



# Lanthanide MOFs

# Photoluminescence, Unconventional-Range Temperature Sensing, and Efficient Catalytic Activities of Lanthanide Metal– Organic Frameworks

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**Abstract:** A luminescent lanthanide metal–organic framework (MOF) based on Eu<sup>3+</sup> and Tb<sup>3+</sup> ions with 2-phenylsuccinate (EuTb-psa) was obtained solvothermally to explore its behavior as a temperature sensor in an unconventional temperature range through the study of the thermal evolution of the hypersensitive  $4f-4f \ {}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition and the luminescence lifetime. The efficiency of the luminescence process was evaluated through the europium intrinsic quantum yield ( $Q_{Eu}$ ), and its variation as a function of temperature is also reported. The optical

# Introduction

Metal–organic frameworks (MOFs) have been the focus of attention in recent decades because their potential applications in a wide variety of fields, such as heterogeneous catalysis,<sup>[1]</sup> ion exchange, and ionic or molecular separation,<sup>[2]</sup> make them promising multifunctional materials.<sup>[3]</sup> Lanthanide ions are special in photonics because of their unique properties,<sup>[4]</sup> particularly with respect to their application in phosphors,<sup>[5]</sup> the generation and amplification of light in lasers,<sup>[6]</sup> optical amplifiers,<sup>[7]</sup> solid-state lighting, full-color displays, and backlights.<sup>[8]</sup>

The sensing and mapping of temperature in an accurate and noninvasive way is vital to understand numerous aspects related to electronic and photonic devices at the micro- and

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properties of four isostructural compounds (Pr-psa, Nd-psa, Gdpsa, and Tb-psa) were investigated and compared with those of related compounds. The energy of the triplet state of the ligand was also estimated. The samples were fully characterized by single-crystal and powder X-ray diffraction, thermal analysis, and vibrational spectroscopy. The heterogeneous catalytic activities of a series of Ln-psa MOFs (with Ln = Sm, Eu, Gd, Tb, EuGd, and EuTb) were evaluated in a one-pot cyanosilylation with benzaldehyde as the substrate.

nanoscale,<sup>[9]</sup> such as thermal-transport phenomena, heat dissipation, heat-transfer profiles, and thermal reactions.<sup>[10]</sup> Furthermore, the optimization of therapeutic treatments such as photodynamic therapy<sup>[11]</sup> requires the determination of exact temperatures in living cells. Few examples of MOFs applied as thermal sensors have been reported since the first study was reported in 2012 by Cui et al., [12-14] who obtained so-called "molecular thermometers" based on temperature-dependent photoluminescence (PL) properties. In this context, Ln MOFs and, more specifically, heterometallic MOFs (HMOFs) have attracted particular interest, mainly for the possibility of tuning the color and spectroscopy by intermetallic variation.<sup>[15]</sup> This is an important point for sensor design. Mixed EuTb MOFs were successfully employed to sense temperatures in the 10-300 K range with tailorable emission colors and showed maximum thermal sensitivities (S) of 3.53 % K<sup>-1.[12a,12b]</sup> Miyata et al. reported the sensor behavior of a TbEu MOF in the temperature range 200-450 K with high thermostability and a higher S value than those of the corresponding Tb or Eu MOFs (0.83 vs. 0.64 or 0.05).<sup>[13b]</sup> Studies of the thermal sensor activity of a nanothermometer based on Ln MOFs in the physiological temperature range (ca. 300–320 K) for potential therapeutic applications have been reported by Carlos and co-workers.<sup>[13a]</sup> Recently, Cui et al.<sup>[12d]</sup> reported the composite system Eu-MOF dye (ZJU-88 perylene), which exhibits an original dual emission accompanied with thermal-sensor activity over the physiological temperature range (293–353 K) and an S value of 1.28 % K<sup>-1</sup>.

In addition, it is worth mentioning that coordination polymers may be designed as active and selective catalysts, as outstanding textural properties and high metal content can be

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achieved. However, their relatively limited thermal and chemical stabilities along with the presence of metallic sites blocked by the organic spacers in many MOF structures have restricted their use in this area. Thus, new synthetic strategies have been applied in the past few years to overcome these drawbacks. A common catalytic "test" reaction to demonstrate the Lewis acidic properties of MOFs is the cyanosilylation of aldehydes and ketones (cyanosilylation reactions, CSRs).<sup>[1]</sup> Trimethylsilyl cyanide (TMSCN) is one of the most useful cyanating reactants for nucleophilic addition to carbonyl compounds to obtain cyanohydrin trimethylsilyl ethers, which are very important intermediate compounds in organic synthesis and biology because they can be transformed into a wide range of building blocks.<sup>[16]</sup> For this reason, the development of efficient catalysts for the cyanosilylation of carbonyl compounds with TMSCN is a relevant topic in chemistry, and many examples of this kind of catalyst have been reported.<sup>[17]</sup> In previous work, Ln MOFs were successfully tested as heterogeneous catalysts for important reactions in green chemistry such as the hydrodesulfurization of thiophene<sup>[18]</sup> and the oxidation of methyl phenyl sulfide.<sup>[19]</sup>

To harness the coordination geometry and PL features of lanthanides, we recently synthesized and characterized 2D Lnpsa MOFs (with Ln = Sm, Eu, and the mixed Eu/Gd; psa = 2phenylsuccinate ion) with interesting and tunable optical properties.<sup>[20]</sup> The Eu-psa bulk material was readily exfoliated by liquid ultrasonication, and the presence of nanolayers was confirmed by scanning electronic microscopy and atomic force microscopy. The aim of the present work was to obtain heterometallic Ln-psa phases with promising PL properties, and here we report the new HMOF EuTb-psa {[Eu<sub>0.8</sub>Tb<sub>1.2</sub>(C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)]}, which was prepared solvothermally from a pH-controlled solution. To establish the structure-properties relationships, the optical properties of [Pr<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)] (Pr-psa), [Nd<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>)<sub>3</sub>- $(H_2O)$ (Nd-psa),  $[Tb_2(C_{10}H_8O_4)_3(H_2O)]$ (Tb-psa), and [Gd<sub>2</sub>(C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)] (Gd-psa) were also explored. The compounds were characterized by FTIR spectroscopy, thermal analysis, and powder and single-crystal X-ray diffraction. The temperature-dependent PL properties of EuTb-psa were determined with respect to the relative intensities and the lifetimes to study its thermal-sensor behavior in an unconventional range. The catalytic behaviors of some members of the Ln-psa series (with Ln = Sm, Eu, Gd, Tb, EuGd and EuTb) were evaluated in CSRs to identify the role that the Lewis acid sites play in the expected carbonyl activation mechanism. The efficiency of the catalytic process was evaluated by green-chemistry metrics.

## **Results and Discussion**

## **Crystal Structure**

The crystallographic data for EuTb-psa is summarized in Table 1. As the compound is isostructural with the previously reported Ln-psa ones, a brief description of its structural features is given here, and a more thorough discussion of the framework can be found in ref.<sup>[20]</sup>



Table 1. Crystal data, structure determination, and refinement summary for EuTb-psa.

Crystal system	monoclinic
Empirical formula	Eu <sub>0.8</sub> Tb <sub>1.2</sub> C <sub>30</sub> H <sub>26</sub> O <sub>13</sub>
Formula mass [g]	906.78
Space group	P21/c
a [Å]	15.3401(6)
b [Å]	18.0835(5)
c [Å]	11.1080(2)
α [°]	90.0
β [°]	100.719(3)
γ [°]	90.0
V [Å <sup>3</sup> ]	3027.62(2)
$\varrho_{calcd.}$ [g cm <sup>-3</sup> ]	1.988
Z	4
7 [K]	150
Absorption coefficient [mm <sup>-1</sup> ]	4.490
Crystal size [mm]	$0.19 \times 0.12 \times 0.04$
T <sub>min.</sub> /T <sub>max.</sub>	3.64/29.27
h	(-20,20)
k	(-23,24)
I	(-14,15)
Reflections collected/unique $[l > 2\sigma(l)]$	10844/7631
Absorption correction	semiempirical
Refined parameters	413
Goodness-of-fit on F <sup>2</sup>	1.052
Refinement method	full-matrix least-squares on F
λ [Å]	0.71073
Final R indices	$R_1 = 0.0561$
$[l > 2\sigma(l)]$	$wR_2 = 0.1420$
R factor (all)	0.087

The asymmetric unit comprises two crystallographically inequivalent Ln<sup>3+</sup> ions and three psa ligands, all of which have a gauche conformation (Figure 1, a). EuTb-psa shows the same metallic positional disorder over two sites found in the analogous EuGd-psa.<sup>[19]</sup> One of the lanthanide ions is surrounded by eight oxygen atoms (hereafter site A), all of which come from carboxylate groups, whereas the other one is nonacoordinated (hereafter site B) through eight oxygen atoms from carboxylate groups and the remaining one from the coordinated water molecule. The coordination polyhedra are consistent with triangulated dodecahedra and monocapped square antiprisms for sites A and B, respectively. From the refinement results, the best model to describe the structure considers that both Ln ions (Eu<sup>3+</sup> and Tb<sup>3+</sup>) are disordered on sites A and B; the relative occupancy of both ions is not easy to distinguish because of their similar scattering factors. However, a small dependence of the agreement factor  $(wR_2)$  on the relative occupancy can be observed. Different structural refinements were performed as a function of Eu occupancy in site A (see Figure S1), and a minimum value for  $wR_2$  was obtained for occupation factors for the Eu<sup>3+</sup> and Tb<sup>3+</sup> ions at site A of 0.25 and 0.75, respectively, which produces 0.55 and 0.45 for the Eu<sup>3+</sup> and Tb<sup>3+</sup> ions, respectively, at site B. The Ln-O bond lengths fall in the ranges 2.287(6)-2.636(5) Å for [LnO<sub>8</sub>] and 2.362(6)–2.603(5) Å for the [LnO<sub>9</sub>] polyhedron. As can be seen in Figure 1 (b), the secondary building units (SBUs) consist of infinite zigzag chains of edge-sharing polyhedra running along the [001] direction. The compound can be classified as I<sup>1</sup>O<sup>1</sup> according to the classification proposed by Cheetham et al.<sup>[21]</sup> and forms a two-dimensional net with layers topologically described as fes-type nets (Figure 1, c).





Figure 1. (a) ORTEP drawing of the asymmetric unit of EuTb-psa, (b) view of the *cb* plane, and (c) topological net.

#### Luminescence Studies

### Exploring the Room-Temperature PL Properties of Ln-psa MOFs

The following results show the PL study of the Ln-psa series (with Ln = Nd, Tb, Gd, Pr, EuTb) at room temperature. The emission was monitored at  $\lambda = 1069$  nm (9355 cm<sup>-1</sup>) and the excitation wavelength was varied between 250 and 850 nm to produce an excitation spectrum for Nd-psa (see Figure 2, top). The peaks labeled a-j could be assigned to the corresponding transitions within the 4f shell of the Nd<sup>3+</sup> ion and are listed in Table 2. Upon excitation at  $\lambda = 584$  nm (17123 cm<sup>-1</sup>) in the  ${}^{2}G_{7/2}$ ,  ${}^{4}G_{5/2} \leftarrow {}^{4}I_{9/2}$  transitions, the typical narrow Nd<sup>3+</sup> emission peaks in the near-IR (NIR) region are observable (Figure 2, bottom). The peaks labeled k-m are assigned to the corresponding electronic transitions in Table 2. The emission at  $\lambda$  = 1069 nm shows a monoexponential decay profile upon excitation at  $\lambda =$ 355 nm with a pulsed light source. From the luminescence decay profile (see Figure S2), it is possible to calculate a luminescence decay time of  $(0.426 \pm 0.007)$  µs, which is the shortest one for this set of MOFs.

The excitation spectrum of Tb-psa was recorded in the range  $\lambda = 250-525$  nm, and the emission was monitored at  $\lambda = 541.6$  nm (Figure 3, top). At short wavelengths, a rather intense broad band is visible with a maximum at  $\lambda = 270.4$  nm (36982 cm<sup>-1</sup>). This value was selected as the excitation wavelength to record the emission spectrum shown in Figure 3 (bottom), in which the typical narrow Tb<sup>3+</sup> peaks yield a strong green emission. The aforementioned band most likely originates from the  $\pi \rightarrow \pi^*$  transitions of the phenyl groups; the fact that this band is more intense than the 4f–4f lines indicates a





Figure 2. Excitation spectrum monitored at  $\lambda$  = 1069 nm (top) and emission spectrum ( $\lambda_{exc}$  = 584 nm) of Nd-psa (bottom).

rather effective antenna effect. The narrow and less-intense peaks in the excitation spectrum correspond to transitions within the 4f shell of the Tb<sup>3+</sup> ion. The corresponding assignment of the <sup>25+1</sup>L<sub>J</sub> $\leftarrow$ <sup>7</sup>F<sub>6</sub> excitation and the <sup>5</sup>D<sub>4</sub> $\rightarrow$ <sup>7</sup>F<sub>J</sub> (J = 6–0) emission electronic transitions is shown in Table 2. The emission at  $\lambda = 541.6$  nm shows a monoexponential decay profile (Figure S3), and the calculated luminescence lifetime is (1.625 ± 0.008) ms. When the emission spectrum of Tb-psa is compared with that previously reported for Tb-dms<sup>[22]</sup> (dms = 2,3-dimethylsuccinate), a decrease in intensity of ca. 4.5 times for the <sup>5</sup>D<sub>4</sub> $\rightarrow$ <sup>7</sup>F<sub>5</sub> transition is noticeable for the first compound along with a slightly shorter  $\tau_{obs}$ . This behavior can be explained in terms of the coordinated water content, which can effectively quench the Tb<sup>3+</sup> luminescence through the relaxation of OH groups.<sup>[23]</sup>

The excitation spectrum of Gd-psa exhibits a structured broad and weak band that is ascribed to the typical  $\pi \rightarrow \pi^*$  transitions of aromatic compounds. Upon UV excitation, a greenish blue emission with  $\lambda_{max} = 441$  nm can be observed (see Figures 4 and 5), as was reported for other Gd MOFs.<sup>[24]</sup> The emission at  $\lambda = 441$  nm shows a monoexponential decay profile



Figure 3. Excitation spectrum monitored at  $\lambda$  = 541.6 nm (top) and emission spectrum obtained with  $\lambda_{exc}$  = 270.4 nm (bottom) of Tb-psa.





	Excitation			Emission			
Label	Wavelength [nm]	Energy [cm <sup>-1</sup> ]	Transition	Label	Wavelength [nm]	Energy [cm <sup>-1</sup> ]	Transition
			Pr-psa				
a	452	22124	${}^{3}P_{2}\leftarrow {}^{3}H_{4}$	d	545	18348	${}^{3}P_{0} \rightarrow {}^{3}H_{5}$
b	466	21459	<sup>1</sup> I <sub>6</sub> , <sup>3</sup> P <sub>1</sub> ← <sup>3</sup> H <sub>4</sub>	e	587	17036	$^{1}D_{2}\rightarrow ^{3}H_{4}$
с	481.5	20768	<sup>3</sup> P <sub>0</sub> ← <sup>3</sup> H <sub>4</sub>	f	610.5	16380	${}^{3}P_{0} \rightarrow {}^{3}H_{6}$
				g	630	15873	${}^{3}P_{0} \rightarrow {}^{3}F_{2}$
				h	712.5	14035	${}^{3}P_{0} \rightarrow {}^{3}F_{3}$
			Tb-psa				
а	318.2	31427	${}^{5}H_{6}$ , ${}^{5}D_{0} \leftarrow {}^{7}F_{6}$	i	487.9	20496	${}^{5}D_{4} \rightarrow {}^{7}F_{6}$
b	325.0	30769	${}^{5}D_{1} \leftarrow {}^{7}F_{6}$	j	541.6	18464	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$
с	341.7	29265	<sup>5</sup> L <sub>8</sub> , <sup>5</sup> L <sub>7</sub> , <sup>5</sup> L <sub>6</sub> , <sup>5</sup> G <sub>2</sub> , <sup>5</sup> G <sub>3</sub> ← <sup>7</sup> F <sub>6</sub>	k	582.8	17158	${}^{5}D_{4} \rightarrow {}^{7}F_{4}$
d	351.3	28466	<sup>5</sup> L <sub>9</sub> , <sup>5</sup> G <sub>4</sub> , <sup>5</sup> D <sub>2</sub> ← <sup>7</sup> F <sub>6</sub>	I.	621.4	16093	${}^{5}D_{4} \rightarrow {}^{7}F_{3}$
e	359.1	27847	${}^{5}G_{5} \leftarrow {}^{7}F_{6}$	m	645.2	15499	${}^{5}D_{4} \rightarrow {}^{7}F_{2}$
f	369.1	27093	<sup>5</sup> L <sub>10</sub> ← <sup>7</sup> F <sub>6</sub>	n	667.8	14974	${}^{5}D_{4} \rightarrow {}^{7}F_{1}$
g	377.6	26483	<sup>5</sup> G <sub>6</sub> , <sup>5</sup> D <sub>3</sub> ← <sup>7</sup> F <sub>6</sub>	0	679.5	14717	${}^{5}D_{4} \rightarrow {}^{7}F_{0}$
h	486.8	20542	${}^{5}D_{4}\leftarrow {}^{7}F_{6}$				
			Nd-psa				
а	331	30211	<sup>2</sup> L <sub>17/2</sub> , <sup>4</sup> D <sub>7/2</sub> , <sup>2</sup> I <sub>13/2</sub> ← <sup>4</sup> I <sub>9/2</sub>	k	893	11198	${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$
b	353	28329	<sup>2</sup> L <sub>15/2</sub> , <sup>4</sup> D <sub>1/2</sub> , <sup>2</sup> I <sub>11/2</sub> , <sup>4</sup> D <sub>5/2</sub> , <sup>4</sup> D <sub>3/2</sub> ← <sup>4</sup> I <sub>9/2</sub>	I	1069	9355	${}^{4}F_{3/2} \rightarrow {}^{4}I_{11/2}$
с	431	23202	<sup>2</sup> P <sub>1/2</sub> , <sup>2</sup> D <sub>5/2</sub> ← <sup>4</sup> I <sub>9/2</sub>	m	1340	7463	${}^{4}F_{3/2} \rightarrow {}^{4}I_{13/2}$
d	468	21368	${}^{4}G_{11/2}$ , ${}^{2}D_{3/2}$ , ${}^{2}P_{3/2}$ , ${}^{2}G_{9/2}$ , ${}^{2}K_{15/2} \leftarrow {}^{4}I_{9/2}$				
e	526	19011	<sup>4</sup> G <sub>9/2</sub> , <sup>4</sup> G <sub>7/2</sub> , <sup>2</sup> K <sub>13/2</sub> ← <sup>4</sup> I <sub>9/2</sub>				
f	583	17153	<sup>2</sup> G <sub>7/2</sub> , <sup>4</sup> G <sub>5/2</sub> ← <sup>4</sup> I <sub>9/2</sub>				
g	630	15873	<sup>2</sup> H <sub>11/2</sub> ← <sup>4</sup> I <sub>9/2</sub>				
h	686	14577	<sup>4</sup> F <sub>9/2</sub> ← <sup>4</sup> I <sub>9/2</sub>				
i	744	13441	<sup>4</sup> S <sub>3/2</sub> , <sup>4</sup> F <sub>7/2</sub> ← <sup>4</sup> I <sub>9/2</sub>				
j	802	12469	${}^{2}\text{H}_{9/2}, {}^{4}\text{F}_{5/2} \leftarrow {}^{4}\text{I}_{9/2}$				
			EuTb-psa				
а	298.3	33523	${}^{5}I_{4} \leftarrow {}^{7}F_{1}, {}^{5}F_{4} \leftarrow {}^{7}F_{0} (Eu^{3+})$	n	488.5	20471	${}^{5}\text{D}_{4} \rightarrow {}^{7}\text{F}_{6} \text{ (Tb}^{3+}\text{)}$
b	302.7	33036	<sup>5</sup> F <sub>2</sub> ← <sup>7</sup> F <sub>0</sub> , <sup>5</sup> F <sub>1</sub> ← <sup>7</sup> F <sub>1</sub> (Eu <sup>3+</sup> )	0	541.6	18464	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$ (Tb <sup>3+</sup> )
с	317.9	31456	<sup>5</sup> H <sub>7</sub> ← <sup>7</sup> F <sub>6</sub> (Tb <sup>3+</sup> )/ <sup>5</sup> H <sub>6</sub> ← <sup>7</sup> F <sub>0</sub> (Eu <sup>3+</sup> )	р	579.5	17256	${}^{5}D_{0}\rightarrow {}^{7}F_{0}(Eu^{3+})$
d	324.8	30788	<sup>5</sup> H <sub>7</sub> ← <sup>7</sup> F <sub>1</sub> (Eu <sup>3+</sup> )	q	592.5	16878	${}^{5}D_{0}\rightarrow {}^{7}F_{1}(Eu^{3+})$
e	339.5	29455	<sup>5</sup> L <sub>7</sub> ← <sup>7</sup> F <sub>6</sub> (Tb <sup>3+</sup> )	r	616.1	16231	${}^{5}D_{0}\rightarrow {}^{7}F_{2}(Eu^{3+})$
f	341.6	29274	<sup>5</sup> L <sub>8</sub> ← <sup>7</sup> F <sub>6</sub> (Tb <sup>3+</sup> )	S	651.8	15342	${}^{5}D_{0}\rightarrow {}^{7}F_{3}(Eu^{3+})$
g	350.9	28498	<sup>5</sup> G <sub>4</sub> , <sup>5</sup> L <sub>9</sub> ← <sup>7</sup> F <sub>6</sub> (Tb <sup>3+</sup> )	t	698.5	14316	${}^{5}D_{0}\rightarrow {}^{7}F_{4}(Eu^{3+})$
h	358.7	27878	<sup>5</sup> G <sub>5</sub> ← <sup>7</sup> F <sub>6</sub> (Tb <sup>3+</sup> )	u	756.6	13217	${}^{5}D_{0}\rightarrow {}^{7}F_{5}(Eu^{3+})$
i	361.4	27670	<sup>5</sup> D₄← <sup>7</sup> F₀ (Eu <sup>3+</sup> )	v	804.9	12424	${}^{5}D_{0}\rightarrow {}^{7}F_{6}(Eu^{3+})$
j	369.2	27086	<sup>5</sup> L <sub>10</sub> ← <sup>7</sup> F <sub>6</sub> (Tb <sup>3+</sup> )				
k	376.3	26575	<sup>5</sup> G <sub>6</sub> ← <sup>7</sup> F <sub>6</sub> (Tb <sup>3+</sup> )				
I.	379.5	26351	${}^{5}G_{6}, {}^{5}G_{5} \leftarrow {}^{7}F_{1} (Eu^{3+})/{}^{5}D_{3} \leftarrow {}^{7}F_{6}(Tb^{3+})$				
m	393.6	25407	${}^{5}L_{6} \leftarrow {}^{7}F_{0}$ (Eu <sup>3+</sup> )				

#### Table 2. Assignment of the 4f-4f transitions in the excitation and emission spectra of Pr-psa, Nd-psa, Tb-psa, and EuTb-psa.

(Figure S4), and the calculated luminescence lifetime is  $(0.557 \pm 0.04)$  µs. One important issue in the photophysical characterization of Gd<sup>3+</sup> complexes is that the triplet-state energy of the ligand (<sup>3</sup>T\*) can be calculated on the basis of the lower-wavelength emission edge of the corresponding emission spectrum.<sup>[25]</sup> Gd<sup>3+</sup> complexes provide an optimum situation as the  ${}^{6}P_{7/2}$  state of the Gd<sup>3+</sup> ion lies at too high energy to be populated by most organic linkers. Moreover, the combination of paramagnetic and heavy-atom effects facilitates the probability of ligand phosphorescence. Thus, the triplet-state energy of H<sub>2</sub>psa in Gd-psa was determined to be 24968 cm<sup>-1</sup>, which is similar to that reported for the p-terphenyl-3,3",5,5"tetracarboxylic acid (H<sub>4</sub>ptptc) ligand in a Gd MOF.<sup>[26]</sup> This value successfully explains the ligand sensitization (antenna effect) in Tb-psa as well as the absence of such an effect in the analogous Eu-psa, Sm-psa,<sup>[19]</sup> and Nd-psa compounds. For efficient energy transfer, the energy gap between the triplet-state energy of the

ligand and the resonant level of the trivalent lanthanide ions,  $\Delta(^{3}T^{*}-Ln^{3+}),^{[27]}$  must be in the 4000  $\pm$  500 cm $^{-1}$  range. The corresponding energy values of the resonant level are 32066 (Gd $^{3+}$ ), 17850 (Sm $^{3+}$ ), 19020 (Eu $^{3+}$ ), and 21000 cm $^{-1}$  (Tb $^{3+}$ ); therefore, an energy-transfer process is feasible in the latter case.

The emission of Pr-psa was monitored at  $\lambda = 610.5$  nm (16380 cm<sup>-1</sup>), and the excitation wavelength was varied between  $\lambda = 250$  and 500 nm to record an excitation spectrum (Figure 6, top). The peaks labeled a-c could be assigned to transitions within the 4f shell of the Pr<sup>3+</sup> ion (see Table 2). A few peaks could not be assigned to any known Pr<sup>3+</sup> transitions, and the broad band with a maximum at  $\lambda = 378.5$  nm was assigned to the  $\pi \rightarrow \pi^*$  transition of the psa ligand. The intensity of this peak is weaker than that of peak "b". Therefore, direct 4f-4f transitions are indicated rather than a contribution of energy transfer from  $\pi \rightarrow \pi^*$  transitions. Upon excitation at  $\lambda = 466$  nm







Figure 4. Excitation (top) and emission (bottom) spectra of Gd-psa.



Figure 5. CIE 1931 chromaticity diagram showing the (x, y) color coordinates for the Ln-psa compounds after irradiation with the corresponding excitation wavelength: (0.31, 0.62) for Tb-psa, (0.26, 0.30) for Gd-psa, (0.49, 0.50) for Pr-psa, and (0.62, 0.35) for EuTb-psa. The picture shows selected samples before and after UV irradiation.

(21459 cm<sup>-1</sup>) in the <sup>1</sup>I<sub>6</sub>, <sup>3</sup>P<sub>1</sub> $\leftarrow$ <sup>3</sup>H<sub>4</sub> transitions, the sample shows the typical narrow Pr<sup>3+</sup> emission peaks (see Figure 6, bottom). The peaks labeled d–h are assigned to the corresponding electronic transitions in Table 2. No peaks are visible in the NIR range for this sample. Upon excitation at  $\lambda = 466$  nm with a pulsed light source, the decay curve of the emission at  $\lambda =$ 610.5 nm can be satisfactorily fitted with a single exponential function with  $\tau_{obs} = (1.908 \pm 0.004) \mu s$ . The luminescence decay profile is given in Figure S5. In spite of the adequate proximity between the <sup>3</sup>T\* state of the ligand and the <sup>3</sup>P<sub>0</sub> resonant level of the Pr<sup>3+</sup> ions (20700 cm<sup>-1</sup>), a small  $\tau_{obs}$  value along with a poor luminescence intensity were obtained in comparison with those of the other visible emitters of this series of Ln-psa compounds. For this reason, it can be assumed that part of the energy is lost through nonradiative processes such as back energy transfer, as was seen in [Pr-(1,4-BDC)] (1,4-BDC = 1,4-benz-enedicarboxylate).<sup>[28]</sup>

#### **Optical Temperature-Sensing Behavior of EuTb-psa**

The excitation spectra of EuTb-psa at seven different temperatures (from cryogenic to room temperatures) were recorded in the  $\lambda$  = 250–450 nm range, and the emission was monitored at  $\lambda = 615.8$  nm (16239 cm<sup>-1</sup>, Figure 7, a). All of the peaks in the spectra can be assigned to transitions within the 4f shells of the Eu<sup>3+</sup> or Tb<sup>3+</sup> ions. No significant differences are observed in the excitation spectra with increasing temperature. Upon excitation at  $\lambda = 378$  nm (26455 cm<sup>-1</sup>) in the temperature range 13.5–313.5 K, the sample shows only the typical narrow Eu<sup>3+</sup> emission peaks; 378 nm was chosen as the excitation wavelength because the Eu<sup>3+</sup> and Tb<sup>3+</sup> ions both absorb at this wavelength. The assignment of the excitation and emission peaks to the corresponding electronic transitions according to Carnall et al.<sup>[29]</sup> is displayed in Table 2. At 313.5 K, the excitation–emission spectra and chromaticity of EuTb-psa (x, y = 0.62, 0.35) are quite similar to those of the analogous Eu-psa (x, y = 0.66, 0.34) and EuGd-psa (x, y = 0.66, 0.34,<sup>[20]</sup> see Figures S6, S7 and Table S1). At the lowest temperature, two additional very weak peaks assigned to the  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$  and  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transitions of the Tb<sup>3+</sup> ion (Figure 7, b) are identified. The presence of strong Tb<sup>3+</sup> transition peaks in the excitation spectrum and only two Tb<sup>3+</sup> peaks in the emission spectrum at 13.5 K suggests an efficient transfer of energy from the excited 4f states of the Tb<sup>3+</sup> ions to the corresponding Eu<sup>3+</sup> ones. This process is known as metal-to-metal charge transfer (MMCT) and was also observed for mixed EuTb MOFs in which the Tb<sup>3+</sup> ions were sensitized through template molecules.<sup>[30]</sup> Other examples of MMCT were described for codoped Gd MOFs with luminescence colors tunable by controlled variation of the atomic ratio of the Eu/Tb dopants and 4,4'-bipyridine<sup>[31]</sup> or 3,5-disulfobenzoate<sup>[8]</sup> ligands.

As can be observed in the inset of Figure 7 (b), the  ${}^{5}D_{4} \rightarrow {}^{7}F_{6}$ and  ${}^{5}D_{4} \rightarrow {}^{7}F_{5}$  Tb<sup>3+</sup> transitions mentioned above become so weak with increasing temperature that they cannot be detected



Figure 6. Excitation spectrum monitored at  $\lambda$  = 610.5 nm (top) and emission spectrum ( $\lambda_{exc}$  = 466 nm) (bottom) of Pr-psa.







Figure 7. (a) Excitation and (b) emission spectra at different temperatures, (c) thermal evolution of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  hypersensitive transition, and (d) relative intensity as function of temperature for EuTb-psa.

in the subsequent spectra, and only the Eu<sup>3+</sup> emission peaks are distinguished.

Temperature sensing with thermographic phosphors is usually discriminated in decay-time and intensity algorithms.<sup>[32]</sup> The decay-time methods exploit the temperature dependence of the lifetime of an emitting level and the intensity ratio of one or more transitions to detect temperature.<sup>[33]</sup> The principal advantage of using the ratio between the luminescence intensities ( $l_1/l_2$ ) of two transitions as a measurement of absolute temperature is that one single emission spectrum contains all the information to compute it.<sup>[34]</sup>

To study the thermal-sensor activity of lanthanide-based materials, some authors have employed a particular 4f-4f hypersensitive transition<sup>[35]</sup> or both the intensity ratio and the lifetime<sup>[36]</sup> as temperature-dependent parameters. The luminescence performance of EuTb-psa towards temperature was studied both in terms of intensity ratio (1/10, 10 is the intensity of the hypersensitive transition at the lowest temperature) and  $\tau$ . Furthermore, from Figure 7 (c), it can be assessed that the intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition decreases by more than 60 % when the temperature increases from 13.5 to 313.5 K. Moreover, the relationship between the relative intensity  $(I/I_0)$  and temperature follows the first-order exponential decay formula:  $I/I_0$  = 0.339 + 0.853 exp(-T/51.276) (see Figure 7, d). The R value, defined as  $I({}^{5}D_{0} \rightarrow {}^{7}F_{2})/I({}^{5}D_{0} \rightarrow {}^{7}F_{1}), [{}^{4b]}$  is an acceptable approximation of the electronic environments of Eu<sup>3+</sup> ions in diverse inorganic compounds. As can be seen in Figure S8, it remains practically unchanged throughout the temperature range 63.5-313.5 K. In other words, we found it to be almost independent of the temperature; therefore, the geometric structure of EuTbpsa should be retained in the studied temperature range. One important variable for a thermal sensor is the sensitivity (S) defined as  $(\partial / \partial T) / I_0$ .<sup>[37]</sup> The S value of EuTb-psa was determined

to be 0.366 % K<sup>-1</sup> from an average slope calculated from the points at 13.5 and 313.5 K. This value is comparable to those obtained by Cui et al.<sup>[12a]</sup> for  $[(Tb_{0.9931}Eu_{0.0069})_2(DMBDC)_3-(H_2O)_4]$ -DMF·H<sub>2</sub>O (0.38 % K<sup>-1</sup>; DMBDC = 2,5-dimethoxy-1,4-benzenedicarboxylate; DMF = *N*,*N*-dimethylformamide) and Carlos et al.<sup>[13a]</sup> for  $[Tb_{0.99}Eu_{0.01}(1,4-BDC)_{1.5}(H_2O)_2]$  (0.31 % K<sup>-1</sup>). The performance of EuTb-psa is compared with those of other intensity-based MOF thermal sensors in Table 3. In addition, the lifetime drops rapidly as the temperature increases, and  $\partial \tau/\partial T$  is -0.14 % K<sup>-1</sup> in the studied temperature range (see Figure 8, top).

As can be seen from Figure 8 (bottom), the nonradiative deexcitation probability of the  ${}^{5}D_{0}$  level could be successfully fitted by the Mott–Seitz model, which was previously used to explain the deactivation by NH groups in a Eu<sup>3+</sup>/Tb<sup>3+</sup> codoped hybrid material<sup>[38]</sup> and relates the temperature dependence of the experimental lifetimes ( $\tau_{obs}$ ) through [Equation (1)]

$$1/\tau_{\rm obs} = 1/\tau_0 + k \exp(-\Delta E/k_{\rm B}T) \tag{1}$$

where  $\tau_0$  is the lifetime at T = 0 K, k is the migration energy rate,  $\Delta E$  is the energy gap between the <sup>5</sup>D<sub>0</sub> level and the deexcitation states, and  $k_{\rm B}$  is the Boltzmann constant.

Thus, it can be assumed that the behavior previously described is induced by thermally activated nonradiative mechanisms, that is, the coupling of the  $Ln^{3+}$  excited states to vibrational overtones of OH oscillators, which provide an efficient pathway for energy transfer. As a consequence, it results in a radiationless deactivation of the  $Ln^{3+}$  excited state.<sup>[39]</sup> This observation is supported by the increment of the nonradiative empirical constant ( $k_{nr}$ ) presented in Table 4. The other photophysical parameters for EuTb-psa at different temperatures are also shown.

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MOF type	MOF thermal sensor	Δ <i>T</i> [K]	S [% K <sup>-1</sup> ]	Temperature-dependence algorithm	Reference
EuTb MOF	[(Eu <sub>0.0138</sub> Tb <sub>1.9862</sub> )(DMBDC) <sub>3</sub> (H <sub>2</sub> O) <sub>4</sub> ]•DMF•H <sub>2</sub> O	50-200	0.38	I <sub>Tb</sub> /I <sub>Eu</sub>	[12a]
EuTb MOF	[Eu <sub>0.1</sub> Tb <sub>0.9</sub> (PIA)(HPIA)(H <sub>2</sub> O) <sub>2.5</sub> ]	100-300	3.53	I <sub>Tb</sub> /I <sub>Eu</sub>	[12b]
EuTb MOF	[Eu <sub>0.043</sub> Tb <sub>0.957</sub> (H <sub>2</sub> cpda)(Hcpda)(H <sub>2</sub> O)]•6H <sub>2</sub> O	40-300	not reported	I <sub>Tb</sub> /I <sub>Eu</sub>	[12c]
Eu-MOF⊃guest	[Eu <sub>2</sub> (QPTCA)(NO <sub>3</sub> ) <sub>2</sub> (DMF) <sub>4</sub> ]•(EtOH) <sub>3</sub> ⊃perylene	293-353	1.28	I <sub>liq</sub> /I <sub>Eu</sub>	[12d]
EuTb MOF	$[Eu_{0.8}Tb_{1.2}(psa)_3(H_2O)]$	13.5-313.5	0.366	I <sub>Eu</sub> /I <sub>o</sub>	this study
EuTb MOF	[Eu <sub>0.01</sub> Tb <sub>0.99</sub> (BDC) <sub>1.5</sub> (H <sub>2</sub> O) <sub>2</sub> ]	298-318	0.31	I <sub>Tb</sub> /I <sub>Eu</sub>	[13a]
EuTb MOF	[Eu <sub>0.086</sub> Tb <sub>0.914</sub> (PDA) <sub>3</sub> (H <sub>2</sub> O)]•2H <sub>2</sub> O	10-325	5.96	I <sub>Tb</sub> /I <sub>Eu</sub>	[13b]
EuTb MOF	[Eu <sub>0.102</sub> Tb <sub>0.898</sub> (notpH <sub>4</sub> )(NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> ]•8H <sub>2</sub> O	20-300	3.9	I <sub>Tb</sub> /I <sub>Eu</sub>	[13c]
EuGd MOF and	$[Ln_{0.14}Gd_{6.86}(3,5-DSB)_4(OH)_9(H_2O)_{15}]$ •4H <sub>2</sub> O (Ln = Eu or	10-300	32	$I_{\text{triplet}}/I_{\text{Eu}}$ and $I_{\text{triplet}}/I_{\text{Tb}}$	[14a]
TbGd MOF	Tb)				
EuTb MOF	[Eu <sub>0.01</sub> Tb <sub>0.99</sub> (hfa) <sub>3</sub> (dpbp)]	200-450	0.83	I <sub>Eu</sub> /I <sub>Tb</sub>	[14b]
Eu <sup>3+</sup> ,Tb <sup>3+</sup> @MOF	[Eu <sup>3+</sup> ,Tb <sup>3+</sup> @In(OH)(bpydc)]	283-333	4.97	I <sub>Tb</sub> /I <sub>Fu</sub>	[14c]
EuTb MOF	[Eu <sub>0.2</sub> Tb <sub>0.8</sub> (L1) <sub>2</sub> (COO)(H <sub>2</sub> O) <sub>2</sub> ]•H <sub>2</sub> O	40-300	0.17	I <sub>Tb</sub> /I <sub>Eu</sub>	[14d]
EuTb MOF	[Eu <sub>0.01</sub> Tb <sub>0.99</sub> (BDC) <sub>0.5</sub> (DSTP)]•2H <sub>2</sub> O	77–275	3.9	I <sub>Tb</sub> /I <sub>Fu</sub>	[14e]
EuTb MOF	[Eu <sub>0.001</sub> Tb <sub>0.999</sub> -BPDC-ad]	100-300	1.23	log(I <sub>Tb</sub> /I <sub>Eu</sub> )	[14f]
Eu <sup>3+</sup> @MOF	$Eu^{3+}@[Zr6(\mu^{3}-O)_{4}(OH)_{4}(bpydc)_{12}]$	293-353	2.99	I <sub>lia</sub> /I <sub>Eu</sub>	[14g]
EuTb MOF	[Eu <sub>0.13</sub> Tb <sub>1.87</sub> (HL2) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]-5.5H <sub>2</sub> O	4–50	31	I <sub>Tb</sub> /I <sub>Eu</sub>	[14h]

Table 3. Operating temperature range ( $\Delta T$ ), maximum sensitivity (S), and temperature-dependence algorithms<sup>[a]</sup> for selected thermal sensors based on MOFs.

[a] hfa = hexafluoroacetylacetonato; dpbp = 4,4'-bis(diphenylphosphoryl)biphenyl; H<sub>3</sub>cpda = 5-(4-carboxyphenyl)-2,6-pyridinedicarboxylic acid; QPTCA = 1,1' :4',1'':4'',1'''-quaterphenyl-3,3''',5,5'''-tetracarboxylate; 3,5-DSB = disulfobenzoate; notpH<sub>6</sub> = 1,4,7-triazacyclononane-1,4,7-triyl-tris(methylenephosphonic acid); bpydc = 2,2'-bipyridine-5,5'-dicarboxylate; L1 = 1,3-bis(4-carboxyphenyl)imidazolium; L2 = 5-hydroxy-1,2,4-benzenetricarboxylate; H<sub>2</sub>DSTP = 2,4-(2,2':6',2''terpyridin-4'-yl)benzenedisulfonic acid; OA = oxalate;  $I_{Tb} = {}^{5}D_{4} \rightarrow {}^{7}F_{5}$  transition (Tb<sup>3+</sup>);  $I_{Eu} = {}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition (linker or guest molecule);  $I_{o}$  = intensity of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition (Eu<sup>3+</sup>) at the lowest temperature;  $I_{triplet}$  = triplet ligand phosphorescence.



Figure 8. Top: Temperature dependence (13.5–313.5 K) of the Eu<sup>3+ 5</sup>D<sub>0</sub> lifetimes (black stars) in EuTb-psa. The red line corresponds to the best fit of the experimental <sup>5</sup>D<sub>0</sub> lifetimes using the Mott–Seitz temperature dependence [Equation (1)]. Bottom: Luminescence decay traces at different temperatures.

Table 4. Photophysical parameters of EuTb-psa at different temperatures.

T [K]	$I_{\rm tot}/I_{\rm MD}$	$\frac{1/\tau_{\rm r}=k_{\rm r}}{[{\rm s}^{-1}]}$	$ au_{r}$ [s]	$k_{exp}$ [s <sup>-1</sup> ]	k <sub>nr</sub> [s <sup>-1</sup> ]	$ au_{obs}$ [ms]	Q <sub>Ln</sub> [%]
13.5	8.71	191	0.00522	928	737	1.077(8)	20.6
63.5	7.72	170	0.00589	1003	833	0.996(10)	16.9
113.5	8.28	182	0.00549	1071	889	0.934(7)	16.9
163.5	7.91	174	0.00575	1108	935	0.902(20)	15.7
213.5	7.49	165	0.00607	1131	967	0.884(5)	14.6
263.5	7.31	161	0.00622	1132	972	0.883(4)	14.18
313.5	7.59	167	0.00599	1196	1029	0.836(9)	13.94

Another important parameter for Eu compounds is the intrinsic quantum yield ( $Q_{Eu}$ ), which gives an approximation of the efficiency of the luminescence process.<sup>[40]</sup> Nevertheless, the study of this parameter as a function of temperature for Eu MOFs has not been reported previously. The  $Q_{Eu}$  values were calculated from Equations (2), (3), and (4).

$$Q_{\rm Eu}$$
 [%] = 100 $k_{\rm r}/(k_{\rm r} + k_{\rm nr})$  or  $Q_{\rm Eu}$ = 100 $k_{\rm r}/k_{\rm exp}$  (2)

$$k_{\rm r} = (1/\tau_{\rm r}) = A_{\rm MD,0} n^3 (I_{\rm tot}/I_{\rm MD})$$
(3)

$$k_{\rm exp} = 1/\tau_{\rm obs} \tag{4}$$

Here,  $A_{MD,0}$  is the spontaneous emission probability of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition (14.65 s<sup>-1</sup>), *n* is the refractive index (1.5),  $I_{tot}$  is the total integrated emission of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J = 0-6) transitions, and  $I_{MD}$  is the integrated emission of the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition. Haquin et al. gave an example of implementing the intrinsic quantum yield to study the intermetallic quenching phenomena in mixed carboxylate Ln MOFs (Eu, Tb, and Eu/Tb).<sup>[41]</sup>

The variation of  $Q_{Eu}$  [%] is shown in Figure 9 for the 13.5–313.5 K temperature range, in which it was possible to identify



Figure 9. Variation of Q<sub>Eu</sub> [%] with temperature for EuTb-psa.

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an adjustable temperature zone (100–313.5 K) with a first-order exponential equation (denoted by a blue ellipse) with the following relationship:  $Q_{Eu}$  [%] = 13.491 + 12.033 exp(-*T*/92.645).

The photophysical characterization data of all of the Ln-psa compounds at room temperature are shown in Table 5. According to this data, it is possible to establish criteria for the design of functional luminescent materials. Owing to their strong luminescence, pure red or green colors, and long lifetimes, Eu<sup>3+</sup>and Tb<sup>3+</sup>-based MOFs (Eu-psa, Tb-psa, EuTb-psa, EuGd-psa)<sup>[19]</sup> are promising candidates for the elaboration of photoluminescent sensors for a variety of chemical entities (such as anions, small molecules, and explosives)<sup>[42]</sup> with the hypersensitive transitions as sensing algorithms. Furthermore, the controlled doping of neutral matrixes, usually Gd<sup>3+</sup>- or Y<sup>3+</sup>-based compounds, with Eu<sup>3+</sup> and Tb<sup>3+</sup> ions can lead to materials with fewer nonradiative processes such as concentration guenching. The heterometallic systems EuGd-psa and EuTb-psa have increased experimental lifetimes in comparison with that of Eupsa as well as a decrease in their nonradiative constants (the corresponding  $k_{nr}$  value for Eu-psa is 1318 s<sup>-1</sup>).<sup>[20]</sup> The  $\tau_{obs}$  values of the Eu MOFs are shown in Table 5. Applications that require fast response such as scintillation<sup>[43]</sup> (the emission of light during short times) and displays involve small lifetime values. In this sense, Pr-psa, Nd-psa, Gd-psa, or Sm-psa could be employed to elaborate devices with such characteristics. A simplified energy diagram that summarizes the different radiative processes studied in this family of compounds is presented in Figure 10.

Table 5. Summary of the photophysical features of Ln-psa compounds at room temperature.

Ln-psa	$ au_{ m obs}$	Q <sub>Ln</sub> [%]	Emission color	Reference
Pr-psa	1.908(4) μs	-	yellow	this study
Nd-psa	0.426(7) µs	-	red (NIR)	this study
Sm-psa	3.5(01) µs	-	yellow-orange	[20]
Eu-psa	0.587(20) ms	22.6	red	[20]
EuGd-psa	0.872(9) ms	32.5	red	[20]
Gd-psa	0.557(40) μs	-	green-blue	this study
EuTb-psa	0.836(9) ms	13.9	red	this study
Tb-psa	1.625(8) ms	-	green	this study



Figure 10. Simplified energy diagram showing the most important  ${}^{25+1}L_{J}$  energy levels of the Pr<sup>3+</sup>, Nd<sup>3+</sup>, Sm<sup>3+</sup>, Eu<sup>3+</sup>, and Gd<sup>3+</sup> ions in the Ln-psa series (ET = energy transfer).

#### **Catalytic Study**

CSRs are important carbon–carbon bond-forming processes that are catalyzed by Lewis acids and Lewis acids/bases that can be used in homogeneous, heterogeneous, or enzymatic catalysis. MOFs are important heterogeneous catalysts for Lewis acid reactions owing to their unique reactivity and selectivity under mild reaction conditions.<sup>[44]</sup> Rare-earth and indium polymeric frames (RPFs and InPF) are good Lewis acid catalysts for CSRs under solvent-free conditions.<sup>[45]</sup>

The catalytic activities of several members of the Ln-psa series (Ln = Sm, Eu, Gd, Tb, Eu/Gd, and Eu/Tb) were tested in the one-pot CSR of benzaldehyde (BA) with TMSCN under mild conditions and low catalyst loads (see Scheme 1). As was mentioned above, all of these compounds belong to an isostructural series, and we previously reported the structural features of Sm-psa, Eu-psa, and EuGd-psa.<sup>[20]</sup>



Scheme 1. CSR of aldehydes with TMSCN.

Gd-psa shows the highest activity with a turnover frequency (TOF) of 112 h<sup>-1</sup> (TOF: the number of molecules reacting per active site in unit time,<sup>[46]</sup> calculated as mmol substrate/mmol catalyst per unit time) followed by EuGd-psa, EuTb-psa, Sm-psa, Tb-psa, and Eu-psa with values of 104, 103, 96, 88, and 84  $h^{-1}$ , respectively. The presence of different metal centers does not influence the reactivity significantly. The Lewis acidity of lanthanide metals is closely related to their ionic radii; in some cases, reactions that involve acid catalysts are well-defined because the reactivity increases with a decrease of the ionic radii. In our case, the catalytic performance of the Ln-psa compounds does not fit this trend. The corresponding kinetic profiles are depicted in Figure 11, and a graphical comparison of the TOF values is presented in Figure S9. The negative results for other products indicate that reactions such as aldol condensation and aldehyde acetalization do not occur and demonstrate the high selectivities of these catalysts.



Figure 11. Kinetic profiles of Ln-psa for the CSR. The black curve shows the kinetic profile of the reaction system without catalyst.

These results allow us to propose the mechanism shown in Scheme 2, which can be explained as consistent with the following steps: (1) contact between the metallic centers and the aldehyde molecules through a coordination interaction involving the oxygen atom of the carbonyl group and the lanthanide ion leads to a positive charge on the carbonyl carbon atom





(carbon activation), (2) nucleophilic attack of the TMSCN is favored by the carbon activation, and (3) molecular rearrangement results in the formation of the main product.



Scheme 2. Proposed mechanism for Ln-psa-catalyzed cyanosilylation of aldehydes.

According to the crystallographic data, which determine the presence of two metal centers with different coordination numbers in the asymmetric unit ([LnO<sub>8</sub>] and [LnO<sub>9</sub>]), it is possible to propose that the reaction mechanism occurs through the activation of the carbonyl group by unsaturated metallic centers, as was described previously for similar compounds.<sup>[45]</sup>

The effect of different substituents on the aromatic ring of the carbonyl compound was explored by studying the EuTbpsa-catalyzed reaction; to this end, *p*-tolualdehyde and 4chlorobenzaldehyde were selected as substrates (see Figure 12). The influence of the substituent was analyzed through the TOF values and the time needed to reach 100 % conversion. Regarding the conditions required for the first step of the proposed mechanism to occur, a lower Lewis basic character of the carbonylic oxygen atom of the substrate or the presence of voluminous substituents able to obstruct the interaction with the lanthanide ions would be disadvantageous for the desired process. The calculated TOF values are 104 and 107 h<sup>-1</sup> for 4chlorobenzaldehyde and *p*-tolualdehyde, respectively. The cor-



Figure 12. Kinetic profiles of CSRs with EuTb-psa as the catalyst and different substrates.

responding kinetic curves clearly show that the reaction is significantly faster with *p*-tolualdehyde as the substrate; therefore, both steric (Cl volume < CH<sub>3</sub> volume) and electronic factors play important roles in the resulting behavior. Similar results were evidenced when InPFs were used as heterogeneous catalysts in CSR reactions.<sup>[45c]</sup>

#### **Recycling Test**

To analyze if Ln-psa compounds behave as true heterogeneous catalysts, Sm-psa was selected for recyclability experiments with the conditions described in the Experimental Section. According to the obtained results, the catalytic activity remained unaltered after the reactions. The catalyst was analyzed by powder XRD (PXRD), and no appreciable structural changes with respect to the pattern recorded before three catalytic cycles were detected (see Figures 13 and S10).



Figure 13. Kinetic profiles of three consecutive CSR cycles with Sm-psa as catalyst.

#### **Green-Chemistry Parameters**

Owing to the new trends in modern chemistry, Anastas and Warner<sup>[47]</sup> introduced the concept of Green Chemistry to overcome the health and environmental problems generated by the chemical industry through the design of innovative and environmentally friendly chemical reactions that lead to cleaner processes. Basically, this concept emphasizes the efficient use of the starting materials (preferably recycled ones) and minimization of waste generation as well as the use of toxic or hazardous reagents in the manufacture and application of chemicals. In this context, a chemical process can be evaluated by calculating the so-called green parameters.<sup>[48]</sup> Thus, the atomic economy (AE), mass intensity (MI), reaction mass efficiency (RME), and carbon efficiency (CE) parameters have been proposed as a measure of environmental sustainability in terms of minimizing the theoretical amount of waste. The green metrics, ideally AE  $\approx$  100 %, MI  $\approx$  1, RME  $\approx$  100 %, and CE  $\approx$  100 %, were calculated through the procedures reported in ref.<sup>[47]</sup>, and their definitions can be found in the Supporting Information (Equations 1-3). According to the results obtained for six homo- and heterometallic Ln-psa compounds (see Table 6), Gd-psa exhibits the highest degree of greenness in the catalytic performance.



Table 6. Green parameters calculated for the CSR with Ln-psa as catalysts.<sup>[a]</sup>

Ln-psa	МІ	RME [%]	CE [%]
Sm-psa	7.1	77.1	81.1
Eu-psa	8.1	67.4	70.9
Gd-psa	6.0	90.4	95.1
Tb-psa	7.7	70.9	74.6
EuGd-psa	6.5	84.0	88.4
EuTb-psa	6.6	82.8	87.2

[a] The AE values have been omitted as they are identical for all of the compounds (99.8 %).

## Conclusions

A heterometallic MOF, EuTb-psa, exhibits red luminescence and was obtained by solvothermal synthesis. Most of the observed transitions in the spectrum at 13.5 K could be identified with those from Eu<sup>3+</sup> ions, whereas the Tb<sup>3+</sup> emission is hardly seen and gradually disappears with increasing temperature to 313.5 K. Thus, the Tb<sup>3+</sup> luminescence is efficiently quenched by a mechanism of metal-to-metal charge transfer (MMCT) from the Tb<sup>3+</sup> to Eu<sup>3+</sup> centers; consequently, the luminescence is practically based on Eu<sup>3+</sup> ions. The thermal-sensor activity of EuTb-psa was evaluated in the range 13.5–313.5 K as a function of the emission intensity of the hypersensitive  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition and the luminescence lifetime, which yielded sensitivities of ca. 0.366 % K<sup>-1</sup> and -0.14 % K<sup>-1</sup>, respectively. Moreover, the variation of the intrinsic quantum yield with temperature for a Eu-containing MOF has also been reported. The PL features of Pr-psa, Nd-psa, Tb-psa, and Gd-psa were also studied, and the triple-state energy (<sup>3</sup>T\*) of the H<sub>2</sub>psa ligand could be estimated through the emission spectrum of the latter MOF; therefore, the sensitization observed for Tb-psa could be explained. The lighter members of the lanthanide series exhibit shorter lifetime values, whereas the longer values found for the heavier ions make them suitable for the construction of optical devices of different types.

Furthermore, the isostructural Ln-psa series with  $Ln^{3+} = Sm$ , Eu, Gd, Tb, Eu/Gd, and Eu/Tb has been tested in heterogeneous catalysis for the CSR of benzaldehyde without prior catalyst activation. The Lewis acidic nature of the MOFs allowed their use in CSRs, and the highest activities were obtained for Gd-psa followed by the heterometallic MOFs. The mechanism can be explained by an activation of the carbonyl substrate by the metallic centers. The use of low catalyst loading (5 mmol-%) and the recyclability of these phases make these materials suitable candidates for applications in green chemistry.

Finally, this work confirms the multifunctional character of this Ln-psa series, which is principally derived from the existence of active Lewis acid sites and emissive metal centers.

## **Experimental Section**

**EuTb-psa:** EuTb-psa was prepared by a solvothermal method. 2-Phenylsuccinic acid (2 mmol) and each lanthanide chloride (0.75 mmol) were dissolved in a mixture of distilled water (30 mL) and ethanol (30 mL). The pH was adjusted to 3–3.5 with 4,4'-bipyridine (2 mmol). The solution was heated at 160 °C in a 120 mL Teflon-lined Parr bomb for 3 d, and then the reactor was cooled



immediately to room temperature. Colorless plate-shaped crystals suitable for single-crystal X-ray diffraction were obtained (see Figure S11). The Eu<sup>3+</sup>/Tb<sup>3+</sup> molar ratio (40.07/59.93) in EuTb-psa was determined by inductively coupled plasma mass spectrometry (ICP-MS) and energy-dispersive X-ray spectroscopy (EDS, see inset of Figure S11); 45 % yield based on Eu. Eu<sub>0.8</sub>Tb<sub>1.2</sub>C<sub>30</sub>H<sub>26</sub>O<sub>13</sub> (906.75): calcd. C 39.72, H 2.86, O 22.95; found C 40.03, H 2.71, O 23.21.

 $[Pr_2(C_{10}H_8O_4)_3(H_2O)]$  (Pr-psa),  $[Nd_2(C_{10}H_8O_4)_3(H_2O)]$  (Nd-psa),  $[Tb_2(C_{10}H_8O_4)_3(H_2O)]$  (Tb-psa), and  $[Gd_2(C_{10}H_8O_4)_3(H_2O)]$  (Gd-psa) were prepared by the procedure that we reported previously.<sup>[19]</sup> and microcrystalline powders were obtained. The stoichiometries of Pr-psa, Nd-psa, Tb-psa, and Gd-psa were confirmed by thermal and elemental analyses (see Table S2); 41, 48, 43, and 35 % yields based on Pr, Nd, Tb, and Gd, respectively.  $Pr_2C_{30}H_{26}O_{13}$  (876.33): calcd. C 41.10, H 2.96, O 23.75; found C 41.22, H 2.88, O 23.71. Nd<sub>2</sub>C<sub>30</sub>H<sub>26</sub>O<sub>13</sub> (883.00): calcd. C 40.79, H 2.94, O 23.57; found C 40.72, H 2.89, O 23.48. Tb<sub>2</sub>C<sub>30</sub>H<sub>26</sub>O<sub>13</sub> (912.37): calcd. C 39.48, H 2.85, O 22.81; found C 39.63, H 2.79, O 23.01.  $Gd_2C_{30}H_{26}O_{13}$  (909.02): calcd. C 39.62, H 2.86, O 22.89; found C 39.71, H 2.77, O 23.10. The isostructural nature of these phases and their purity were confirmed by comparison of their respective PXRD patterns with that simulated for EuTb-psa (see Figure S12).

Single-Crystal Structure Determination: A single crystal of EuTbpsa was mounted on an Agilent Gemini A four-circle kappa-diffractometer equipped with an Enhance Mo X-ray source operated at 2 kW power (50 kV, 40 mA) to generate Mo- $K_{\alpha}$  radiation ( $\lambda$  = 0.71073 Å) and an Agilent EOS area detector. The diffraction data were collected over a sphere of reciprocal space in a combination of  $\varphi$  and  $\omega$  scans to reach a resolution of 0.8 Å (29.2° in  $\theta$ ) with the CrysAlisPro software suite (each exposure of 112 s covered 1° in  $\omega$ ). The unit-cell dimensions were determined by a least-squares fit of reflections with  $l > 2\sigma(l)$ . A semiempirical absorption and scale correction based on equivalent reflections was performed with SAD-ABS.<sup>[49]</sup> Space-group determinations were performed with XPREP.<sup>[50]</sup> The structures were solved by direct methods and refined by anisotropic full-matrix least-squares techniques with SHELXL-20.<sup>[51]</sup> The crystal data and a summary of the conditions for data collection and structure refinement are given in Table 1. The hydrogen atoms of the coordinated water molecule were refined with constraints. All calculations were performed with the following: SMART software for data collection, the SAINT plus program<sup>[52]</sup> for integration and scale correction of data, SHELXTL<sup>[47]</sup> to resolve and refine the structure and to prepare material for publication, and ATOMS<sup>[53]</sup> and MERCURY 2.0<sup>[54]</sup> for molecular graphics.

CCDC 1412860 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Powder X-ray Diffraction:** The X-ray powder diffractograms were obtained with a Rigaku D-MAX-IIIC diffractometer with Cu- $K_{\alpha}$  radiation ( $\lambda = 1.5418$  Å) and NaCl and quartz as external calibration standards. The best-counting statistics were achieved with a scanning step of 0.02° between 5° and 60° Bragg angles with an exposure time of 5 s per step.

**Thermal Analysis:** Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed with Shimadzu TGA-51 and DTA-50 apparatus under flowing air at 50 mL min<sup>-1</sup> at a heating rate of 10 °C min<sup>-1</sup> (see Figures S13–17). X-ray powder diffraction was applied for further characterization of the pyrolysis products.

**Solid-State Luminescence Measurements**: The steady-state and time-resolved luminescence measurements were performed with an Edinburgh Instruments FLSP920 spectrometer with a 450 W xe-



non lamp as the steady-state excitation source and a 60 W pulsed xenon lamp as the time-resolved excitation source (operating at a pulse frequency of 100 Hz). The emission was detected by a Hamamatsu R928P PMT photomultiplier tube for the visible range and a Hamamatsu R5509-72 photomultiplier operating at 193 K for the NIR range. The excitation spectra were corrected for the emission profile of the xenon lamp, whereas the emission spectra were corrected for the detector response curve. All measurements were performed at a step size of 0.1 nm. For the Gd-psa and Nd-psa samples, the time-resolved measurements were performed with a Continuum® Surelite I laser (450 mJ at 1064 nm) operating at a repetition rate of 10 Hz and with the third harmonic (355 nm) as the excitation source and the detectors mentioned above. For Pr-psa, the timeresolved measurements were performed with a Continuum® Surelite I-10 Nd:YAG-pumped OPO Plus laser system tuned to 466 nm and the visible photomultiplier detector mentioned above. The temperature of the measurements for EuTb-psa was controlled with an ARS closed-cycle cryostat in the temperature range 13.5-313.5 K (measurements were taken every 50 K). In all cases, the corresponding lifetime values were calculated in triplicate, and the standard errors were added.

**Catalytic study**: A typical procedure for the cyanosilylation of benzaldehyde was as follows: Into a Pyrex-glass screw-cap vial, the catalyst (10 mg, 5 mmol-%) was placed with dichloromethane (DCM, 1 mL) as the solvent at room temperature. After that, BA (0.026 mL) and TMSCN (0.05 mL) in a 1:1.5 molar ratio were added. The reaction mixture was stirred constantly at 800 rpm under a N<sub>2</sub> atmosphere. The conversion of BA and the product yield were periodically determined by GC analysis. When the reaction was complete, the catalyst was separated through the centrifugation of the reaction mixture. The identities of all products were confirmed by comparison of their GC retention times and GC–MS analysis. GC analysis was performed with a Konik HRGC 400 B gas chromato-graph-mass spectrometer equipped with a cross-linked 95 % dimethyl–5 % diphenyl polysiloxane (Teknokroma TRB-5MS) column of 30 m length.

**FTIR Spectroscopy**: The FTIR spectra (Figure S18) were recorded with a Nicolet Protégé 460 spectrometer in the  $\tilde{v} = 4000-225$  cm<sup>-1</sup> range with 64 scans and a spectral resolution of 4 cm<sup>-1</sup> by the KBr pellet technique.

**Supporting Information** (see footnote on the first page of this article): powder XRD patterns, TG-DTA curves, FTIR spectra, and luminescence decay traces.

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