A Multifunctional Dual-Luminescent Polyoxometalate@Metal-Organic Framework EuW10@UiO-67 Composite as Chemical Probe and Temperature Sensor

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A multifunctional dual-luminescent polyoxometalate@metal-organic framework EuW$_{10}$@UiO-67 composite as chemical probe and temperature sensor

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13   **Thermometer, Europium.**

14   **Abstract**

15   The luminescent $[EuW_{10}O_{36}]^{9-}$ 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$_{10}$@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$_{10}$@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$_{10}$@UiO-67 acts as a sensor for the detection of metallic cations, with a high selectivity for Fe^{3+}.

24 Noticeably, the recyclability of the reported material has been established. Finally, it is shown that

25 the dual-luminescent EuW$_{10}$@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^{III} and Tb^{III} 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 $[EuW_{10}O_{36}]^{9-}$

42 (EuW$_{10}$) 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$_{10}$ are characterized by a large Eu^{III} 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$_{10}$ 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$_{10}$ 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 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 EuW$_{10}$@UiO-67 composite to act as sensor for

73 metallic cations and AAs was investigated. Considering the dual-luminescent properties of

74 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

2   Experimental section

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^{-1}) at a heating rate of 5°C min^{-1} up to 800°C. N$_2$

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$_{10}$@UiO-67 powder (1.5 mg)

97   into aqueous solution (3 mL, 10^{-2} mol L^{-1}) of MCl$_x$ (M^{n+} = Na$^+$, K$^+$, Ni^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Mn^{2+} and

98   Fe^{3+}) 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$_9$[EuW$_{10}$O$_{36}$]·32H$_2$O (EuW$_{10}$)

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$_9$[EuW$_{10}$O$_{36}$]·(DODACl)$_2$ ((DODA)EuW$_{10}$).**   The

110 dimethyldioctadecylammonium (DODA) salt of EuW$_{10}$ was synthesized according to a procedure

111 developed by L. Wu. et al. for (DODA)$_{13}$H$_2$[Eu(BW$_{11}$O$_{39}$)$_2$]·25H$_2$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$_9$[EuW$_{10}$O$_{36}$]·32H$_2$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$_4$. 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)$_9$[EuW$_{10}$O$_{36}$]·(DODACl)$_2$ (C$_{418}$H$_{880}$N$_{11}$EuW$_{10}$O$_{36}$Cl$_2$; M.W.: 8699 g mol^{-1}): C

118 57.71 (57.45), H 10.20 (10.51), N 1.77 (1.66). IR (ATR): ν (cm^{-1}) 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$_6$O$_4$(OH)$_4$][C$_{14}$H$_8$O$_4$]$_{5.8}$[EuW$_{10}$O$_{36}$]$_{0.04}$·7H$_2$O (EuW$_{10}$@UiO-67).** ZrCl$_4$ (116 mg,

122 0.5 mmol), biphenyl-dicarboxylic acid (121 mg, 0.5 mmol), (DODA)EuW$_{10}$ (429 mg, 4.93 10^{-5} 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 μL) 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$_6$O$_4$(OH)$_4$][C$_{14}$H$_8$O$_4$]$_{5.8}$[EuW$_{10}$O$_{36}$]$_{0.04}$·7H$_2$O (C$_{81.2}$H$_{64.4}$O$_{39.64}$Zr$_6$W$_{0.4}$Eu$_{0.04}$; M.W.: 2301 g mol^{-1}) :

129 C 42.38 (42.50), H 2.82 (3.21). IR (ATR): ν (cm^{-1}) 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$_{10}$@UiO-67 material**

134 We recently evidenced that the [PW$_{12}$O$_{40}$]$^{3-}$ Keggin (Salomon et al., 2015), the [P$_2$W$_{18}$O$_{62}$]$^{6-}$

135 Dawson (Salomon et al., 2015) as well as the sandwich [(FeW$_9$O$_{34}$)$_2$Fe$_4$(H$_2$O)$_2$]$^{10-}$ (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$_{10}$ 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$_{10}$@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$_{10}$@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$_{10}$@UiO-67 and of EuW$_{10}$@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$_{10}$@UiO-67   the   formula

153   [Zr$_6$O$_4$(OH)$_4$][C$_{14}$H$_8$O$_4$]$_{5.8}$[EuW$_{10}$O$_{36}$]$_{0.04}$·7H$_2$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^{-1} 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$_{10}$, this loading being lower than for [(FeW$_9$O$_{34}$)$_2$Fe$_4$(H$_2$O)$_2$]$^{10-}$ (1/10)

162   (Salomon et al., 2016). The N$_2$ sorption isotherms experiments were conducted for both UiO-

163   67 and EuW$_{10}$@UiO-67 (Figure 1c and Table S1). As expected, the surface area is lower for

164   EuW$_{10}$@UiO-67 (S$_{BET}$ = 1900 m².g^{-1}) than for UiO-67 (S$_{BET}$ = 2400 m².g^{-1}), 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$_{10}$@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$_{10}$@UiO-67 (2400 x 0.95 = 2280 m².g^{-1}), is significantly different from the experimental

169   value of EuW$_{10}$@UiO-67 (1900 m².g^{-1}), suggesting that EuW$_{10}$ 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$_{10}$@UiO-67**

176   The photophysical properties of EuW$_{10}$@UiO-67 were thoroughly investigated at room

177   temperature. Firstly, the solid-state photoluminescence (PL) properties of the pure EuW$_{10}$ and

178   UiO-67 compounds were studied separately before considering the EuW$_{10}$@UiO-67

179   composite. As expected, the excitation spectra of EuW$_{10}$ (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^{3+} ion (Yamase and

182   Sugeta, 1993). Under photoexcitation at λ_{exc} = 280 nm, EuW$_{10}$ shows a red luminescence

183   (Figure S6) associated to the typical $^5D_0$ → $^7F_{0-4}$ transitions of Eu^{3+} ions in the 587-700 nm

184   range, indicating an efficient intramolecular energy transfer from ligand to Eu^{3+}. As this latter

185   ion is located in a slightly distorted square antiprismatic site close to D$_{4d}$ point symmetry, the

186    $^5D_0$→$^7F_2$ electric dipole transition (611-620 nm) gets a very weak intensity compared to that

187   of the $^5D_0$→$^7F_1$ 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 π→π* transitions centred on the

191   biphenyldicarboxylate linker. For the EuW$_{10}$@UiO-67 composite, the excitation spectrum,

192   monitored within the $^5D_0$ → $^7F_4$ (700 nm) Eu^{3+} transition (Figure 2), shows the LMCT broad

193   band (λ_{max} = 280 nm) and the weakly intense sharp lines of the Eu^{3+} f-f transitions of EuW$_{10}$

194   as well as the excitation bands of UiO-67 (λ_{max} = 336 nm). The presence of the LMCT band is

195   a strong indication of the integrity of EuW$_{10}$ in the composite, whereas the presence of the

196   excitation bands of UiO-67, within the $^5D_0$ → $^7F_4$ Eu^{3+} transition, quite evidences an

197   intermolecular MOF-to-Eu^{3+} energy transfer. Then, upon UV excitation at 336 nm, the

198   emission spectrum of EuW$_{10}$@UiO-67 corresponds to the association of the red emission of

199   EuW$_{10}$ 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 $^5D_0$→$^7F_2$ transition to the $^5D_0$→$^7F_1$ transition is significantly increased

202   compared to that observed for pure EuW$_{10}$. In addition, the symmetry-forbidden electric

203   dipole $^5D_0$→$^7F_0$ transition (580 nm) which does not appear in pure EuW$_{10}$ is distinguishable in

204   the PL spectrum of EuW$_{10}$@UiO-67. These results unambiguously reveal that the site

205   symmetry of the Eu^{3+} ion in EuW$_{10}$ decreases when the POM is introduced into the MOF

206   pores (Sugeta et al., 1993).

207   **3.3   EuW$_{10}$@UiO-67 as sensor for metallic cations and amino-acids**

208   The luminescent sensing properties of EuW$_{10}$@UiO-67 were first investigated for the

209   detection of metal ions (Na$^+$, K$^+$, Ni^{2+}, Cr^{3+}, Cu^{2+}, Al^{3+}, Mn^{2+} and Fe^{3+}) present in aqueous

210   solutions (10^{-2} M) as chloride salts. The PL properties of suspensions of EuW$_{10}$@UiO-67 into

211   the metallic solutions (8.5 μM in Eu^{3+}) were monitored at λ_{exc} = 336 nm and the luminescence

212   intensity variations of the most intense $^5D_0 \rightarrow {}^7F_2$ 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 Eu^{3+} f-f bands compared to their

215   intensity when EuW$_{10}$@UiO-67 is simply immersed in deionized water. The same effect is

216   also observable on the organic ligand emission at 471 nm. Strikingly, Fe^{3+} ions can quench

217   the whole emission of the composite, which becomes non-emissive under UV-light. This high

218   selectivity regarding Fe^{3+} ions offers an interesting perspective to use EuW$_{10}$@UiO-67 as an

219   efficient luminescent chemical probe for 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 Fe^{3+} concentration was then conducted. The quenching effect can be quantitatively

222   rationalized by the Stern-Volmer equation : $I_0/I = 1 + K_{SV}[Fe^{3+}]$, where I_0 and I are the

223   fluorescence intensities of the $^5D_0 \rightarrow {}^7F_2$ transition of the Eu^{3+} ion in the EuW$_{10}$@UiO-67

224   suspension in the absence or presence of Fe^{3+}, respectively. K_{SV} is the quenching constant,

225   which is calculated as 2667 L.mol^{-1} with a very good linear correlation (R) of 0.9993,

226   indicating the strong quenching effect from Fe^{3+} (Figure S9). The concentration limit for the

227   detection is estimated to be 37 μM, corresponding to the concentration for which the

228   fluorescence intensity variation is less than 10%. To assess the robustness of the

229   EuW$_{10}$@UiO-67 composite, we have checked its recyclability after immersion into a 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$_{10}$@UiO-67 exhibits a high robustness enabling to be

235   reusable to detect Fe^{3+} ions in an aqueous solution. In short, although the amount of the

236   EuW$_{10}$ 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$_{10}$@UiO-67 was also tested as chemical probe for basic amino-acids (AAs), such as

239   glycine, β-alanine, L-histidine, L-tryptophan, L-arginine, and γ-aminobutyric acid (Table S2).

240   Aqueous solutions of AAs were prepared (10^{-2} M) and EuW$_{10}$@UiO-67 was dispersed (8.5

241   μM in Eu^{3+}) to further monitor the luminescence properties at λ_{exc} = 336 nm. The emission

242   spectra are depicted in Figure S8b. As already noticed for the pure $[Eu(SiW_{10}MoO_{39})_2]^{13-}$

243   POM in homogeneous aqueous solutions (Li et al., 2014), distinct luminescence

244   enhancements are observed when the EuW$_{10}$@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   EuW$_{10}$@UiO-67 as self-calibrated-ratiometric luminescent thermometer**

252   As both the biphenyldicarboxylate linker of UiO-67 and EuW$_{10}$ act as emitters, we further

253   evaluated the capability of EuW$_{10}$@UiO-67 to be used as a self-calibrated ratiometric

254   luminescent thermometer. For that, the integrated areas of the ligand (I_{Ligand}) and $^5D_0\rightarrow^7F_2$

255   Eu^{3+} (I_{Eu}) emissions were used to define the thermometric parameter $\Delta = I_{Ligand}/I_{Eu}$ permitting

256   the conversion of emission intensities into absolute temperature. The temperature dependence

257   of the EuW$_{10}$@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_{Ligand} and I_{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 Δ in the 200 – 300 K

262   range is presented in Figure S11, where the solid line represents the temperature calibration

263   curve. The parameter Δ 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 R² 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 EuW$_{10}$@UiO-67 exhibits a

271   maximum relative sensitivity S_m of ca. 0.26% 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$_{10}$@UiO-67 is able to act as a sensor ([Eu^{3+}] = 8.5 µM) 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^{3+}, while an enhancement of the
279   EuW$_{10}$@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$_{10}$@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**

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

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427

428 **10. Figure Captions**

429

430 **FIGURE 1** (a) Polyhedral representations of EuW_{10} and an octahedral cage of EuW_{10}@UiO-
431 67; blue octahedra: WO_6, pink sphere: Eu, orange polyhedra: ZrO_8, black sphere: C, (b) SEM
432 image of crystals of EuW_{10}@UiO-67 and EDS mapping for zirconium and tungsten, (c) N_2
433 adsorption/desorption isotherms (77K, $P/P_0 = 1$ atm.) of UiO-67 (black) and the
434 EuW_{10}@UiO-67 composite (red).

435

436 **FIGURE 2.** Room-temperature excitation spectra of EuW_{10}@UiO-67 monitored at $\lambda_{em} = 471$ nm
437 (red line) and at $\lambda_{em} = 700$ nm (blue line) and excitation spectrum of EuW_{10} (black dotted line)
438 monitored at $\lambda_{em} = 700$ nm. Inset: the asterisk represents the $^7F_0 \rightarrow {}^5L_6$ excitation band of the Eu^{3+}
439 ion.

440

441   **FIGURE 3** (a) Room-temperature emission spectrum monitored at λ_{exc} = 336 nm of EuW$_{10}$@UiO-

442   67. The asterisk highlights the $^5D_0\rightarrow{}^7F_0$ transition related to the Eu^{3+} ion; (b) CIE chromaticity

443   diagram for EuW$_{10}$@UiO-67 excited at 336 nm.

444   **FIGURE 4** Luminescence intensity variations of the $^4D_0\rightarrow{}^7F_2$ transition (λ_{exc} = 336 nm) of

445   EuW$_{10}$@UiO-67 interacting with different metal ions and amino-acid aqueous solutions (C = 10^{-2}

446   mol.L^{-1}) (glyc. = glycine, ala. = β-alanine, hist = L-histidine, trypt. = L-tryptophan, buty. = γ-

447   aminobutyric acid, arg. = L-arginine).

448

449   **FIGURE 5** Emission spectra of compound EuW$_{10}$@UiO-67 in the range 150-300 K with the

450   excitation fixed at 336 nm.

451

452

453