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# **Electronic Supplementary Information (ESI)**

# PMMA or PVDF films with β-diketonate *tetrakis* Eu<sup>III</sup> or Tb<sup>III</sup> complexes

# used as downshifting coatings of near-UV LEDs

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# Electronic Supplementary Information (ESI1) – Chemicals, syntheses, characterization, and photophysical parameters

## Chemicals

Hydrochloric acid (HCl, Aldrich, 37%), ethanol (C<sub>2</sub>H<sub>5</sub>OH, Synth, 99.5%), europium oxide (Eu<sub>2</sub>O<sub>3</sub>, Aldrich, 99.99%), terbium oxide (Tb<sub>4</sub>O<sub>7</sub>, Aldrich, 99.99%), sodium hydroxide (NaOH, Cinética, 97%), 1,3diphenyl-1,3-propanedione (Hdbm,C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>, Aldrich, 98%), didodecyl dimethylammonium ([C<sub>26</sub>H<sub>56</sub>N]Br, Sigma-Aldrich, 98%), acetylacetone (Hacac, C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, Sigma-Aldrich, 99%) dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, Synth, 99.99%), acetone (C<sub>3</sub>H<sub>6</sub>O, Synth, 99.99%), PMMA (Aldrich, Mw ~ 120000), and PVDF (ATOCHEM) were used as start reactants without any further purification.

#### Syntheses

#### (C<sub>26</sub>H<sub>56</sub>N)[Eu(dbm)<sub>4</sub>] synthesis

Prior the complex synthesis, lanthanide chloride (LnCl<sub>3</sub>) solutions were prepared from the lanthanide oxide dissolution in HCl (1 mol L<sup>-1</sup>); for TbCl<sub>3</sub>, some drops of H<sub>2</sub>O<sub>2</sub> were also added up to the oxide dissolution. ( $C_{26}H_{56}N$ )[Eu(dbm)<sub>4</sub>] was synthesized by adding the Hdbm ligand to the counterion (4:1.5 in mol) in ethanol (30 mL). Then, NaOH (1 mol L<sup>-1</sup>) aqueous solution was added (1:1 in relation to the ligand), which changed from a transparent solution to light yellow due to the β-diketone deprotonation. EuCl<sub>3</sub> solution was then stoichiometrically added (1:4, Eu<sup>III</sup>:ligand) dropwise and this solution was left under stirring for 4 hours at 25 °C which changed its color from light yellow to a transparent solution. The solution volume was then reduced by evaporation under heating, and after that, the solution was placed in an ice bath, then the precipitate was vacuum filtered and dried in a desiccator. Color: light orange; Yield: 83.8%; MALDI TOF of C<sub>60</sub>H<sub>44</sub>EuO<sub>8</sub><sup>-</sup> m/z found (calcd): 1045.22(1045.23) [[Eu(dbm)<sub>4</sub>]<sup>-</sup>-C<sub>26</sub>H<sub>56</sub>N<sup>+</sup>]<sup>-</sup> (Figure S1). Elemental analysis for C<sub>86</sub>H<sub>99</sub>EuNO<sub>8</sub> (MW = 1426.67 g mol<sup>-1</sup>) calcd (found): C, 72.40% (72.22%); N, 0.98% (0.95%); H, 6.99% (7.03%); FTIR-ATR (cm<sup>-1</sup>) 2923-2852 (u CH<sub>2</sub>); 1594 (v<sub>s C=0</sub>); 1551 ( $\phi$  ring); 1454 ( $\delta$  CH + C=Oas}; 430 (u O-Eu) (Figure S2).

#### Na[Tb(acac)<sub>4</sub>] synthesis

For the Na[Tb(acac)<sub>4</sub>] synthesis, Hacac ligand was mixed with water and then, NaOH aqueous solution (1 mol L<sup>-1</sup>, 1:1 relative to the ligand) was added for ligand deprotonation, changing the solution color from transparent to pale yellow. Then, an ethanolic solution of TbCl<sub>3</sub> (4:1, relative to the ligand) was slowly dripped into the ligand solution which changed its color from pale yellow to transparent; this  $(C_{26}H_{56}N)$ [solution was kept under magnetic stirring for 4 hours at 25 °C. The complex obtained by solvent

evaporation was filtered and washed with a low amount of ethanol and dried in a desiccator. Color: white; Yield: 80.4%; Elemental analysis for  $C_{20}H_{28}TbNaO_8$  (MW = 578.35 g mol<sup>-1</sup>) calcd (found): C, 41.53% (41.35%); H, 4.88% (4.89%); FTIR-ATR (cm<sup>-1</sup>) 2922 ( $\upsilon$  CH<sub>3</sub>); 1587 ( $v_{s C=0}$ ); 1515 ( $v_{as C=C}$ ); 1190 ( $\delta$  CH); 424 ( $\upsilon$  O-Tb) (Figure S2).

#### PMMA films preparation

PMMA films with Eu(dbm)<sub>4</sub>] or Na[Tb(acac)<sub>4</sub>] complexes were prepared as reported by our research group for the ( $C_{26}H_{56}N$ )[Eu(dbm)<sub>4</sub>] system<sup>1</sup>. To prepare the films with ( $C_{26}H_{56}N$ )[Eu(dbm)<sub>4</sub>], a solution of the complex in chloroform (0.404 mg mL<sup>-1</sup>) was prepared while the weight amount of the complex in PMMA (wt%) was changed according to the Table S1 by considering the final weight (PMMA + complex) of 115 mg. PMMA and the complex was mixed with chloroform (2 mL), which was kept under magnetic stirring until halve the volume. After that, the solution was deposited by the "drop-casting" method on a glass substrate (22 x 22 mm<sup>2</sup>) which were dried in a saturated chloroform atmosphere to prevent the film from becoming opaque. For the Na[Tb(acac)<sub>4</sub>] films, stoichiometric amount of the complex was weighed as represented in the Table S1 Films with 0.10wt.% and 0.25wt.% were not prepared because the complex amount is too small for weighing, in addition to the fact that it is insoluble, making it impossible to prepare the solution. The film deposition procedure was the same as described for ( $C_{26}H_{56}N$ )[Eu(dbm)<sub>4</sub>] films.

#### **PVDF** films preparation

For the PVDF films with  $(C_{26}H_{56}N)[Eu(dbm)_4]$ , a DMF suspension (0.404 mg mL<sup>-1</sup>) was prepared while the weight amount of the complex in PVDF (wt%) was changed according to the Table S1 by considering the final weight (PVDF + complex) of 250 mg. Initially, PVDF was dissolved in DMF (2 mL), which was heated at ~80 °C, under magnetic stirring, until the polymer was completely dissolved, and its volume was reduced to 1 mL. The solution was then brought back to room temperature and the ( $C_{26}H_{56}N)[Eu(dbm)_4]$ complex was added. After 10 minutes, the mixture was deposited in a Petri dish (40 x 12 mm) and dried in an oven at 60 °C for 15 hours. For the PVDF/Na[Tb(acac)\_4] series, the film deposition procedure was the same as described for films with ( $C_{26}H_{56}N)[Eu(dbm)_4]$ .

		PMMA films / mg			PVDF films / mg		
wt.%	PMMA	Eu complex	Tb complex	PVDF	Eu complex	Tb complex	
0	115.0	-	-	250.0	-	-	
0.1	114.9	$0.1^{[*]}$	-	249.7	0.3 <sup>[**]</sup>	-	
0.25	114.7	0.3[*]	-	249.4	0.6 <sup>[**]</sup>	-	
0.50	114.4	0.6[*]	0.6	248.7	1.3	1.3	
0.75	114.1	0.9 <sup>[*]</sup>	0.9	248.1	1.9	1.9	
1.0	113.8	1.2	1.2	247.5	2.5	2.5	
2.0	112.7	2.3	2.3	245.0	5.0	5.0	
5.0	109.2	5.8	5.8	237.5	12.5	12.5	

Table S1. Relation of complex and PMMA or PVDF amount used to prepare the films.

[\*] Amount obtained from the 0.404 mg mL<sup>-1</sup> solution of the complex in chloroform.

[\*\*] Amount obtained from the 0.404 mg mL<sup>-1</sup> suspension of the complex in DMF.

#### LED prototype assembling

The 1 wt% films were used as coating of near-UV emitting LEDs ( $\lambda_{max}$ =395 ± 10 nm, SMD type), Figure 1. For that, a piece of the film with size of 0.1×0.1 cm was fixed on the LED surface by using a cyanoacrylate glue.

### Characterization

**FTIR.** FTIR spectra were measured in a Perkin Elmer Frontier instrument equipped with a diamond ATR module within the 4000 – 400 cm<sup>-1</sup> range recorded using 120 scans and resolution of 0.5 cm<sup>-1</sup>.

**Absorption spectroscopy.** The UV-Vis absorption spectra were performed in a Shimadzu model UV-1800 spectrometer, double beam, within the 900 – 200 nm spectral range and monitoring step of 1 nm.

**Diffuse reflectance spectroscopy (DRS).** To obtain the reflectance spectra, an absorption spectrophotometer in the UV/Vis/NIR region with integrating sphere, Lambda 1050 from Perkin Elmer was used.

**Thermogravimetry.** The thermogravimetric analysis measurements were performed in a TA Instruments, model SDT-500, under conditions from 10 °C/min to 1200 °C, with air flow at 100 mL min<sup>-1</sup>.

**C, H, N elemental analysis**. Elemental analysis measurements were performed by the Flash EA 1112 CHNS elemental analyzer.

**MALDI-TOF.** MALDI-TOF analyzes were performed on a Bruker Daltonics autoflex III smartbeam equipment.

**Photoluminescence.** Excitation and emission spectra (298 K) were carried out in a Horiba Jobyn Yvon Fluorolog spectrofluorimeter (model FL3-221) while spectra were corrected accordingly to lamp intensity and detector. Emission decay curves were measured in the same equipment using phosphorimeter and pulsed Xe bulb.

**Emission quantum yield.** The photoluminescence quantum yield (PLQY) obtained in triplicate was measured using an integrating sphere (Labsphere<sup>®</sup>) with a diameter of 5 inches and a solid-state laser with an emission at 375 nm. The photoluminescence signal was evaluated by a USB2000 + mini-spectrometer (Ocean Optics<sup>®</sup>).

**LED device characterization.** Emission spectra and radiant stability of LED prototypes were measured in a PerkinElmer model LS55 spectrometer while the CW Xe lamp (9.9 W) for excitation was kept off.

**Photophysical parameters.** For Eu<sup>III</sup> systems, experimental  $\Omega_2$  and  $\Omega_4$  (Equation S1) Judd-Ofelt intensity parameters, radiative (Equation S2) and non-radiative decay probabilities (*A*), and intrinsic emission quantum yield ( $\Phi_{Eu}^{Eu}$ , Equation S3) were obtained from the emission spectrum through the free LUMPAC<sup>\*</sup> software. In these equations,  $\omega$  is the angular frequency of incident radiation,  $\chi = n(n+2)^2/9$  is the Lorentz local-field correction, *n* is the refractive index of the medium (1.500 for complexes),  $|\langle {}^7F_j || U^{(\lambda)} || {}^5D_0 \rangle|^2$  is 0.0032 or 0.0023 for *J* = 2 and 4, respectively,  $A_{0\lambda}$  is the spontaneous emission probability,  $A_{01}=14,6\cdot n^3$ ,  $\tau$  is the emitting state lifetime, and  $S_{01}$  is the area under the band assigned to the  ${}^5D_0 \rightarrow {}^7F_J$  transition. In this approach, the  $\Omega_6$  parameter is not calculated because the  ${}^5D_0 \rightarrow {}^7F_6$  transition is not observed in the monitored emission range.<sup>2</sup> For Tb<sup>III</sup> systems, these greatnesses were not calculated since this method is only applied for Eu<sup>III</sup>, which has a purely magnet dipole transition that can be used as reference for the calculation from the emission spectrum.

$$\Omega_{\lambda} = \frac{3hc^{3}A_{0\lambda}}{8\pi e^{2}\omega^{3}\chi \left|\left\langle {}^{7}F_{J}\right|\right| U^{(\lambda)} \left|\right| {}^{5}D_{0}\right\rangle \right|^{2}} (S1)$$
$$A_{0J} = A_{01} \left(\frac{v_{01}}{v_{0J}}\right) \left(\frac{S_{0J}}{S_{01}}\right) (S2)$$
$$\Phi_{Eu}^{Eu} = \frac{A_{rad}}{A_{Total}} = \frac{\tau_{total}}{\tau_{rad}} (S3)$$

Supplementary note S2 – Structural characterization of complexes



**Figure S1.** MALDI-TOF spectrum of  $(C_{26}H_{56}N)[Eu(dbm)_4]$ . The structure of the molecular anion is also provided as insert in the figure.



**Figure S2.** FTIR spectra of (a)  $(C_{26}H_{56}N)[Eu(dbm)_4]$  and (b) Na[Tb(acac)\_4] compared to the respective free ligand. Main assignments are depicted in the figure <sup>3,4,5,6</sup>.



Supplementary note S3 – Thermal characterization of complexes

**Figure S3.** Thermogravimetric analyses (TG) of  $(C_{26}H_{56}N)[Eu(dbm)_4]$  and Na[Tb(acac)\_4]. For  $(C_{26}H_{56}N)[Eu(dbm)_4]$ , the first thermal event at around 250 °C corresponded to the  $\beta$ -diketone decomposition and the second one at 490 °C was assigned to the counter-ion thermolysis. For Na[Tb(acac)\_4], all three thermal events observed in the TG curve were assigned to acac decomposition. Moreover, after 500 °C, the plateau in the TG curves corresponds to Eu<sub>2</sub>O<sub>3</sub> or Tb<sub>4</sub>O<sub>7</sub> formation.

## Supplementary note S4 – Spectroscopic features of complexes



**Figure S4.** (a) UV-Vis absorption spectrum of  $(C_{26}H_{56}N)[Eu(dbm)_4]$  in chloroform. (b) Diffuse reflectance spectrum of powder Na[Tb(acac)\_4] since it has poor solubility in all tested solvents.



**Figure S5.** Emission decay curves (298 K) from powder ( $C_{26}H_{56}N$ )[Eu(dbm)<sub>4</sub>] and Na[Tb(acac)<sub>4</sub>] complexes emission. For ( $C_{26}H_{56}N$ )[Eu(dbm)<sub>4</sub>],  $\lambda_{exc}$  = 395 nm and  $\lambda_{em}$  = 615 nm; for Na[Tb(acac)<sub>4</sub>],  $\lambda_{exc}$  = 320 nm and  $\lambda_{em}$  = 542 nm. Curves were adjusted by a monoexponential function ( $R^2 > 0.95$ ).

Supplementary note S5 – Structure and thermal behavior of films



Figure S6. SEM images (1000x magnification) of 1wt.% films, (a)  $(C_{26}H_{56}N)[Eu(dbm)_4]/PVDF$ , and (b)  $Na[Tb(acac)_4]/PVDF$ .



Figure S7. Powder XRD of PVDF films with different amount of (a)  $(C_{26}H_{56}N)[Eu(dbm)_4]$  and (b) Na[Tb(acac)\_4] complexes.



Figure S8. DSC scan of PVDF film with 0.5wt.% of  $(C_{26}H_{56}N)[Eu(dbm)_4]$ .



**Figure S9.** FTIR spectra of PMMA complexes with different wt.% of (a)  $(C_{26}H_{56}N)[Eu(dbm)_4]$  or (b) Na[Tb(acac)\_4] and PVDF films with different wt.% of (c)  $(C_{26}H_{56}N)[Eu(dbm)_4]$  or (d) Na[Tb(acac)\_4]. Assignments of PMMA vibrational modes: (1) stretching of CH<sub>3</sub> and CH<sub>2</sub>, (2)  $\upsilon$ (C=O) stretching band of non-conjugated ester, (3) the  $\upsilon$ (O-CH<sub>3</sub>) of the ester group, (4) to stretching vibration modes of the C-O-C group, (5) in-plane C-H angle deformation, (6)  $\alpha$ -methyl group vibrations. Assignments of PVDF vibrational modes: (7) CH<sub>2</sub> in-plane or out-of-plane bending or scissoring, (8) C-F stretching, (9) CH<sub>2</sub> rocking and CF<sub>2</sub> asymmetric stretching, (10) CF<sub>2</sub> bending and CCC skeletal vibration, (11) CF<sub>2</sub> bending and wagging.<sup>7</sup>



Supplementary note S6 – Spectroscopic properties of films

**Figure S10.** Diffuse reflectance spectra of (a) PMMA films with  $Na[Tb(acac)_4]$ , (b) PVDF with  $Na[Tb(acac)_4]$ , and (c) PVDF with  $(C_{26}H_{56}N)[Eu(dbm)_4]$ .



**Figure S11.** Commission internationale de l'éclairage (CIE) 1931 color space representing the emission color of (a) (C<sub>26</sub>H<sub>56</sub>N)[Eu(dbm)<sub>4</sub>]/PMMA, (b) Na[Tb(acac)<sub>4</sub>]/PMMA, (c) (C<sub>26</sub>H<sub>56</sub>N)[Eu(dbm)<sub>4</sub>]/PVDF, and (d) Na[Tb(acac)<sub>4</sub>]/PVDF films.



**Figure S12.** Emission decay curves (298 K) of PVDF or PMMA films with  $(C_{26}H_{56}N)[Eu(dbm)_4]$  or Na[Tb(acac)\_4] complexes. For  $(C_{26}H_{56}N)[Eu(dbm)_4$ ,  $\lambda_{exc}$  = 395 nm and  $\lambda_{em}$  = 615 nm; for Na[Tb(acac)\_4],  $\lambda_{exc}$  = 320 nm and  $\lambda_{em}$  = 542 nm. Curves were adjusted by a monoexponential function ( $R^2 > 0.95$ ).

**Table S2.** <sup>5</sup>D<sub>0</sub> state lifetime ( $\tau$ ), Judd-Ofelt intensity parameters ( $\Omega$  and  $\Omega_4$ ), radiative ( $A_{rad}$ ) and nonradiative ( $A_{nrad}$ ) decay probabilities, absolute emission quantum yield ( $\Phi_L^{Eu}$ ), intrinsic emission quantum yield ( $\Phi_{Eu}^{Eu}$ ), and sensibilization efficiency ( $\eta = \Phi_L^{Eu}/\Phi_{Eu}^{Eu}$ ) for PMMA and PVDF films with (C<sub>26</sub>H<sub>56</sub>N)[Eu(dbm)<sub>4</sub>], the sensitization efficiency quantifies the energy transfer efficiency from ligand to Eu<sup>III</sup>[8].

wt.%	τ / ms	$\Phi^{Eu}_{Eu} / \%$	Φ <sup>Eu</sup> / %	η / %	Ω2 / 10 <sup>-20</sup> cm <sup>2</sup>	Ω4 / 10 <sup>-20</sup> cm <sup>2</sup>	A <sub>rad</sub> / s <sup>-1</sup>	Anrad / S <sup>-1</sup>
	(C <sub>26</sub> H <sub>56</sub> N)[Eu(dbm) <sub>4</sub> ]							
	0.97 <sup>[I]</sup>	63[1]	6.4[2]	-	19 <sup>[1]</sup>	1.2 <sup>[I]</sup>	652[1]	374[1]
(C26H56N)[Eu(dbm)4]/PMMA								
0.1	0.44	_[3]	_[3]	_[3]	_[3]	_[3]	_[3]	_[3]
0.25	0.26	15	0.20	1.3	17	1.1	574	3280
0.5	0.27	14	0.40	2.8	15	1.2	521	3117
0.75	0.33	25	2.2	8.6	23	1.5	764	2243
1.0	0.63	51	22	43	25	1.8	815	773
2.0	0.67	56	40	71	26	1.2	835	648
(C <sub>26</sub> H <sub>56</sub> N)[Eu(dbm) <sub>4</sub> ]/PVDF								
0.1	0.49	_*	_*	_*	_*	_*	_*	_*
0.25	0.42	_*	_*	_*	_*	_*	_*	_*
0.5	0.57	54	2.7	5.0	32	6.5	944	809
0.75	0.64	62	14	22	33	6.3	970	591
1.0	0.55	48	5.8	11	30	5.7	879	938
2.0	0.58	59	21	35	35	5.9	1011	712

<sup>[1]</sup> Powder complex.

<sup>[2]</sup> Chloroform solution.

<sup>[3]</sup> It was not possible to obtain the values because the emission intensity was too low.

**Table S3.** <sup>5</sup>D<sub>4</sub> state lifetime ( $\tau$ ) and absolute emission quantum yield ( $\Phi_L^{Tb}$ ) for PMMA and PVDF films series with Na[Tb(acac)<sub>4</sub>].

wt.%	τ / ms	$\Phi_L^{Tb}$ / %		
Solid Na[Tb(acac)4]				
	1.9	100		
Na[Tb(acac)4]/PMMA				
0.5	1.3	13		
0.75	1.3	5.5		
1.0	1.2	4.7		
2.0	1.2	25.8		
5.0	1.2	48.2		
Na[Tb(acac)4]/PVDF				
0.5	0.89	1.2		
0.75	0.98	4.9		
1.0	0.98	0.9		
2.0	1.1	7.1		
5.0	1.12	16.7		

wt.%	thickness (mm)		
(C26H56N)[Eu(dbm)4]/PMMA			
0.1	0.2		
0.25	0.2		
0.5	0.2		
0.75	0.2		
1.0	0.2		
2.0	0.2		
5.0	0.2		
(C <sub>26</sub> H <sub>56</sub> N)[Eu(dbm) <sub>4</sub> ]/PVDF			
0.1	0.1		
0.25	0.1		
0.5	0.1		
0.75	0.1		
1.0	0.1		
2.0	0.1		
5.0	0.1		
Na[Tb(acac)4]/PMMA			
0.5	0.2		
0.75	0.1		
1.0	0.1		
2.0	0.2		
5.0	0.1		
Na[Tb(acac)4]/PVDF			
0.5	0.1		
0.75	0.1		
1.0	0.1		
2.0	0.1		
5.0	0.1		

**Table S4.** Thickness in mm of films based on Eu<sup>III</sup> and Tb<sup>III</sup> complexes incorporated in PMMA and PVDF polymers.

## Supplementary references

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