



### Luminescent Nanothermometers

# Luminescent Nanothermometers Obtained by Post-Synthetic Modification of Metal-Organic Framework MIL-68

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**Abstract:** Metal-organic frameworks (MOFs) bearing lanthanide ions are excellent platforms for designing luminescent thermometers. However, so far, post-synthetic modification of MOFs linkers has not been explored as a route to produce such thermometers, despite its potential to design the lanthanide coordination sphere and, thus, tune the emission properties of the material. Here, nanocrystals of MIL-68-NH<sub>2</sub> were post-syntheti-

### Introduction

Metal-organic frameworks (MOFs) are hybrid materials built up from organic linkers and metal ions.<sup>[1]</sup> Certain MOFs features, such as a high surface area, large pore volume and a widely tuneable composition make them promising materials for many applications including gas storage<sup>[2]</sup> and separation,<sup>[3]</sup> catalysis<sup>[4]</sup> and photocatalysis,<sup>[5]</sup> optical,<sup>[6]</sup> and in the biomedical area.<sup>[7]</sup> Recently, post-synthetic modification, i.e., the modification of a MOF after its synthesis preserving the essential features of the framework structure, was used as a route to obtain light emitting materials via coordination of the parent MOF to a trivalent lanthanide ion (Ln<sup>3+</sup>).<sup>[8]</sup> These materials have, among other, the ability to sense with high sensitivity certain metal ions in solution.<sup>[9]</sup>

MOF MIL-68, first reported by the group of Férey,<sup>[10]</sup> consists of infinite *trans*-connected chains of octahedral units  $MO_4(OH)_2$ (M = Ga or In), linked to each other via the terephthalate ligands, generating triangular (ca. 6.0 Å wide) and hexagonal (ca. 16.0 Å) one-dimensional channels (Figure S1). MIL-68 aminofunctionalized at the terephthalate ligand (MIL-68-NH<sub>2</sub>), later disclosed,<sup>[11]</sup> is of particular interest because it opens up a simple route for post-synthetic modification. MIL-68-NH<sub>2</sub> has a BET surface area in excess of 1200 m<sup>2</sup> g<sup>-1</sup> and a good thermal stabil-

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cally modified via a cross-linking reaction with 1,4-Bis{4-[(*E*)-3-(*N*,*N*-dimethylamino)prop-2-enoyl]phenoxy}butane (HL), followed by coordination to  $Eu^{3+}$  and  $Tb^{3+}$  ions. The luminescence properties of the material were assessed.  $Tb_{90}Eu_{10}$ -MIL-68-HL was found to be an excellent cryogenic (< 100 K) ratiometric luminescent nanothermometer exhibiting a maximum relative sensitivity of 9.4 % K<sup>-1</sup> at 12 K.

ity.<sup>[11]</sup> It is also a good adsorbent for  $H_2,\ CO_2,^{[11]}$  and rhod-amine  $B,^{[12]}$  and is a photocatalyst in the reduction of  $Cr^{VI}$  to  $Cr^{III,[13]}$ 

Measuring temperature with accuracy is of interest in a broad range of areas, such as industrial manufacturing and monitoring processes, health, and safety. Molecular luminescent thermometers have advantages over the traditional liquid-filled and bimetallic thermometers, because they exhibit high spatial resolution and sensitivity, fast response, are essentially non-invasive, and are inert to strong electric or magnetic fields.<sup>[14]</sup> MOFs are excellent platforms for designing luminescent thermometers. Work on the development of lanthanide-bearing MOFs luminescent thermometers based on the intensity ratio of two separate electronic emissions, providing self-calibrated temperature readout, has been reviewed.<sup>[15]</sup>

Surprisingly, to the best of our knowledge, the post-synthetic modification of MOFs linkers has not yet been explored as an avenue to produce lanthanide-bearing luminescent thermometers, despite its potential to rationally tune the lanthanide coordination sphere and, thus, the emission properties of the material. As a proof of concept, here MIL-68-NH<sub>2</sub> was post synthetically modified via a cross-linking reaction followed by coordination to Eu<sup>3+</sup> and Tb<sup>3+</sup>, in appropriate ratios. The ensuing dual emission allowed ratiometric temperature sensing with considerable sensitivity in the cryogenic range (< 100 K).

### **Results and Discussion**

#### Synthesis of MIL-68-NH<sub>2</sub>

MIL-68-NH<sub>2</sub> was prepared by addition of indium nitrate to 2aminoterephthalic acid in the presence of DMF at room temperature. A solution of DABCO (1,4-diazabicyclo[2.2.2]octane) in DMF was added drop wise to this solution yielding a white crystalline powder. The chemical formula of MIL-68-NH<sub>2</sub> ascertained from elemental analysis was [In(OH)(C<sub>8</sub>H<sub>5</sub>NO<sub>4</sub>)].



#### Synthesis and Molecular Structure of HL

HL linker was synthesized using  $\alpha, \omega$ -bis(4-acetylphenoxy)butane as starting material, obtained by reacting the potassium salt (following treatment of 4-hydroxyacetophenone with ethanolic potassium hydroxide) with butane dibromobutane in boiling DMF. Solvent-less heating of this compound with DMF/ DMA afforded the corresponding bis(enaminone) derivative (Figure S2). <sup>1</sup>H NMR spectra of HL show one singlet at  $\delta = 3.0$ due to the *N*,*N* dimethylamino protons, and two doublets at  $\delta = 5.7$  and  $\delta = 7.8$  characteristic of olefinic–CH=CH-N protons with the same coupling constant J = 12 Hz (typical for *trans*configuration), in addition to the other butane and aromatic moieties resonances.

Using ChemBio3D, the molecular structure of HL was predicted with mode MM2 (Energy Minimization with hindered rotation). As shown in Figure S3, the distance between the two terminal nitrogen atoms is 14.3 Å, suggesting the HL molecule may me admitted into MIL-68-NH<sub>2</sub> channels.

#### Post-Synthetic Cross-Linking Modification of MIL-68-NH<sub>2</sub>

MIL-68-NH<sub>2</sub> was chemically cross-linked to the HL linker (Scheme 1). Proof for the modification is forthcoming from <sup>1</sup>H NMR spectra, after sample digestion (DCI/D<sub>2</sub>O/[D<sub>6</sub>]DMSO) (Figures S4–11), which display the linker resonances [7.35 ( $\delta$ , <sup>1</sup>H, *J* 8.3 and 1.3 Hz, H-4), 7.62 ( $\delta$ , <sup>1</sup>H, *J* 1.3 Hz, H-1), 7.85 ( $\delta$ , <sup>1</sup>H, *J* 8.3 Hz, H-5)], while the peaks at  $\delta$  = 6.85 and  $\delta$  = 7.50 are ascribed to the HL aromatic ring. The aliphatic methylene group resonates at  $\delta$  = 3.2 (s, 2H, -CH<sub>2</sub>). <sup>1</sup>H peaks integration indicates a modification rate of ca. 100 %. HMBC, COSY, NOSY, HSQC provide further proof for MOFs modification. According to NMR, Fourier transform infrared and elemental analysis, the chemical



Scheme 1. Post-synthetic modification of MIL-68-NH<sub>2</sub> with HL, followed by the complexation of MIL-68-HL with  $Ln^{3+}$  ions. The exact nature of the  $Ln^{3+}$  coordination sphere is unknown.



composition of MIL-68-HL was  $In(OH)(C_{19}H_{14}NO_6)$ . Thus, one molecule of HL linker binds to two aminoterephthalate molecules.

In absence of suitable single crystals, the determination of the unit-cell parameters of MIL-68-NH<sub>2</sub> and ensuing modified materials was carried out from powder X-ray diffraction. No significant differences were observed between MIL-68-NH<sub>2</sub>, MIL-68-HL, Eu-MIL-68-HL, Tb-MIL-68-HL, Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL (Figure 1). The pattern of MIL-68-NH<sub>2</sub> was indexed in the orthorhombic system (*Cmcm* space group) with the following cell parameters: a = 21.782 Å, b = 37.804 Å, c = 7.215 Å, V = 5941.2 Å<sup>3</sup>, and Figure of Merit F(n = 30) = 37.0.<sup>[11]</sup>



Figure 1. Powder X-ray diffraction patterns of a) MIL-68-NH $_2$ , b) MIL-68-HL, c) Eu-MIL-68-HL, d) Tb-MIL-68-HL, e) Tb $_{90}$ Eu $_{10}$ -MIL-68-HL.

Consider the infrared spectra in Figure 2. MIL-68-NH<sub>2</sub> exhibits the typical bands of the carboxylic acid function in the region of 1400–1700 cm<sup>-1</sup>. The absorption band of the carboxyl groups of the ligand coordinated to the indium metal appears at 1558 cm<sup>-1</sup>. Moreover, the presence of occluded DMF molecules is also evidenced by the C=O band at 1671 cm<sup>-1</sup>.



Figure 2. FTIR spectra of MIL-68-NH<sub>2</sub>, MIL-68-HL, Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL.

The band at 1256 cm<sup>-1</sup> is ascribed to the N–C stretching vibration and the two weak peaks at 3380 and 3472 cm<sup>-1</sup> to  $NH_2$ symmetric and asymmetric stretching vibrations. Importantly, the



carbonyl group of MIL-68-HL is observed at 1727 cm<sup>-1</sup> but absent from the Ln-bearing samples, supporting carbonyl Ln-coordination. The following chemical compositions of Ln-bearing samples were determined by energy-dispersive X-ray spectroscopy (EDS) and elemental analysis:  $In(OH)(C_{29}H_{43}N_3EUO_{17}S_5)$ ;  $In(OH)(C_{29}H_{43}N_3TbO_{17}S_5)$ ,  $In(OH)(C_{29}H_{43}N_3EUO_{17}S_5)$  for, respectively, Eu-MIL-68-HL, Tb-MIL-68-HL and  $Tb_{90}Eu_{10}$ -MIL-68-HL. The ratio between indium, and europium and terbium was determined by EDS and confirmed by atomic absorption spectroscopy.

TEM and SEM images of MIL-68-NH<sub>2</sub>, Eu-MIL-68-HL, Tb-MIL-68-HL and  $Tb_{90}Eu_{10}$ -MIL-68-HL are shown in, respectively, Figure 3 and S12. MIL-68-NH<sub>2</sub> presents itself as thin sheets from tens to hundred nanometres wide. Following HL-modification and Ln-coordination, rods are observed, 100–200 nm wide.



Figure 3. TEM images of a) MIL-68-NH<sub>2</sub>, b) Eu-MIL-68-HL, c) Tb-MIL-68-HL, d)  $Tb_{90}Eu_{10}$ -MIL-68-HL.

#### **Luminescence Thermometry**

The excitation spectra of Eu-MIL-68-HL and Tb-MIL-68-HL were recorded at room temperature (ca. 295 K) monitoring the strongest Eu<sup>3+</sup> <sup>5</sup>D<sub>0</sub> $\rightarrow$ <sup>7</sup>F<sub>2</sub>, and the Tb<sup>3+</sup> <sup>5</sup>D<sub>4</sub> $\rightarrow$ <sup>7</sup>F<sub>5</sub> emission transitions (Figure 4). Both spectra are dominated by a broad UV band (240–330 nm) attributed to a superposition of the  $\pi$ - $\pi$ \* transitions of the organic ligands and a ligand-to-metal charge-transfer band. The additional sharp lines in the spectra of Eu-MIL-68-HL and Tb-MIL-68-HL are ascribed to the intra-4f<sup>6</sup> <sup>7</sup>F<sub>0,1</sub> $\rightarrow$ <sup>5</sup>D<sub>1-4</sub>, <sup>5</sup>L<sub>6</sub> and <sup>5</sup>G<sub>2-6</sub> transitions of Eu<sup>3+</sup>, and to the intra-4f<sup>8</sup> <sup>7</sup>F<sub>6</sub> $\rightarrow$ <sup>5</sup>D<sub>2-4</sub> and <sup>5</sup>G<sub>J</sub> transitions of Tb<sup>3+</sup>.

The emission spectra of Eu-MIL-68-HL and Tb-MIL-68-HL recorded at 295 K and excited at 312 nm (ligand band) are shown in Figure 5. The sharp Eu<sup>3+</sup> and Tb<sup>3+</sup> emission lines are assigned to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{0-4}$  and  ${}^{5}D_{4} \rightarrow {}^{7}F_{6-0}$  transitions, respectively. The





Figure 4. Excitation spectra of Eu-MIL-68-HL ( $\lambda_{Em.}$  = 613.5 nm) and Tb-MIL-68-HL ( $\lambda_{Em.}$  = 545 nm) recorded at 295 K.

emission spectrum of Eu-MIL-68-HL shows a dominance of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  over the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, a unique  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  transition, and exhibits three and five Stark components for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transitions. These features indicate the presence of a single low-symmetry Ln<sup>3+</sup> local environment. The emission spectrum of Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL recorded at 295 K under ambient pressure consists on, essentially, the overlap of the Eu-MIL-68-HL and Tb-MIL-68-HL spectra (Figure S13).



Figure 5. Emission spectra of Eu-MIL-68-HL and Tb-MIL-68-HL recorded at 295 K with the excitation fixed at 312 nm.

However, when the sample is submitted to a  $5 \times 10^{-3}$  mbar vacuum the corresponding emission spectrum completely changes (Figure S13) witnessing a phase transformation prompted by the release of the solvent molecules from the porous structure. Consequently, to prevent any phase transformation under high vacuum, in the low temperature measurements the vacuum system was initialized at a temperature below 260 K, allowing to freeze the sample. At the very low pressure ( $5 \times 10^{-6}$  mbar) used on the temperature dependent measurements the as-synthesised sample is only stable up to 240 K.





The excitation spectra of Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL, at ambient temperature and 12 K, were monitored both in the Eu<sup>3+</sup> ( ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  at 613.5 nm) and Tb<sup>3+</sup> ( ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  at 545 nm) strongest transitions (Figure S14). While the 295 K spectrum monitoring the Tb<sup>3+</sup> emission is similar to the spetrum of Tb-MIL-68-HL (Figure 4), the spectrum monitoring the Eu<sup>3+</sup> emission shows a prominence of the Tb<sup>3+</sup> intra 4f lines over the Eu<sup>3+</sup> ones. This is clear evidence for Tb<sup>3+</sup>-to-Eu<sup>3+</sup> energy transfer, which enabled the ratiometric thermometry. For that, an excitation wavelength of 312.3 nm was selected, on the ligand-to-Ln<sup>3+</sup> energy-transfer UV band, corresponding to the minimum overlap of the Tb<sup>3+</sup> and Eu<sup>3+</sup> 12 K excitation spectra, and very close to the Tb<sup>3+</sup> and Eu<sup>3+</sup> excitation maxima at room-temperature (Figure S14). Therefore, the 312.3 nm excitation afforded a good emission output and maximized the temperature sensitivity of the system.

The temperature dependence of  $Tb_{90}Eu_{10}$ -MIL-68-HL emission in the 12–240 K range, with the excitation fixed at 312.3 nm, is shown in Figure 6a.

into absolute temperature T. For each temperature, four consecutive emission spectra were collected and used to determine the average thermometric parameter and the corresponding standard deviation (95 % confidence).  $I_{\rm Tb}$  and  $I_{\rm Eu}$  parameters were determined by integrating the emission spectra in the 535-557 nm and 605-629 nm wavelength intervals, respectively. Figure 6b exhibits the distinct  $I_{Tb}$  and  $I_{Eu}$  temperature dependence. The Tb<sup>3+</sup> emission decreases in the temperature range studied, particularly in the 12-60 K interval where it shows logarithmic temperature dependence, reaching at 240 K 19% of the emission observed at 12 K. In contrast, the Eu<sup>3+</sup> emission increases 1.6-fold from 12 K to 240 K. The decrease of the Tb<sup>3+</sup> emission and concomitant increase of the Eu<sup>3+</sup> emission is evidence for a thermally activated  $Tb^{3+}$ -to-Eu<sup>3+</sup> energy transfer. In accord, whereas the Eu<sup>3+ 5</sup>D<sub>0</sub> decay curves are single exponentials with the corresponding emission lifetimes slightly decreasing from 12 K ( $0.56 \pm 0.01$  ms) to 295 K ( $0.50 \pm 0.01$  ms), the Tb<sup>3+ 5</sup>D<sub>4</sub> decay curves are obviously not single exponentials and the corresponding averaged lifetime strongly decreases



Figure 6. a) Emission spectra of Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL in the 12–240 K range with the excitation fixed at 312.3 nm. b) Corresponding temperature dependence of  $I_{\rm Tb}$  (green) and  $I_{\rm Eu}$  (red) parameters.

The integrated areas of the green  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  ( $I_{Tb}$ ), and red  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  ( $I_{Eu}$ ) transitions were used to define the thermometric parameter  $\Delta = I_{Tb}/I_{Eu}$  and to convert the emission intensities



Figure 7. a) Variation of  $\Delta$  as a function of temperature in the 12–240 K range for Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL excited at 312.3 nm. The solid line is the calibration curve obtained by fiting the experimental data to equation (4) ( $r^2 > 0.999$ ). The error in  $\Delta$  results from the propagation of the errors in  $I_{Tb}$  and  $I_{Eu}$ . b) Corresponding relative thermal sensitivity in the same temperature range.



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from 0.82 ms to 0.31 ms, in the same temperature range (Figure S15).

Figure 7a shows the temperature dependence of the thermometer parameter  $\Delta$  in the 12–240 K range for Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL. The data is well fitted by the classical Mott–Seitz model considering two competitive non-radiative recombination channels:<sup>(15,16]</sup>

where  $\Delta_0$  is the  $\Delta$  parameter at T = 0 K,  $\alpha = W_0/W_R$  is the ratio between the non-radiative ( $W_0$  at T = 0 K) and radiative ( $W_R$ ) rates, and  $\Delta E_1$  and  $\Delta E_2$  are the activation energies for the two non-radiative channels. Fitting the experimental  $\Delta$  values with Equation (1) yields  $\Delta_0 = 1.51 \pm 0.04$ ,  $\alpha_1 = 10.3 \pm 0.2$ ,  $\Delta E_1 =$  $21.1 \pm 0.3$  cm<sup>-1</sup>,  $\alpha_2 = 26.5 \pm 2.2$  and  $\Delta E_2 = 249 \pm 13$  cm<sup>-1</sup>.

$$\Delta(T) = \frac{\Delta_0}{1 + \alpha_1 \exp(-\Delta E_1/k_B T) + \alpha_2 \exp(-\Delta E_2/k_B T)}$$
(1)

The two non-radiative recombination channels responsible for the temperature sensing, associated with  $\Delta E_1$  and  $\Delta E_2$ , are presumably the Tb<sup>3+</sup>-to-Eu<sup>3+</sup> energy transfer and the energy migration between two neighbouring Tb<sup>3+</sup> sites. The relative sensitivity,  $S_r = (\partial \Delta / \partial T) / \Delta$ ,<sup>[17]</sup> a figure of merit used to compare the performance of thermometers, is plotted in Figure 7b. Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL presents a maximum relative sensitivity ( $S_m$ ) of 9.4 %K<sup>-1</sup> at 12 K, which gradually decreases with the temperature increase reaching a value of 1 %K<sup>-1</sup> at 52.3 K and a minimum of 0.26 %K<sup>-1</sup> at 240 K.

Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL presents the second best  $S_m$  reported so far for ratiometric luminescent thermometers operative in the cryogenic temperature range (T < 100 K).<sup>[16,18]</sup> Concerning the  $S_m$  parameter, Tb<sub>90</sub>Eu<sub>10</sub>-MIL-68-HL is only outperformed by Tb<sub>0.95</sub>Eu<sub>0.05</sub>HY (HY = 5-hydroxy-1,2,4-benzenetricarboxylic acid), with  $S_m$  of 31.0 %K<sup>-1</sup> at 4 K.<sup>[18a]</sup>

### Conclusions

In conclusion, post-synthetic modification of Ln-based Metal-Organic Frameworks has been shown to be a suitable tool to design ratiometric luminescent nanothermometers. This concept was illustrated with MIL-68-NH<sub>2</sub>, by cross-linking with an appropriate ligand (HL) and coordinating to  $Eu^{3+}$  and  $Tb^{3+}$ .  $Tb_{90}Eu_{10}$ -MIL-68-HL is a new cryogenic ratiometric luminescent thermometer with a very good maximum relative sensitivity of 9.4 % K<sup>-1</sup> at 12 K, which is the second best reported so far for related temperature sensors. Many other wide-pore MOFs and a variety of cross-linking molecules are available to engineer luminescent thermometers. Work along these lines is in progress.

### **Experimental Section**

**Materials:** 2-Aminoterephthalic acid (99 %, Aldrich), indium nitrate hydrate (Merck), *N,N*-dimethylformamide (DMF, 99.9 %, Aldrich), chloroform (99.5 %, Aldrich), 4-Hydroxyacetophenone (99 %, Aldrich), europium nitrate hexahydrate [Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O] (99.99 %, Aldrich), terbium nitrate hexahydrate [Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O] (99.99 %, Aldrich).

**Synthesis of MIL-68-NH<sub>2</sub>:** MIL-68-NH<sub>2</sub> was obtained by precipitation. 0.325 g (1.08 mmol) of indium nitrate and 0.227 g (1.25 mmol) of 2-aminoterephthalic acid were dissolved in 20 mL of DMF. The reaction mixture was stirred for 5 min, then 1 mL (1.38 mmol) of 1.38 M DABCO solution (0.192 g of DABCO in 1 mL of DMF) was added dropwise. The reaction mixture was stirred for 20 h at room temperature. The precipitate obtained was washed with DMF then soaked in CHCl<sub>3</sub> for 24 h. filter and dry in air. <sup>1</sup>H NMR 300 MHz, (DCl/D<sub>2</sub>O/[D<sub>6</sub>]DMSO)  $\delta$ : 7.06 (d, 1H, *J* = 8.2Hz), 7.40 (s, 1H), 7.79 (d, 1H, *J* = 8.2Hz).

Synthesis of HL (1,4-Bis{4-[(E)-3-(N,N-dimethylamino)prop-2enoyl]phenoxy}butane): 4- Hydroxyacetophenone (20 mmol) was dissolved in a hot ethanolic KOH solution [prepared by dissolving 1.12 g (20 mmol) of KOH in 20 mL of absolute ethanol], and the solvent was then removed in vacuo. The remaining material was dissolved in DMF (15 mL) and butane dibromides (10 mmol) added. The reaction mixture was refluxed for 5 minutes during which KCI was separated. The solvent was then removed in vacuo and the remaining material poured over crushed ice. The solid obtained was recrystallized from ethanol to give colourless crystals. A mixture of bis(acetyl) derivatives (10 mmol) and dimethylformamide-dimethylacetal (DMF/DMA) (5.4 g, 45 mmol) was refluxed for 10 h. The reaction mixture was left to cool to room temperature and the resulting yellow solid products were collected by filtration, washed with ethanol, dried, and finally recrystallized from ethanol to afford the corresponding bis(enaminone) derivatives as pale yellow crystals respectively. Yield 2.49 g (57 %); m.p. 200-202 °C; IR (KBr) 1640 cm<sup>-1</sup> (C=O), 1600 cm<sup>-1</sup> (C=C); <sup>1</sup>H NMR (CDCl<sub>3</sub>) 2.0 (d, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 3.02 (s, 12H,4 NCH<sub>3</sub>), 4.1 (s, 4H, OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O), 5.71 (d, J = 12Hz, 2H, 2 N-CH=CH-CO), 6.90 (d, J = 9 Hz, 4H, ArH),7.78 (d, J = 12 Hz, 2H, 2N-CH=CH-CO), 7.89 (d, J = 9 Hz, 4H, ArH); Anal. for C<sub>26</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub> Calcd: C, 71.53; H, 7.39; N, 6.42; found C, 71.80; H, 7.22; N, 6.18 %.

**Synthesis of MIL-68-HL:** A CHCl<sub>3</sub> solution of HL reagent (0.6 g, 6 mmol) was added dropwise at room temperature to MIL-68-NH<sub>2</sub> (1.0 g, 3.3 mmol NH<sub>2</sub> equivalents). The resulting mixture was sealed and kept for 3 days at 70 °C. The powder was washed with CHCl<sub>3</sub> three times and dried at 75 °C in a oven.

**Synthesis of Ln-MIL-68-HL:** A sample *MIL-68-HL* (3.10 g, 3 mmol) was dispersed in three vials containing mixed solvent from ethanol/ DMSO (90:10 v/v) (15 mL). To each portion of this mixture, a solution of Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.366 g, 1 mmol) or Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.373 g, 1 mmol) or mixed lanthanide from Eu(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.0366 g, 0.1 mmol) and Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.335 g, 0.9 mmol) was added dropwise at room temperature and the mixture was stand for 5 days. The sample was washed twice with ethanol and dried in air.

**Characterization:** Powder X-ray diffractograms were collected on a X'Pert MPD Philips diffractometer (Cu- $K_{\alpha}$  X-radiation at 40 kV and 50 mA). EDS measurements were carried out on a Hitachi SU-70 fitted with a field emission gun. Optical microscopy images were obtained on a Leica EZ4HD Digital Microscope-3.0 Megapixel. Fourier transform infrared spectra were measured in the transmission mode on a Mattson 5000 in the range 4000–350 cm<sup>-1</sup>. The pellets were prepared by adding 1–2 mg of MOFs to 200 mg of KBr. The mixture was compressed at a pressure of 10 kPa to form transparent pellets. CNH contents were determined on a LECO CHNS-932 elemental analyser. Solution NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz) using a solution prepared by digesting 7 mg of sample in [D<sub>6</sub>]dimethyl sulfoxide (500 µL) and dilute DCI (100 µL, 35 % DCI).

**Photoluminescence**: The emission and excitation spectra were recorded on a modular double grating excitation spectrofluorimeter



with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a R928 Hamamatsu photomultiplier, for the detection on the visible spectral range, using the front face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorometer and the excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. Time-resolved measurements were carried out with the pulsed Xe-Hg lamp excitation, in front face acquisition mode. The temperature was controlled by a helium-closed cycle cryostat with vacuum system measuring ca.  $5 \times 10-6$  mbar and a Lakeshore 330 auto-tuning temperature controller with a resistance heater. The temperature can be adjusted from ca. 12 to 450 K with a maximum accuracy of 0.1 K. The sample temperature was fixed at a given value using the auto-tuning temperature controller; after waiting a minimum of 5 minutes to thermalize the sample, four consecutive steady-state emission spectra were measured for each temperature; the maximum temperature difference detected during the acquisitions was 0.1 K, the temperature accuracy of the controller.

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#### Luminescent Nanothermometers

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 Luminescent Nanothermometers
 Obtained by Post-Synthetic Modification of Metal-Organic Framework MIL-68



Nanocrystals of MIL-68-NH<sub>2</sub> was successfully modified by post-synthetic modification via a cross-linking reac-

tion. The obtained material makes an excellent cryogenic (< 100 K) ratiometric luminescent nanothermometer.

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