Supplementary Information

LAYERED EXFOLIABLE CRYSTALLINE MATERIALS BASED ON Sm-, Eu- AND Eu/Gd- 2-PHENYLSUCCINATE FRAMEWORKS. CRYSTAL STRUCTURE, TOPOLOGY AND LUMINESCENCE PROPERTIES

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Content

1. Synthesis

Synthesis of psa-MOFs: All reagents were purchased at high purity (AR grade) from Fluka (2-phenylsuccinic acid), Strem Chemicals ($SmCl_3.6H_2O$ 99.9%, $GdCl_3.xH_2O$ 99.9% and $EuCl_3.6H_2O$ 99.9%). All of them were used without further purification.

$[Sm_2(C_{10}H_8O_4)_3(H_2O)]$ and $[Eu_2(C_{10}H_8O_4)_3(H_2O)]$: $SmCl_3 \cdot 6H_2O$ (0.365 g, 1 mmol) was dissolved in distilled water (30 mL) and then added to an ethanolic solution containing phenylsuccinic acid (H_2psa, 0.194 g, 1 mmol, 30 mL) whilst stirring; the resulting pH was raised to 4.5 by 4,4'-bipyridine (0.156 g, 1 mmol) addition. After stirring for 30 minutes, the mixture was sealed in a teflon-lined steal bomb and heated at 160 °C for 3 days, then cooled with water. After filtration, the product was washed with distilled water and dried at room temperature. The same method of preparation was carried out for the synthesis of **Eu-psa**. The starting materials $EuCl_3 \cdot 6H_2O$ (0.366g), H_2psa (0.194g), 4,4'-bipyridine (0.156g) (with the same relation), were introduced into H_2O:ethanol mixture (30mL:30mL). In both cases a large number of rombohedric-shaped crystals suitable for a crystallographic study were obtained.

$[Eu_{1.11}Gd_{0.89}(C_{10}H_8O_4)_3(H_2O)]$: $EuCl_3 \cdot 6H_2O$ (0.276g, 0.75 mmol) and $GdCl_3 \cdot H_2O$ (0.197g, 0.75 mmol) were dissolved in distilled water (30 mL) and then added to an ethanolic solution containing phenylsuccinic acid (H_2psa, 0.38 g, 2 mmol, 30 mL) whilst stirring; the resulting pH was raised to 4.5 by 4,4'-bipyridine (0.312 g, 2 mmol) addition. After stirring for 30 minutes, the mixture was sealed in a teflon-lined steal bomb and heated at 160 °C for 3 days, then cooled with water. After filtration, the product was washed with distilled water and ethanol and dried at room temperature. A large number of rombohedric-shaped crystals suitable for a crystallographic study were obtained.

2. Characterization

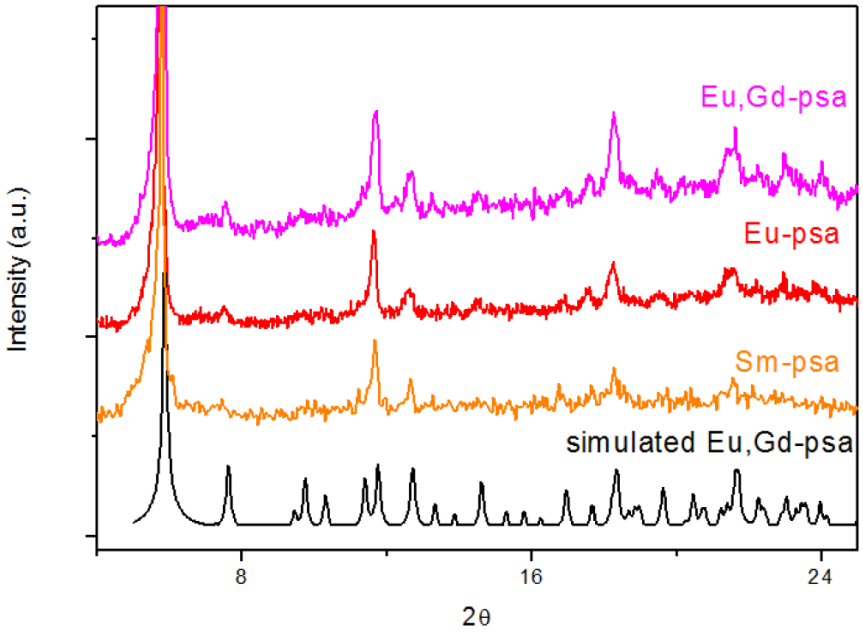

Figure S1: PXRD patterns of the three Ln-psa compounds (preferred orientation could not be completely avoided).

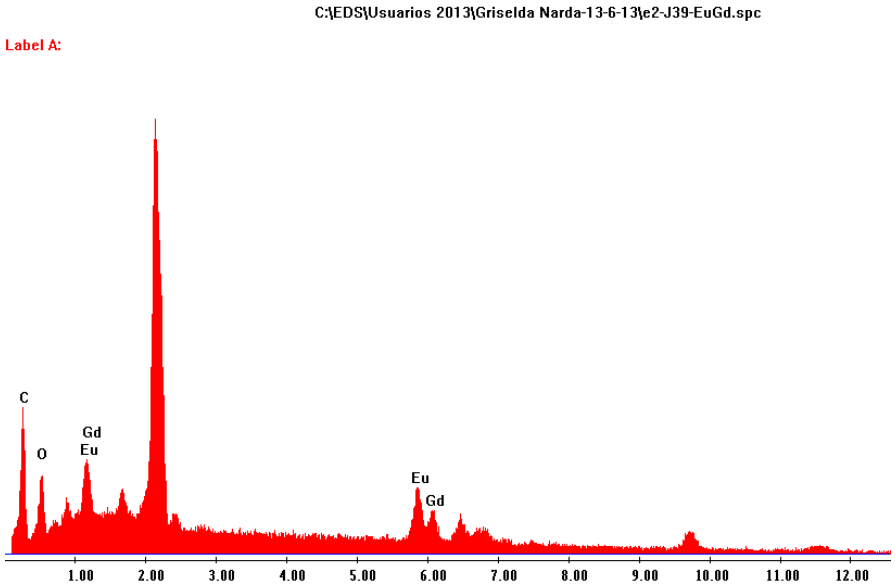

Figure S2: EDAX of Eu,Gd-psa

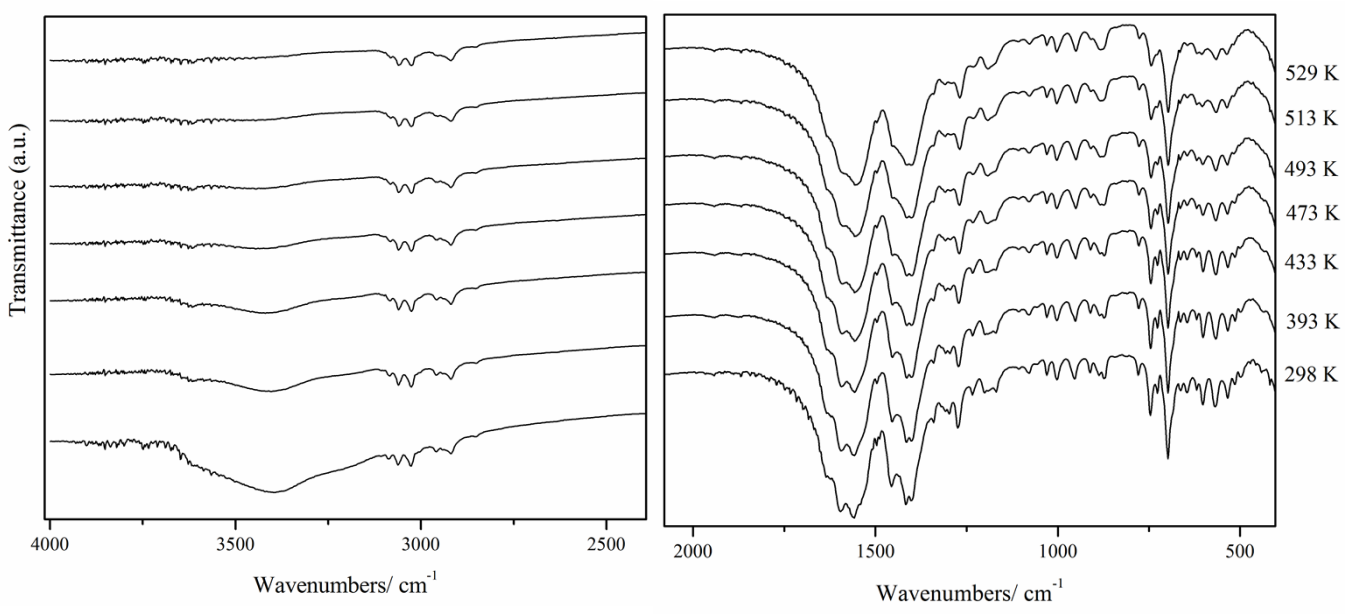

Figure S3: Variable-temperature IR spectra of Eu-psa.

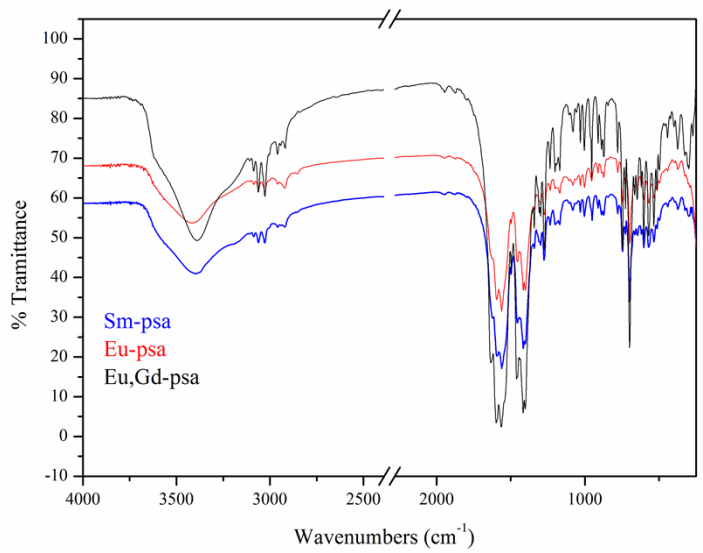

Figure S4: FTIR spectra of Sm-psa, Eu-psa and Eu,Gd-psa.

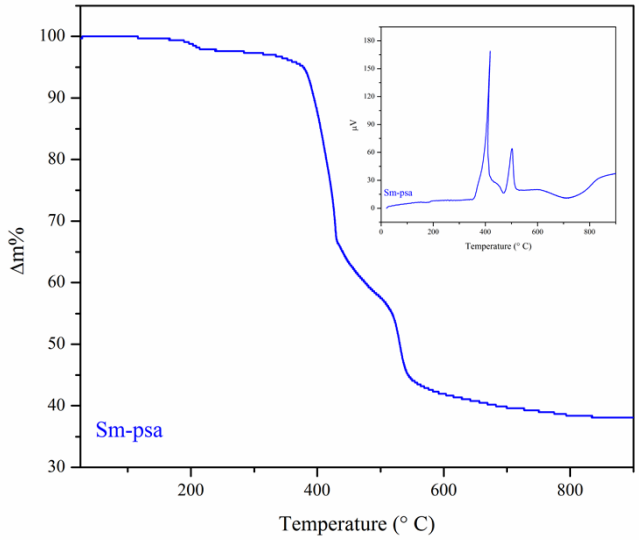

Figure S5: TGA-DTA curves of Sm-psa.

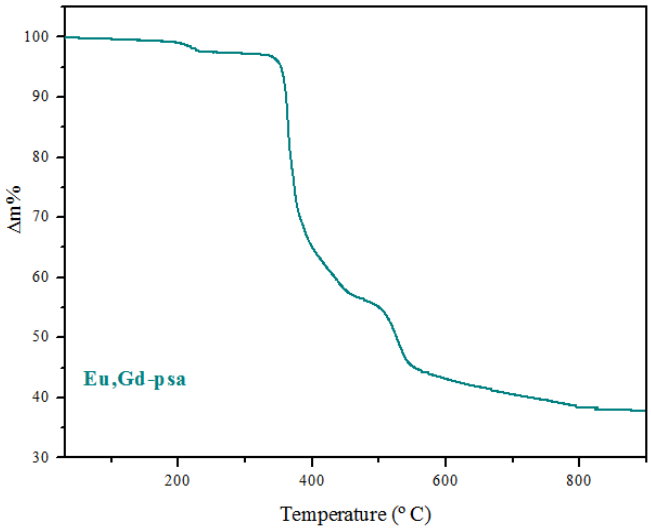

Figure S6: TGA curves of Eu,Gd-psa compound.

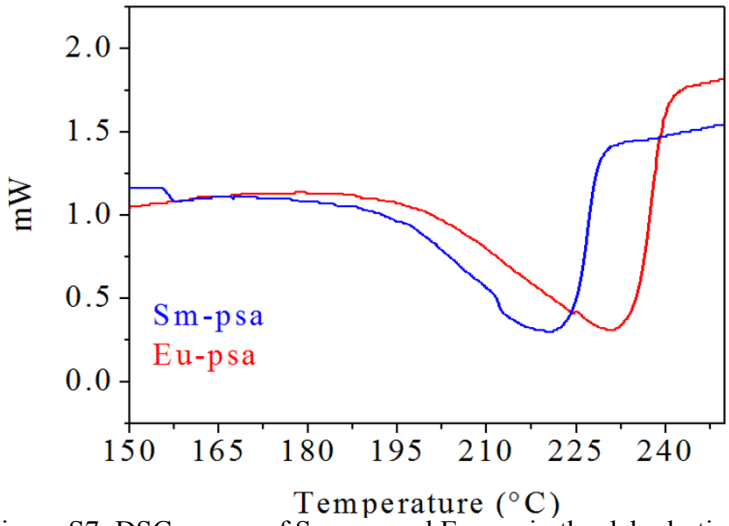

Figure S7: DSC curves of Sm-psa and Eu-psa in the dehydration zone.

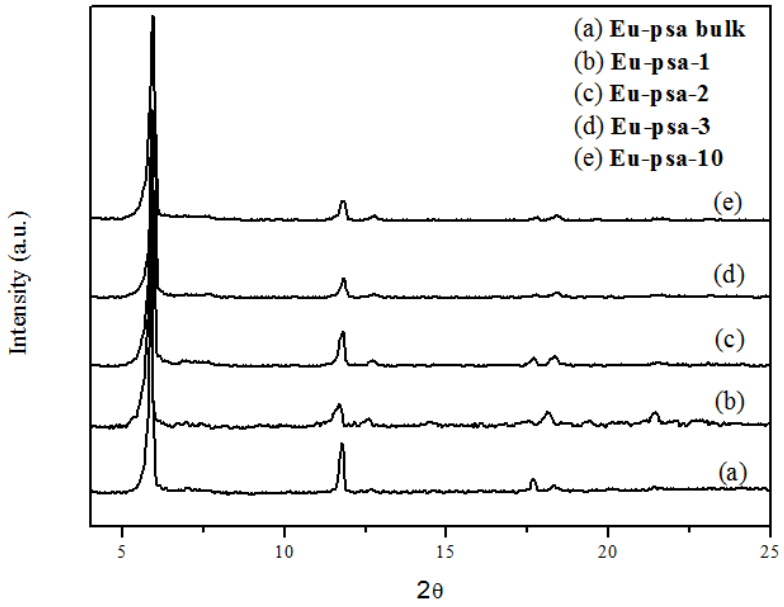

Figure S8: XRPD patterns of Eu-psa prepared with different concentrations of sodium acetate.

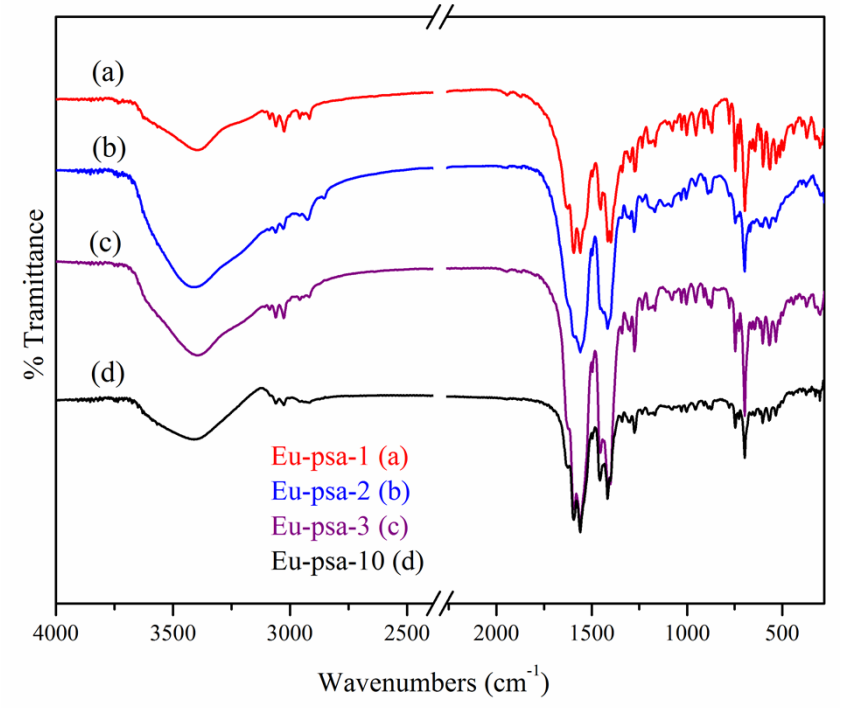

Figure S9: FTIR spectra of Eu-psa-1, Eu-psa-2, Eu-psa-3 and Eu-psa-10 compounds.

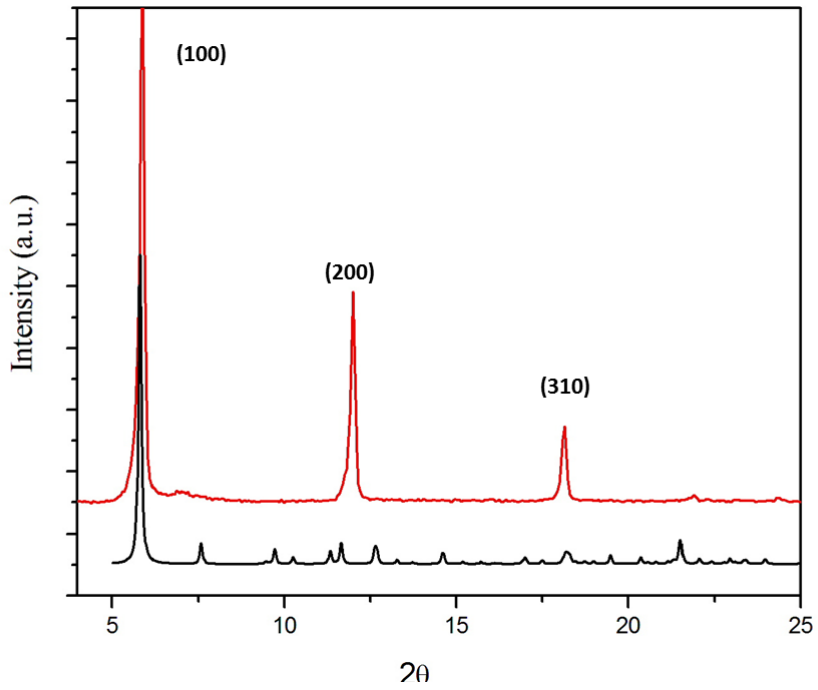

Figure S10: Comparison between the PXRD pattern for exfoliated Eu-psa-10 and the Eu-psa simulated one; the three main reflections strongly affected by the exfoliation process were labeled.

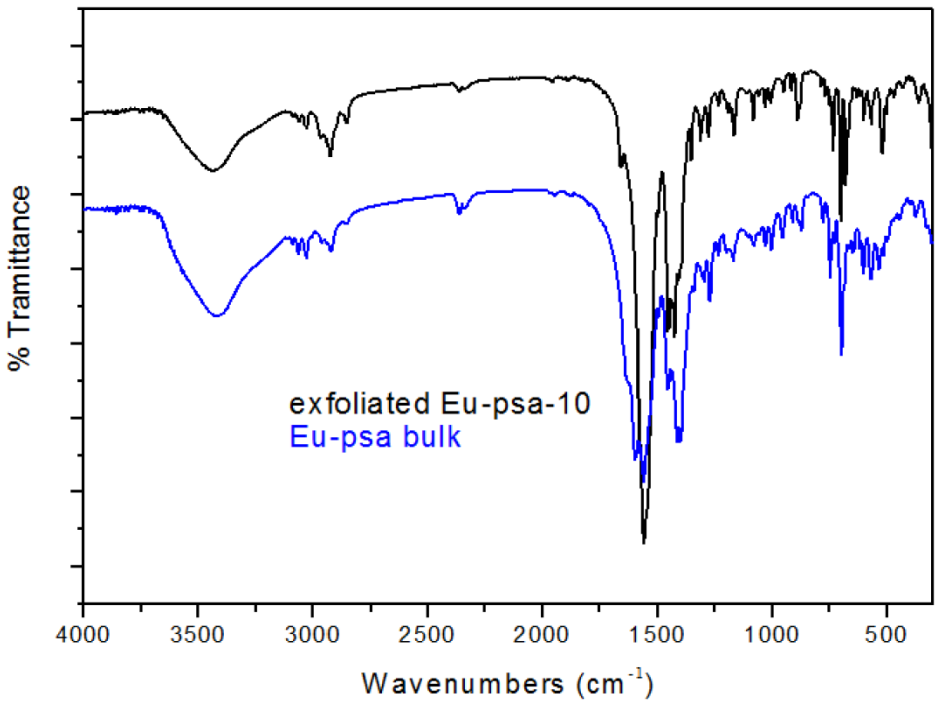

Figure S11: FTIR spectra of Eu-psa and exfoliated Eu-psa-10 samples.

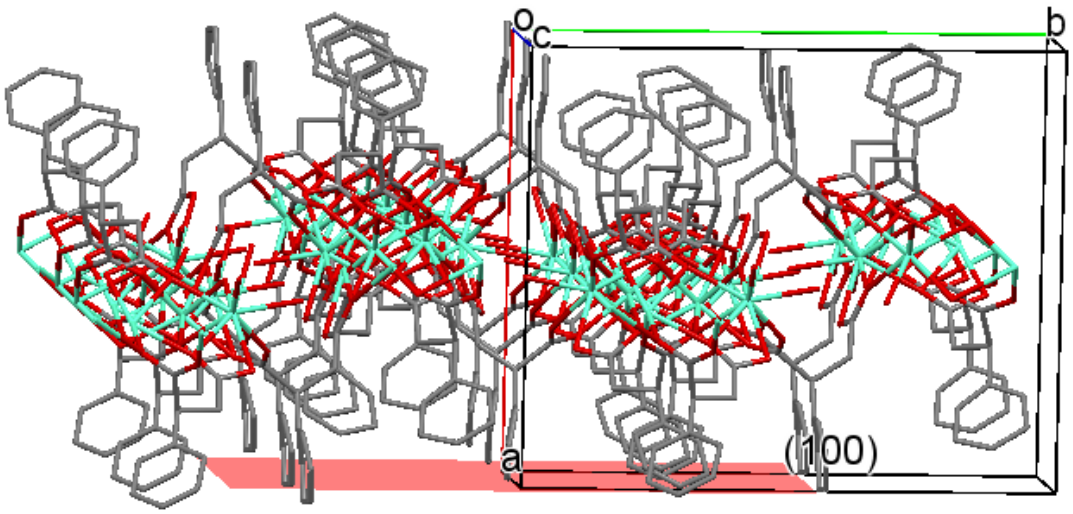

Figure S12: Pairs of *hkl* planes exposed by preferred orientation promoted by the liquid exfoliation.

3. Luminescence properties

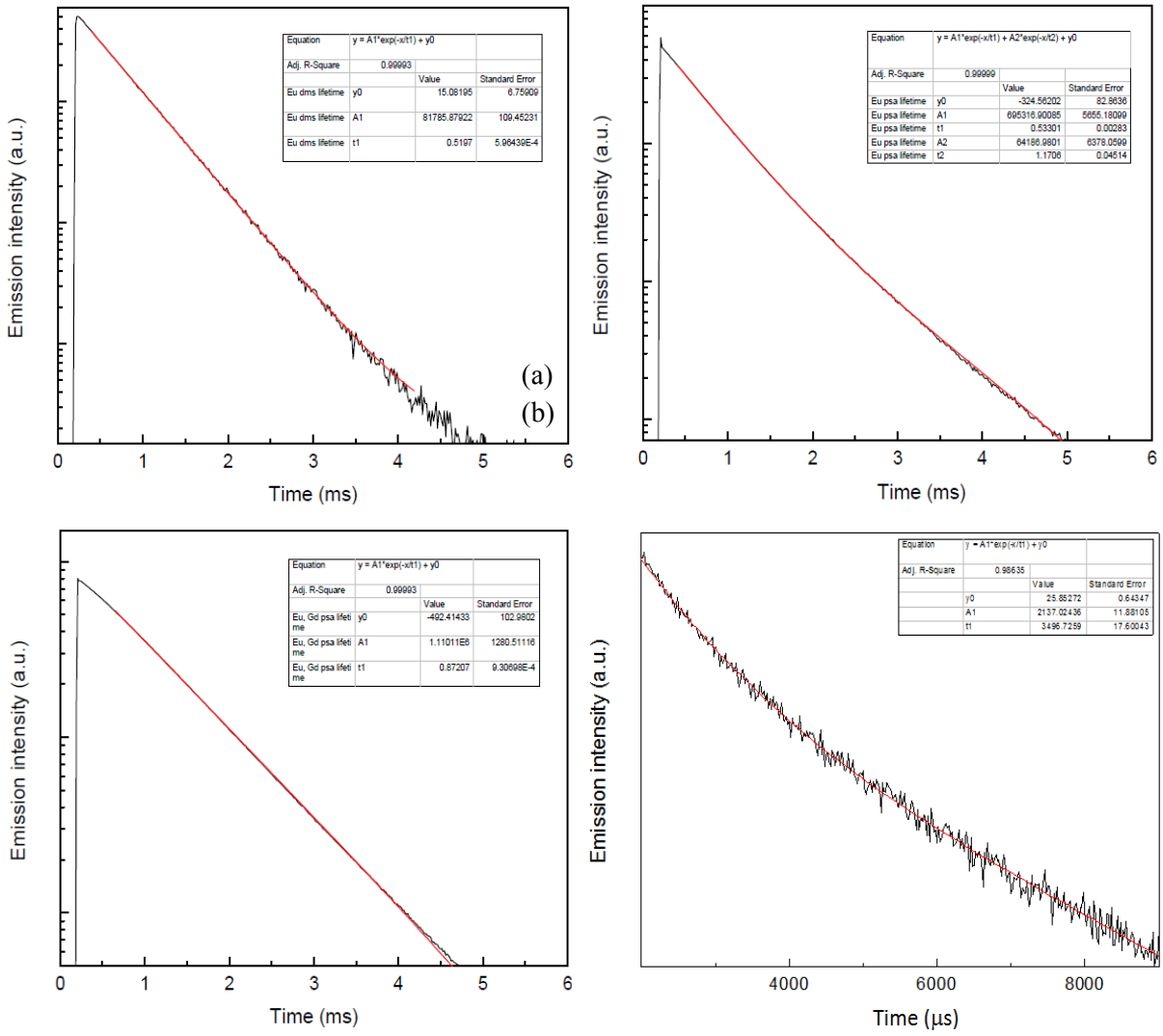

Figure S13: Luminescence decay trace of Eu-2,3-dms (a), Eu-psa (b), Eu,Gd-psa (c) and Sm-psa (d).

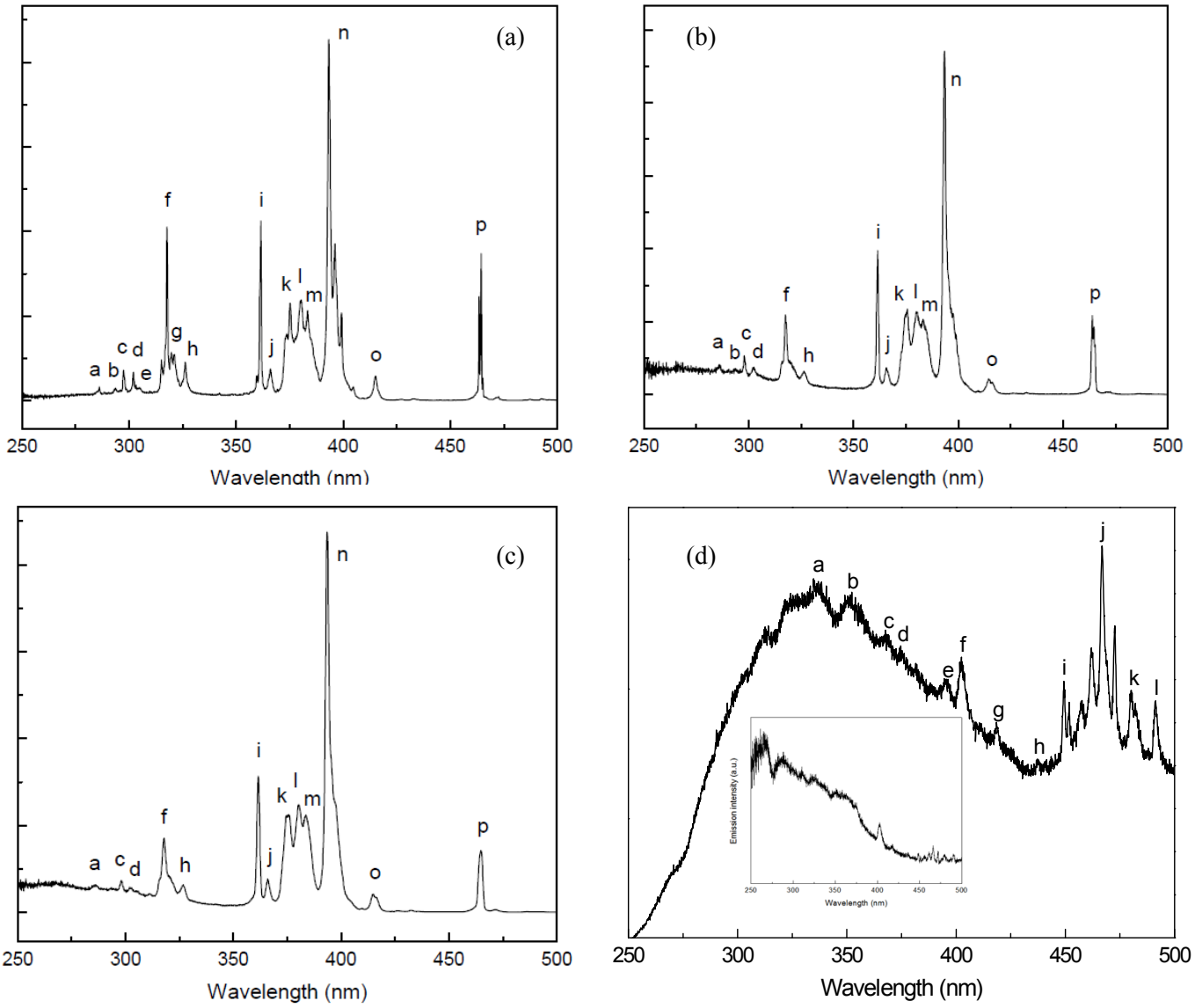

Figure S14: Excitation spectra of Eu-2,3-dms (a), Eu-psa (b), Eu,Gd-psa (c), Sm-psa (d). The inset in (d) shows the excitation spectrum of Sm-psa corrected for detector sensitivity.

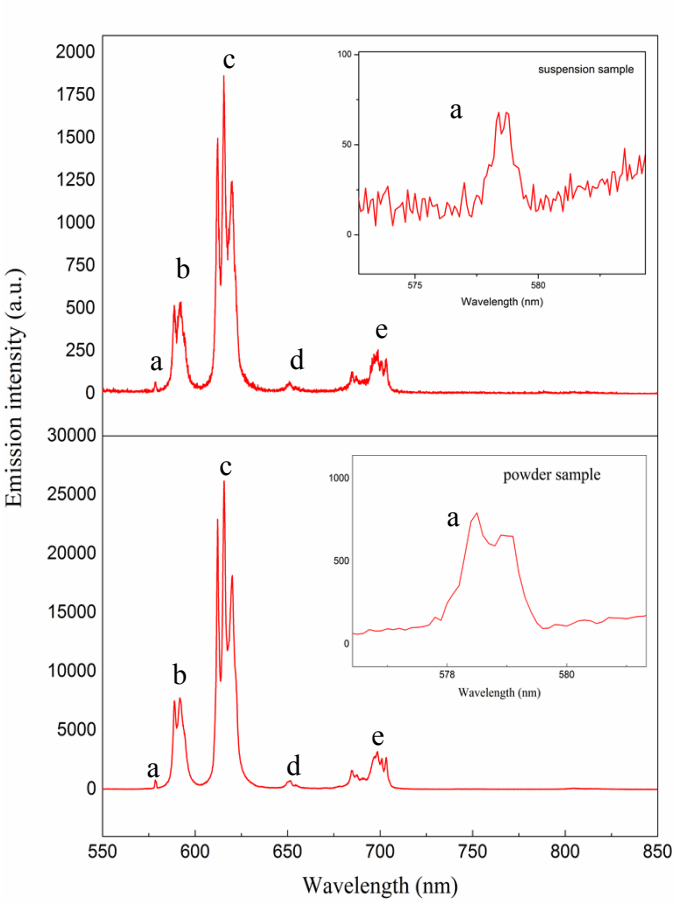

Figure S15: Emission spectra of Eu-psa-10 (suspension) (a) and Eu-psa-10 (powder) (b). In both cases, the insets show the "a" transition.

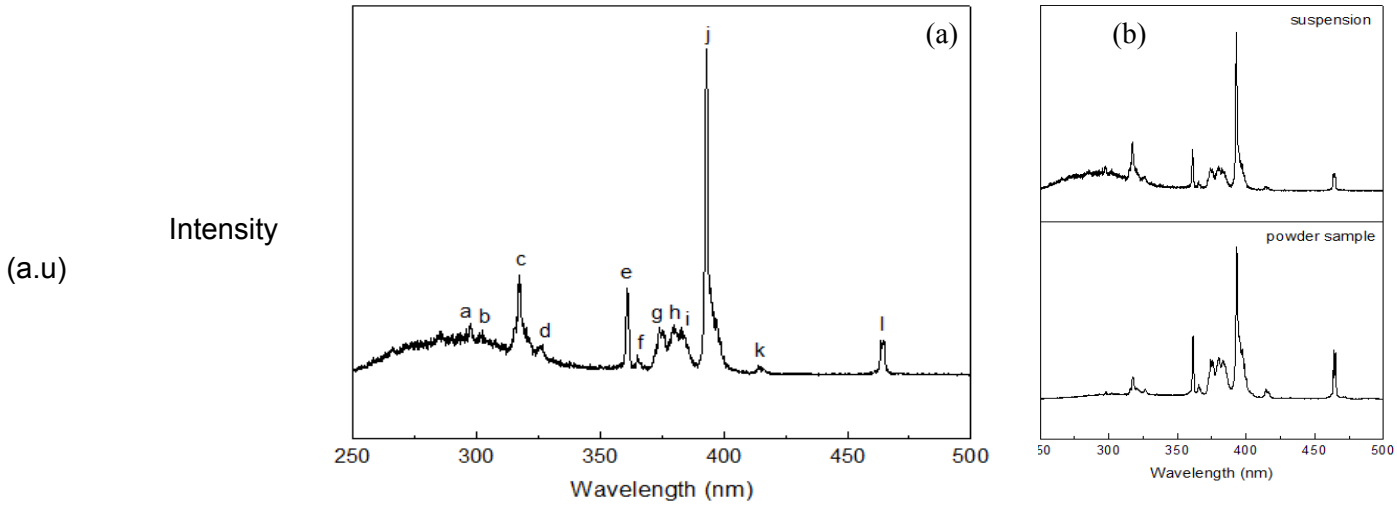

Figure S16: Excitation spectrum of Eu-psa-10 (suspension) monitored at 615.4 nm (a). Comparison of excitation spectra of Eu-psa-10 (suspension and powder sample) (b).

4. Tables

Table S1: Assignment of the 4*f*-4*f* transitions in the excitation spectrum of Sm-psa.

Label	Wavelength (nm)	Energy (cm^{-1})	Transition
a	336.5	29718	$^4G_{5/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4H_{13/2}$←$^6H_{5/2}$
b	350.9	28498	$^4K_{15/2}$, $^4H_{7/2}$←$^6H_{5/2}$
c	367.3	27226	$^4D_{5/2}$, $^6P_{5/2}$, $^4D_{3/2}$, $^4K_{13/2}$←$^6H_{5/2}$
d	374.7	26688	$^6P_{7/2}$←$^6H_{5/2}$
e	395.4	25291	$^4L_{15/2}$, $^4K_{11/2}$←$^6H_{5/2}$
f	402.5	24845	$^6P_{3/2}$, $^4F_{7/2}$, $^4L_{13/2}$←$^6H_{5/2}$
g	418.5	23895	$^6P_{5/2}$, $^4P_{5/2}$←$^6H_{5/2}$
h	437.4	22862	$^4G_{9/2}$←$^6H_{5/2}$
i	449.3	22257	$^4M_{17/2}$, $^4F_{5/2}$←$^6H_{5/2}$
j	466.7	21427	$^4I_{13/2}$←$^6H_{5/2}$
k	480.0	20833	$^4I_{11/2}$, $^4M_{15/2}$←$^6H_{5/2}$
l	491.3	20354	$^4I_{9/2}$, $^4G_{7/2}$←$^6H_{5/2}$

Table S2: Assignment of the 4*f*-4*f* transitions in the emission spectrum of Sm-psa.

Label	Wavelength (nm)	Energy (cm^{-1})	Transition
a	561.7	17803	$^4G_{5/2}$→$^6H_{5/2}$
b	597.8	16728	$^4G_{5/2}$→$^6H_{7/2}$
c	644.7	15511	$^4G_{5/2}$→$^6H_{9/2}$
d	705.0	14184	$^4G_{5/2}$→$^6H_{11/2}$

Table S3: Assignment of labeled electronic transitions corresponding to emission spectra of Eu-MOFs.

Emission			
Label	Wavelength (nm)	Energy (cm^{-1})	Transition
	Eu-2,3-dms		
a	578.5	17286	$^5D_0 \rightarrow {}^7F_0$
b	590.0	16949	$^5D_0 \rightarrow {}^7F_1$
c	615.5	16247	$^5D_0 \rightarrow {}^7F_2$
d	649.2	15404	$^5D_0 \rightarrow {}^7F_3$
e	700.0	14286	$^5D_0 \rightarrow {}^7F_4$
f	744.9	13425	$^5D_0 \rightarrow {}^7F_5$
g	807.6	12382	$^5D_0 \rightarrow {}^7F_6$
	Eu-psa		
a	578.5	17286	$^5D_0 \rightarrow {}^7F_0$
b	591.7	16900	$^5D_0 \rightarrow {}^7F_1$
c	615.8	16239	$^5D_0 \rightarrow {}^7F_2$
d	651.5	15349	$^5D_0 \rightarrow {}^7F_3$
e	698.4	14318	$^5D_0 \rightarrow {}^7F_4$
f	747.9	13371	$^5D_0 \rightarrow {}^7F_5$
g	807.5	12384	$^5D_0 \rightarrow {}^7F_6$
	Eu,Gd-psa		
a	578.9	17274	$^5D_0 \rightarrow {}^7F_0$
b	592.2	16886	$^5D_0 \rightarrow {}^7F_1$
c	582.8	17158	$^5D_0 \rightarrow {}^7F_2$
d	651.0	15361	$^5D_0 \rightarrow {}^7F_3$
e	698.5	14316	$^5D_0 \rightarrow {}^7F_4$
f	751.2	13312	$^5D_0 \rightarrow {}^7F_5$
g	804.1	12436	$^5D_0 \rightarrow {}^7F_6$

Table S4: Assignment of labeled electronic transitions corresponding to excitation spectra of Eu-MOFs.

Excitation			
Label	Wavelenght (nm)	Energy (cm^{-1})	Transition
	Eu-2,3-dms		
a	286.1	34953	$^5I_6$, $^5H_6 \leftarrow {}^7F_0$
			$^5I_7 \leftarrow {}^7F_1$
b	293.6	34060	$^5F_4$, $^5H_5 \leftarrow 7F_1$
			$^5F_4 \leftarrow {}^7F_0$
c	297.4	33625	$^5F_5$, $^5I_4 \leftarrow 7F_1$
d	302.0	33112	$^5F_2 \leftarrow {}^7F_0$
e	304.8	32808	$^5F_3 \leftarrow {}^7F_1$
f	317.7	31476	$^5H_6 \leftarrow {}^7F_0$
			$^5H_4 \leftarrow {}^7F_0$
g	319.7	31279	$^5H_5 \leftarrow {}^7F_1$
h	326.1	30665	$^5H_7 \leftarrow {}^7F_1$
i	361.6	27655	$^5D_4 \leftarrow {}^7F_0$
j	365.9	27330	$^5D_4 \leftarrow {}^7F_1$
k	375.2	26652	$^5G_6$, $^5G_4 \leftarrow {}^7F_0$
l	380.4	26288	$^5G_6$, $^5G_5$, $^5G_3 \leftarrow {}^7F_1$
m	383.4	26082	$^5L_7 \leftarrow {}^7F_1$
			$^5L_6 \leftarrow {}^7F_0$
n	393.3	25426	$^5L_6 \leftarrow {}^7F_1$
o	415.0	24096	$^5D_3 \leftarrow {}^7F_1$
p	464.5	21528	$^5D_2 \leftarrow {}^7F_0$
	Eu-psa		
a	286.0	34965	$^5I_6$, $^5H_6 \leftarrow {}^7F_0$
			$^5I_7 \leftarrow 7F_1$
b	293.8	34037	$^5F_4$, $^5H_5 \leftarrow {}^7F_1$
			$^5F_4 \leftarrow {}^7F_0$
c	297.9	33568	$^5F_5$, $^5I_4 \leftarrow {}^7F_1$
d	302.4	33069	$^5F_2 \leftarrow {}^7F_0$
e	not observed		
f	317.6	31486	$^5H_6 \leftarrow {}^7F_0$
g	not observed		
h	326.4	30637	$^5H_7 \leftarrow {}^7F_1$
i	361.6	27655	$^5D_4 \leftarrow {}^7F_0$
j	365.7	27345	$^5D_4 \leftarrow {}^7F_1$
k	375.7	26617	$^5G_6$, $^5G_4 \leftarrow {}^7F_0$
l	380.1	26309	$^5G_6$, $^5G_5$, $^5G_3 \leftarrow {}^7F_1$

m	383.2	26096	$^5L_7 \leftarrow {}^7F_1$
			$^5L_6 \leftarrow {}^7F_0$
n	393.5	25413	$^5L_6 \leftarrow {}^7F_1$
o	414.5	24125	$^5D_3 \leftarrow {}^7F1$
p	464.0	21552	$^5D_2 \leftarrow {}^7F_0$
	Eu,Gd-psa		
a	286.2	34941	$^5I_6$, $^5H_6 \leftarrow {}^7F_0$
			$^5I_7 \leftarrow 7F_1$
b	not observed		
			$^5F_4 \leftarrow {}^7F_0$
c	298.1	33546	$^5F_5$, $^5I_4 \leftarrow {}^7F_1$
d	301.9	33124	$^5F_2 \leftarrow {}^7F_0$
e	not observed		
f	317.6	31486	$^5H_6 \leftarrow {}^7F_0$
g	not observed		
h	326.4	30600	$^5H_7 \leftarrow {}^7F_1$
i	361.6	27655	$^5D_4 \leftarrow {}^7F_0$
j	365.9	27330	$^5D_4 \leftarrow {}^7F_1$
k	375.7	26617	$^5G_6$, $^5G_4 \leftarrow {}^7F_0$
l	380.3	26295	$^5G_6$, $^5G_5$, $^5G_3 \leftarrow {}^7F_1$
m	383.7	26062	$^5L_7 \leftarrow {}^7F_1$
			$^5L_6 \leftarrow {}^7F_0$
n	393.5	25413	$^5L_6 \leftarrow {}^7F_1$
o	414.9	24102	$^5D_3 \leftarrow {}^7F_1$
p	464.8	21515	$^5D_2 \leftarrow {}^7F_0$

Table S5: Assignment of the 4*f*-4*f* transitions in the excitation spectra of Eu-psa-10 (suspension and powder).

Label	Wavelength (nm)	Energy (cm^{-1})	Transition
a	297.6	33602	$^5I_4 \leftarrow {}^7F_1$, $^5F_4 \leftarrow {}^7F_0$
b	302.4	33069	$^5F_2 \leftarrow {}^7F_0$, $^5F_1 \leftarrow {}^7F_1$
c	317.1	31536	$^5H_6 \leftarrow {}^7F_0$
d	326.4	30637	$^5H_7 \leftarrow {}^7F_1$
e	361.1	27693	$^5D_4 \leftarrow {}^7F_0$
f	366.9	27255	$^5D_4 \leftarrow {}^7F_1$
g	375.5	26631	$^5G_6$, $^5G_4 \leftarrow {}^7F_0$
h	380.2	26302	$^5G_6$, $^5G_5$, $^5G_3 \leftarrow {}^7F_1$
j	393.5	25413	$^5L_6 \leftarrow {}^7F_0$
k	414.1	27693	$^5D_3 \leftarrow {}^7F_1$
l	464.0	21552	$^5D_2 \leftarrow {}^7F_0$

Table S6: Assignment of the 4*f*-4*f* transitions in the emission spectra of Eu-psa-10 (suspension).

Label	Wavelength (nm)	Energy (cm^{-1})	Transition
a	578.4	17289	$^5D_0 \rightarrow {}^7F_0$
b	592.4	16880	$^5D_0 \rightarrow {}^7F_1$
c	615.4	16250	$^5D_0 \rightarrow {}^7F_2$
d	650.3	15378	$^5D_0 \rightarrow {}^7F_3$
e	698.9	14308	$^5D_0 \rightarrow {}^7F_4$