

## Electronic Supporting Information

For

The effect of two additional  $\text{Eu}^{3+}$  lumophors in two novel  
trinuclear europium complexes on their photoluminescent  
properties

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## 1. Synthetic procedures and characterization.

### Synthesis of 1, 3, 5-tris(bromomethyl)- 2, 4, 6-trimethylbenzene

1, 3, 5-tris(bromomethyl)- 2, 4, 6-trimethylbenzene was prepared according to the procedure described in the literature with some modification [1]. Mesitylene (12 g, 100 mmol), paraformaldehyde (10.26 g, 340 mmol) and 75 ml of glacial acetic acid was rapidly added to a 150 ml three neck round bottom flask with 75 ml of HBr/acetic acid solution during magic stirring. The mixture solution was heated to 95 °C and kept at this temperature for 8 h, then poured into 200 ml of water to give amounts of white solid. The product from filtering was washed with 200 ml of anhydrous ethanol, and then was filtered and dried overnight at 60 °C to give 33.5 g of title compound, yield 85%, mp 183-186 °C. FT-IR (KBr) ( $\text{cm}^{-1}$ ): 785, 1446.1, 2922.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.44 (s, 9H, Ar- $\text{CH}_3$ ), 4.56(s, 6H,- $\text{CH}_2\text{Br}$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$ 12.1, 27.5, 134.7, 137.1.

### Synthesis of 1,10-phenanthroline-5,6-Dione.

1,10-phenanthroline-5,6-dione was synthesized according to a modified literature procedure [2]. 1,10-phenanthroline monohydrate (10.16g, 51.3 mmol) and KBr (24.94 g, 209.6 mmol) were added in a 250 ml three-neck round-bottom flask with a reflux condenser, mixture acid of 75 ml concentrated sulfuric acid and 35 ml concentrated nitric acid was added rapidly during stirring, after the mixture acid finished, solution was heated to 125 °C and kept at this temperature for 3 h. After 3 h, heating temperature was reduced to 100 °C, and the reflux condenser was removed to allow bromine vapors escape from the reaction flask, and used the 10 M NaOH solution absorbed the bromine. After being cooled, the mixture was poured into 275 g ice and carefully neutralized to pH = 7 with 5 M sodium hydroxide solution, and cooled to room temperature. Then the yellow turbid solution was filtered, and residual solid was washed four times with 30 ml boiling water every time, and the filtrate was collected. The combined aqueous solution was extracted with 200 ml dichloromethane, dried over anhydrous magnesium sulfate, and evaporated under reduced pressure to give light-yellow solid. The crude product was recrystallized from 250 ml of toluene to

give the yellow needle crystalline. The pure product was dried overnight in vacuum at 60 °C, yield 80%. Mp: 253-256 °C. FT-IR (KBr)  $\nu/\text{cm}^{-1}$ : 3062, 1685, 1576, 1561, 1460, 1414, 1314, 1292, 1205, 1115, 1009, 924, 808, 738.  $^1\text{H}$  NMR (400 MHz  $\text{CDCl}_3$ ),  $\delta$ : 7.58(d, 16 Hz, 2H), 8.50(dd, 8 Hz, 2H), 9.11(dd, 8 Hz, 2H).

### **1,3,5-Tris(4-formylphenoxyethyl)-2,4,6-trimethylbenzene.**

4-hydroxybenzaldehyde (4.2 g, 40 mmol), 1,3,5-tris(2-bromomethyl)-2,4,6-trimethylbenzene (4.0 g, 10 mmol), and potassium carbonate (5.52 g, 20 mmol) were dissolved in 100 ml DMF, and reacted at 90 °C for 24 h. The resulting solution was poured into 600 ml water, then filtered to get white solid, washed with large portion of water and ethanol, then the resulting solid was recrystallized from a mixture of acetic ether to give fine white crystals (4.88 g, 93%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ppm): 2.47 (9H, s, 3 $\times$ CH<sub>3</sub>), 5.22 (6H, s, 3 $\times$  CH<sub>2</sub>), 7.13 (6H, d, aromatic), 7.89 (6H, d, aromatic), 9.93 (3H, s, 3 $\times$ CHO);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ppm): 16.42 (CH<sub>3</sub>), 65.67 (CH<sub>2</sub>), 115.28, 132.48 (aromatic), 130.75, 131.68, 140.16, 164.34 (quaternary aromatic), 191.11 (CHO); MS (ESI)  $m/z = 523.3$  (M+H)<sup>+</sup>. FT-IR (KBr)  $\nu(\text{C}=\text{O})$  1691  $\text{cm}^{-1}$ .

### **References**

- [1] AW van der Made and RH van der Made. A convenient procedure for bromomethylation of aromatic compounds. Selective mono-, bis-, or trisbromomethylation. *J Org Chem* 1993; 58: 1262-1263.
- [2] Hiort C, Lincoln P and Norden B. DNA binding of .DELTA.- and .LAMBDA.-[Ru(phen)<sub>2</sub>DPPZ]<sup>2+</sup>. *J Am Chem Soc* 1993; 115: 3448-3454.

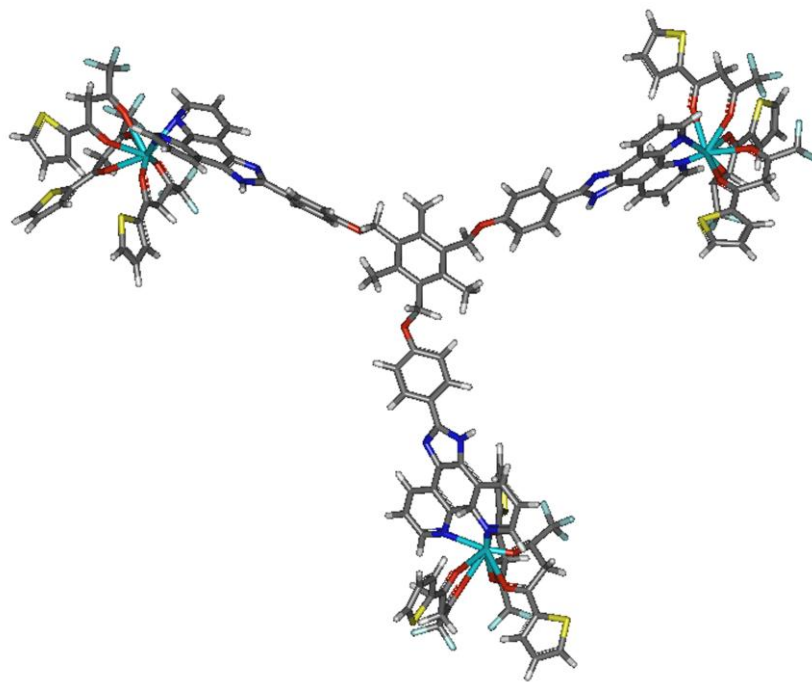
## 2. Additional Tables (Table S1, S2) and Figures (Figure S1-S3).

**Table S1** Spherical atomic coordinates calculated via Sparkle/PM3 coordination polyhedron of the complex  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$

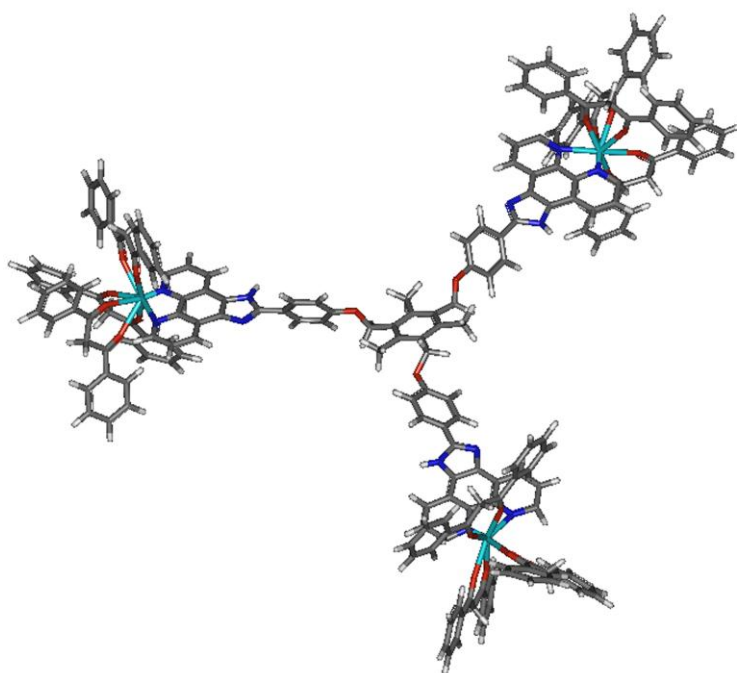
Atom	$R$ (Å)	$\theta$ (degree)	$\varphi$ (degree)
$\text{Eu}^{3+}$	0.000	0.000	0.000
O(TTA)	2.514	69.119	282.869
O(TTA)	2.509	174.373	72.073
O(TTA)	2.501	40.176	7.777
O(TTA)	2.515	73.994	311.405
O(TTA)	2.516	121.345	320.227
O(TTA)	2.505	106.464	24.895
N(trisphen)	2.589	31.551	29.996
N(trisphen)	2.592	92.089	66.728

**Table S2** Spherical atomic coordinates calculated via Sparkle/PM3 coordination polyhedron of the complex  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$

Atom	$R$ (Å)	$\theta$ (degree)	$\varphi$ (degree)
$\text{Eu}^{3+}$	0.000	0.000	0.000
O(DBM)	2.437	55.516	300.503
O(DBM)	2.431	10.763	22.069
O(DBM)	2.427	101.722	345.512
O(DBM)	2.439	157.382	4.829
O(DBM)	2.427	109.124	57.207
O(DBM)	2.425	53.812	39.927
N(trisphen)	2.609	109.524	38.579
N(trisphen)	2.594	78.883	305.578



**Fig. S1** The ground state geometry of the complex  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$  calculated using the Sparkle/PM3 model.



**Fig. S2** The ground state geometry of the complex  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$  calculated using the Sparkle/PM3 model.

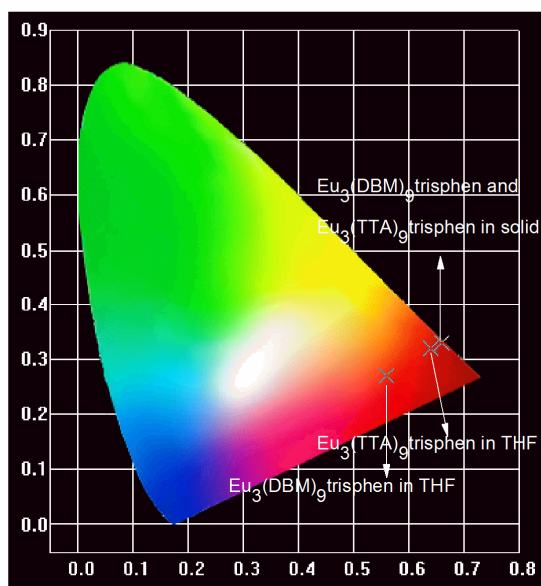


Fig. S3 CIE coordinates diagram of trinuclear europium complexes in solid state and in THF solution.