<sup>3+</sup>) or amino-acids (lysine, L-glycine, β-alanine, L-histidine, L-tryptophane, γ-aminobutyric acid,  
99 L-arginine) at room temperature. The mixtures were magnetically stirred during 5 minutes before  
100 collecting the luminescence data.

101

## 102 2.2 Synthetic procedures

103

104 **Chemicals and reagents.** All available chemicals were purchased from major chemical suppliers and  
105 used as received. The Lindqvist-type europium decatungstate Na<sub>9</sub>[EuW<sub>10</sub>O<sub>36</sub>]·32H<sub>2</sub>O (EuW<sub>10</sub>)  
106 (Sugeta and Yamase, 1993) and the UiO-67 MOF (Salomon et al., 2015) have been synthesized as  
107 previously described.

108

109 **Synthesis of DODA<sub>9</sub>[EuW<sub>10</sub>O<sub>36</sub>]·(DODACl)<sub>2</sub> ((DODA)EuW<sub>10</sub>).** The  
110 dimethyldioctadecylammonium (DODA) salt of EuW<sub>10</sub> was synthesized according to a procedure  
111 developed by L. Wu. et al. for (DODA)<sub>13</sub>H<sub>2</sub>[Eu(BW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]·25H<sub>2</sub>O (Li et al., 2008). A  
112 stoichiometric amount of DODA.Cl (1 equivalent by charge, 3.281 g, 5.6 mmol) was dissolved in 20  
113 mL of chloroform. The solution was then added dropwise to a 10 mL aqueous solution of  
114 Na<sub>9</sub>[EuW<sub>10</sub>O<sub>36</sub>]·32H<sub>2</sub>O (2.082g, 0.62 mmol) under stirring. The mixture was kept under vigorous  
115 stirring for 2 hours. The organic phase was separated and dried with MgSO<sub>4</sub>. The solvent was then

116 evaporated with a rotary evaporator to recover the DODA salt (3.9 g, yield = 72 %). Anal. Calc.  
 117 (found) for (DODA)<sub>9</sub>[EuW<sub>10</sub>O<sub>36</sub>]·(DODACl)<sub>2</sub> (C<sub>418</sub>H<sub>880</sub>N<sub>11</sub>EuW<sub>10</sub>O<sub>36</sub>Cl<sub>2</sub>; M.W.: 8699 g mol<sup>-1</sup>): C  
 118 57.71 (57.45), H 10.20 (10.51), N 1.77 (1.66). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 2916 (s), 2849 (s), 1466 (m), 940  
 119 (m), 922 (m), 836 (m), 753 (s), 718 (s). EDX measurements: atomic ratio calc. (exp.): W/Eu 10.0  
 120 (11.5).

121 **Synthesis of [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>][C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>]<sub>5.8</sub>[EuW<sub>10</sub>O<sub>36</sub>]<sub>0.04</sub>·7H<sub>2</sub>O (EuW<sub>10</sub>@UiO-67).** ZrCl<sub>4</sub> (116 mg,  
 122 0.5 mmol), biphenyl-dicarboxylic acid (121 mg, 0.5 mmol), (DODA)EuW<sub>10</sub> (429 mg, 4.93 10<sup>-5</sup> mol)  
 123 and benzoic acid (1.83 g, 15 mmol) were briefly stirred in 10 mL of dimethylformamide (DMF)  
 124 inside a 23 mL polytetrafluoroethylene-lined vessel. Hydrochloric acid 37% (83  $\mu$ L) was added, and  
 125 the mixture was heated at 120°C for 24 hours. The solid was isolated by filtration of the hot mixture  
 126 and thoroughly washed with DMF, chloroform, dry acetone and dried in an oven at 120°C overnight  
 127 (yield: 60% based on Zr, 118 mg, 4% based on POM). Anal. Calc. (found) for  
 128 [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>][C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>]<sub>5.8</sub>[EuW<sub>10</sub>O<sub>36</sub>]<sub>0.04</sub>·7H<sub>2</sub>O (C<sub>81.2</sub>H<sub>64.4</sub>O<sub>39.64</sub>Zr<sub>6</sub>W<sub>0.4</sub>Eu<sub>0.04</sub>; M.W.: 2301 g mol<sup>-1</sup>) :  
 129 C 42.38 (42.50), H 2.82 (3.21). IR (ATR):  $\nu$  (cm<sup>-1</sup>) 1593 (m), 1545 (m), 1503 (w), 1409 (s), 1180  
 130 (w), 770 (m), 754 (w), 736 (m), 704 (m), 669 (s), 455 (s). EDX measurements: atomic ratio calc.  
 131 (exp.): Zr/W 15.0 (15.6), Eu/W 0.10 (0.13).

### 132 3 Results and Discussion

#### 133 3.1 Synthesis and characterization of the EuW<sub>10</sub>@UiO-67 material

134 We recently evidenced that the [PW<sub>12</sub>O<sub>40</sub>]<sup>3-</sup> Keggin (Salomon et al., 2015), the [P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup>  
 135 Dawson (Salomon et al., 2015) as well as the sandwich [(FeW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>Fe<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>10-</sup> (Salomon et  
 136 al., 2016) polyanions can be incorporated into the pores of the Zr(IV) biphenyldicarboxylate  
 137 UiO-67 MOF. Considering the smallest dimensions of these POMs (ca. 12 Å) and the size of  
 138 the triangular windows of the microporous MOF (ca. 8 Å), no impregnation of the molecular  
 139 units into the preformed MOF could be envisaged and the POM@UiO-67 materials were  
 140 obtained *via* a direct synthesis approach (Salomon et al., 2015; Salomon et al., 2016). The  
 141 same approach has been considered here, as the smallest dimension of EuW<sub>10</sub> is ca. 9 Å. The  
 142 title compound (Figure 1a) was thus synthesized by heating at 120°C in DMF a mixture of the  
 143 dimethyldioctadecyl ammonium (DODA) salt of the POM and the precursors of UiO-67,  
 144 affording EuW<sub>10</sub>@UiO-67 in good yield (60% based on Zr) as a white crystalline powder.

145 As observed in Figure S1, the experimental powder X-ray diffraction (PXRD) pattern of  
 146 EuW<sub>10</sub>@UiO-67 and simulated PXRD pattern of UiO-67 are analogous, showing that the

147 formation of the UiO-67 network can be obtained with the presence of the POM in the  
148 synthetic medium. In addition, the experimental PXRD pattern of the as-synthesized  
149 EuW<sub>10</sub>@UiO-67 and of EuW<sub>10</sub>@UiO-67 stirred for one hour in water at room temperature are  
150 similar, showing that the hybrid is stable in such conditions. EDS mapping evidences both the  
151 presence of MOF and POM (Figure 1b). EDX measurements combined with elemental  
152 analysis and TGA allowed to propose for EuW<sub>10</sub>@UiO-67 the formula  
153 [Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>][C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>]<sub>5.8</sub>[EuW<sub>10</sub>O<sub>36</sub>]<sub>0.04</sub>·7H<sub>2</sub>O, indicating that the material only contains ca.  
154 0.25 wt % in europium. The TGA curve (Figure S2) reveals steps that are attributed to water  
155 removal (weight loss 5.0%, calculated 5.5%), linker decomposition and formation of  
156 inorganic oxides (weight loss 58.6%, calculated 60.5%). The IR spectrum (Figure S3)  
157 confirms that no DODA counterion is present in the MOF, the negative charges introduced by  
158 the POMs being compensated by linker deficiencies (Katz et al., 2013). Also, no vibration at  
159 ca. 1680 cm<sup>-1</sup> is observed, indicating that no free benzoic acid is present in the cavities of the  
160 MOF. In addition, it can be deduced from the formula that only 1/25 of the octahedral cavities  
161 are occupied by EuW<sub>10</sub>, this loading being lower than for [(FeW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>Fe<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>10-</sup> (1/10)  
162 (Salomon et al., 2016). The N<sub>2</sub> sorption isotherms experiments were conducted for both UiO-  
163 67 and EuW<sub>10</sub>@UiO-67 (Figure 1c and Table S1). As expected, the surface area is lower for  
164 EuW<sub>10</sub>@UiO-67 (S<sub>BET</sub> = 1900 m<sup>2</sup>.g<sup>-1</sup>) than for UiO-67 (S<sub>BET</sub> = 2400 m<sup>2</sup>.g<sup>-1</sup>), since a heavy  
165 compound is added and represented 5% of the sample weight. Nevertheless, we note that a  
166 subsequent porosity remains for EuW<sub>10</sub>@UiO-67. Additionally, the value of the normalized  
167 specific surface area, taking into account the contribution of the mass of UiO-67 in  
168 EuW<sub>10</sub>@UiO-67 (2400 x 0.95 = 2280 m<sup>2</sup>.g<sup>-1</sup>), is significantly different from the experimental  
169 value of EuW<sub>10</sub>@UiO-67 (1900 m<sup>2</sup>.g<sup>-1</sup>), suggesting that EuW<sub>10</sub> is located inside the  
170 octahedral cavities and not at the surface of the UiO-67 particles (Table S1). In addition, it is  
171 observed that the porous distribution is not significantly modified, evidencing only one peak  
172 since the hexagonal and tetrahedral cavities are connected by the same triangular windows  
173 (Figure S4).

174

### 175 3.2 Photophysical characterization of EuW<sub>10</sub>@UiO-67

176 The photophysical properties of EuW<sub>10</sub>@UiO-67 were thoroughly investigated at room  
177 temperature. Firstly, the solid-state photoluminescence (PL) properties of the pure EuW<sub>10</sub> and  
178 UiO-67 compounds were studied separately before considering the EuW<sub>10</sub>@UiO-67

179 composite. As expected, the excitation spectra of EuW<sub>10</sub> (Figure S5) is composed by a broad  
180 band centred at 280 nm, corresponding to the O → W ligand-to-metal charge transfer (LMCT)  
181 band, and the sharp lines characteristic of the f-f transitions of the Eu<sup>3+</sup> ion (Yamase and  
182 Sugeta, 1993). Under photoexcitation at  $\lambda_{\text{exc}} = 280$  nm, EuW<sub>10</sub> shows a red luminescence  
183 (Figure S6) associated to the typical  $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$  transitions of Eu<sup>3+</sup> ions in the 587-700 nm  
184 range, indicating an efficient intramolecular energy transfer from ligand to Eu<sup>3+</sup>. As this latter  
185 ion is located in a slightly distorted square antiprismatic site close to D<sub>4d</sub> point symmetry, the  
186  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  electric dipole transition (611-620 nm) gets a very weak intensity compared to that  
187 of the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  magnetic dipole transition (Nogami et al., 1996; Capobianco et al., 1990).  
188 Upon UV excitation at 336 nm, the UiO-67 MOF exhibits a blue emission (Figure S6). Its PL  
189 spectrum (Figure S7) displays a broad band in the 450-600 nm range, with a maximum  
190 wavelength located at 471 nm, attributed to intraligand  $\pi \rightarrow \pi^*$  transitions centred on the  
191 biphenyldicarboxylate linker. For the EuW<sub>10</sub>@UiO-67 composite, the excitation spectrum,  
192 monitored within the  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  (700 nm) Eu<sup>3+</sup> transition (Figure 2), shows the LMCT broad  
193 band ( $\lambda_{\text{max}} = 280$  nm) and the weakly intense sharp lines of the Eu<sup>3+</sup> f-f transitions of EuW<sub>10</sub>  
194 as well as the excitation bands of UiO-67 ( $\lambda_{\text{max}} = 336$  nm). The presence of the LMCT band is  
195 a strong indication of the integrity of EuW<sub>10</sub> in the composite, whereas the presence of the  
196 excitation bands of UiO-67, within the  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  Eu<sup>3+</sup> transition, quite evidences an  
197 intermolecular MOF-to-Eu<sup>3+</sup> energy transfer. Then, upon UV excitation at 336 nm, the  
198 emission spectrum of EuW<sub>10</sub>@UiO-67 corresponds to the association of the red emission of  
199 EuW<sub>10</sub> together with the UiO-67 blue one (Figure 3), and hence, the composite is a good  
200 violet emitter with colour coordinates (x,y) equal to x = 0.356 and y = 0.246. Moreover, the  
201 intensity ratio of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition to the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition is significantly increased  
202 compared to that observed for pure EuW<sub>10</sub>. In addition, the symmetry-forbidden electric  
203 dipole  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition (580 nm) which does not appear in pure EuW<sub>10</sub> is distinguishable in  
204 the PL spectrum of EuW<sub>10</sub>@UiO-67. These results unambiguously reveal that the site  
205 symmetry of the Eu<sup>3+</sup> ion in EuW<sub>10</sub> decreases when the POM is introduced into the MOF  
206 pores (Sugeta et al., 1993).

### 207 3.3 EuW<sub>10</sub>@UiO-67 as sensor for metallic cations and amino-acids

208 The luminescent sensing properties of EuW<sub>10</sub>@UiO-67 were first investigated for the  
209 detection of metal ions (Na<sup>+</sup>, K<sup>+</sup>, Ni<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Al<sup>3+</sup>, Mn<sup>2+</sup> and Fe<sup>3+</sup>) present in aqueous

210 solutions ( $10^{-2}$  M) as chloride salts. The PL properties of suspensions of EuW<sub>10</sub>@UiO-67 into  
211 the metallic solutions ( $8.5 \mu\text{M}$  in  $\text{Eu}^{3+}$ ) were monitored at  $\lambda_{\text{exc}} = 336$  nm and the luminescence  
212 intensity variations of the most intense  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$   $\text{Eu}^{3+}$  transition at 611 nm are depicted in  
213 Figure 4 and Figure S8a. The presence of all studied metal ions in solution systematically  
214 induces a decrease of the luminescence intensity of the  $\text{Eu}^{3+}$  f-f bands compared to their  
215 intensity when EuW<sub>10</sub>@UiO-67 is simply immersed in deionized water. The same effect is  
216 also observable on the organic ligand emission at 471 nm. Strikingly,  $\text{Fe}^{3+}$  ions can quench  
217 the whole emission of the composite, which becomes non-emissive under UV-light. This high  
218 selectivity regarding  $\text{Fe}^{3+}$  ions offers an interesting perspective to use EuW<sub>10</sub>@UiO-67 as an  
219 efficient luminescent chemical probe for  $\text{Fe}^{3+}$  ions that play a relevant role in many biological  
220 processes (Xu et al., 2015). A study of the dependence of the quenching of the luminescence  
221 with the  $\text{Fe}^{3+}$  concentration was then conducted. The quenching effect can be quantitatively  
222 rationalized by the Stern-Volmer equation :  $I_0/I = 1 + K_{\text{SV}}[\text{Fe}^{3+}]$ , where  $I_0$  and  $I$  are the  
223 fluorescence intensities of the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of the  $\text{Eu}^{3+}$  ion in the EuW<sub>10</sub>@UiO-67  
224 suspension in the absence or presence of  $\text{Fe}^{3+}$ , respectively.  $K_{\text{SV}}$  is the quenching constant,  
225 which is calculated as  $2667 \text{ L}\cdot\text{mol}^{-1}$  with a very good linear correlation ( $R$ ) of 0.9993,  
226 indicating the strong quenching effect from  $\text{Fe}^{3+}$  (Figure S9). The concentration limit for the  
227 detection is estimated to be  $37 \mu\text{M}$ , corresponding to the concentration for which the  
228 fluorescence intensity variation is less than 10%. To assess the robustness of the  
229 EuW<sub>10</sub>@UiO-67 composite, we have checked its recyclability after immersion into a  $\text{Fe}^{3+}$   
230 aqueous solution ( $C = 10^{-2}$  M). The emission spectrum of the powder was monitored in the  
231 same conditions (Figure S10) before, directly after immersion, and having washed several  
232 times with ultrapure water, filtered and dried under air the immersed powder. This study  
233 highlights that after washing, the emission of the composite practically recovered its initial  
234 intensity, quite evidencing that the EuW<sub>10</sub>@UiO-67 exhibits a high robustness enabling to be  
235 reusable to detect  $\text{Fe}^{3+}$  ions in an aqueous solution. In short, although the amount of the  
236 EuW<sub>10</sub> emitter is weak into the MOF, the properties of the composite as a chemical probe is  
237 very promising with a good recyclability, never investigated in these systems so far.  
238 EuW<sub>10</sub>@UiO-67 was also tested as chemical probe for basic amino-acids (AAs), such as  
239 glycine,  $\beta$ -alanine, L-histidine, L-tryptophan, L-arginine, and  $\gamma$ -aminobutyric acid (Table S2).  
240 Aqueous solutions of AAs were prepared ( $10^{-2}$  M) and EuW<sub>10</sub>@UiO-67 was dispersed ( $8.5$   
241  $\mu\text{M}$  in  $\text{Eu}^{3+}$ ) to further monitor the luminescence properties at  $\lambda_{\text{exc}} = 336$  nm. The emission

242 spectra are depicted in Figure S8b. As already noticed for the pure  $[\text{Eu}(\text{SiW}_{10}\text{MoO}_{39})_2]^{13-}$   
243 POM in homogeneous aqueous solutions (Li et al., 2014), distinct luminescence  
244 enhancements are observed when the  $\text{EuW}_{10}@\text{UiO}-67$  material is in contact with the various  
245 AAs molecules (Figure 4). The arginine, which is the most basic AA of the investigated  
246 series, induces more than 2.5-fold enhancement of emission intensity. Moreover, the increase  
247 of the emission intensity globally follows the increase of the AA pKa and isoelectric point  
248 (Table S2). This is in line with the fact that the luminescence of Eu-based POMs is quenched  
249 by the surrounding water molecules, which are displaced in presence of protonated AAs due  
250 to electrostatic interactions (Zhou and Yan, 2015).

### 251 3.4 $\text{EuW}_{10}@\text{UiO}-67$ as self-calibrated-ratiometric luminescent thermometer

252 As both the biphenyldicarboxylate linker of  $\text{UiO}-67$  and  $\text{EuW}_{10}$  act as emitters, we further  
253 evaluated the capability of  $\text{EuW}_{10}@\text{UiO}-67$  to be used as a self-calibrated ratiometric  
254 luminescent thermometer. For that, the integrated areas of the ligand ( $I_{\text{Ligand}}$ ) and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$   
255  $\text{Eu}^{3+}$  ( $I_{\text{Eu}}$ ) emissions were used to define the thermometric parameter  $\Delta = I_{\text{Ligand}}/I_{\text{Eu}}$  permitting  
256 the conversion of emission intensities into absolute temperature. The temperature dependence  
257 of the  $\text{EuW}_{10}@\text{UiO}-67$  emission is presented in Figure 5 for the 150 – 300 K range. Five  
258 consecutive emission spectra were collected for each temperature and used to determine  
259 subsequent average data. The  $I_{\text{Ligand}}$  and  $I_{\text{Eu}}$  parameters have been obtained by integrating the  
260 emission spectra in the 438 – 575 nm and 604 – 630 nm wavelength intervals, respectively.  
261 The temperature dependence of the defined thermometric parameters  $\Delta$  in the 200 – 300 K  
262 range is presented in Figure S11, where the solid line represents the temperature calibration  
263 curve. The parameter  $\Delta$  decreases with the temperature according to the following empirical  
264 linear relationship:

265

$$266 \Delta = 1.985 - 0.0029 T$$

267

268 with a correlation coefficient  $R^2$  of 0.998. The corresponding relative sensitivity, defined as  
269  $S_r = |\partial\Delta/\partial T|/\Delta$ , and used as a figure of merit to compare the performance of distinct systems  
270 (Brites et al., 2016) is plotted in Figure S12, showing that  $\text{EuW}_{10}@\text{UiO}-67$  exhibits a  
271 maximum relative sensitivity  $S_m$  of ca. 0.26%  $\text{K}^{-1}$  for the physiological temperature range.

## 272 4 Conclusion

273 In conclusion, we have reported herein an easy to prepare luminescent multifunctional  
274 material made of a metal-organic framework incorporating a europium-containing  
275 polyoxotungstate. Despite the very low amount of POM inserted in the UiO-67 matrix, it has  
276 been shown that EuW<sub>10</sub>@UiO-67 is able to act as a sensor ( $[Eu^{3+}] = 8.5 \mu M$ ) for metallic ions  
277 and amino-acids in water and in heterogeneous conditions. Among a series of cationic  
278 species, a good selectivity has been found for Fe<sup>3+</sup>, while an enhancement of the  
279 EuW<sub>10</sub>@UiO-67 luminescence is observed in presence of amino-acids, the enhancement of  
280 the emission intensity globally following the increase of the amino-acid pKa. Moreover, the  
281 recyclability of EuW<sub>10</sub>@UiO-67 has been demonstrated. In addition, the dual-luminescent  
282 properties – arising both from the POM and from the MOF - lead the reported material to  
283 behave as a self-calibrated ratiometric luminescent thermometer. Considering the huge  
284 number of luminescent POMs and MOFs already available, this first report of a dual-  
285 luminescent POM@MOF material thus opens the way to the development of such optical  
286 sensors.

287

288

## 289 **5 Conflict of Interest**

290 The authors declare that the research was conducted in the absence of any commercial or financial  
291 relationships that could be construed as a potential conflict of interest.

## 292 **6 Author Contributions**

293 All authors have made a substantial, direct and intellectual contribution to the work, and approved it  
294 for publication.

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## 299 **8 Supplementary Material**

300 The Supplementary Material for this article (additional characterizations and optical measurements)  
301 can be found online at: [https://www.frontiersin.org/articles/103389/xxxx/full#supplementary-](https://www.frontiersin.org/articles/103389/xxxx/full#supplementary-material)  
302 material.

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427

## 428 10. Figure Captions

429

430 **FIGURE 1** (a) Polyhedral representations of  $\text{EuW}_{10}$  and an octahedral cage of  $\text{EuW}_{10}@\text{UiO-}$   
431 67; blue octahedra:  $\text{WO}_6$ , pink sphere: Eu, orange polyhedra:  $\text{ZrO}_8$ , black sphere: C, (b) SEM  
432 image of crystals of  $\text{EuW}_{10}@\text{UiO-67}$  and EDS mapping for zirconium and tungsten, (c)  $\text{N}_2$   
433 adsorption/desorption isotherms (77K,  $P/P_0 = 1$  atm.) of UiO-67 (black) and the  
434  $\text{EuW}_{10}@\text{UiO-67}$  composite (red).

435

436 **FIGURE 2.** Room-temperature excitation spectra of  $\text{EuW}_{10}@\text{UiO-67}$  monitored at  $\lambda_{\text{em}} = 471$  nm  
437 (red line) and at  $\lambda_{\text{em}} = 700$  nm (blue line) and excitation spectrum of  $\text{EuW}_{10}$  (black dotted line)  
438 monitored at  $\lambda_{\text{em}} = 700$  nm. Inset: the asterisk represents the  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  excitation band of the  $\text{Eu}^{3+}$   
439 ion.

440

441 **FIGURE 3** (a) Room-temperature emission spectrum monitored at  $\lambda_{\text{exc}} = 336$  nm of EuW<sub>10</sub>@UiO-  
442 67. The asterisk highlights the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition related to the Eu<sup>3+</sup> ion; (b) CIE chromaticity  
443 diagram for EuW<sub>10</sub>@UiO-67 excited at 336 nm.

444 **FIGURE 4** Luminescence intensity variations of the  $^4\text{D}_0 \rightarrow ^7\text{F}_2$  transition ( $\lambda_{\text{exc}} = 336$  nm) of  
445 EuW<sub>10</sub>@UiO-67 interacting with different metal ions and amino-acid aqueous solutions ( $C = 10^{-2}$   
446 mol.L<sup>-1</sup>) (glyc. = glycine, ala. =  $\beta$ -alanine, hist = L-histidine, trypt. = L-tryptophan, buty. =  $\gamma$ -  
447 aminobutyric acid, arg. = L-arginine).

448

449 **FIGURE 5** Emission spectra of compound EuW<sub>10</sub>@UiO-67 in the range 150-300 K with the  
450 excitation fixed at 336 nm.

451

452

