

# Versatile platform for lanthanide(III)-containing organogelators: fabrication of the Er(III)-incorporated polymer nanocomposite from an organogel template

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## General Experimental

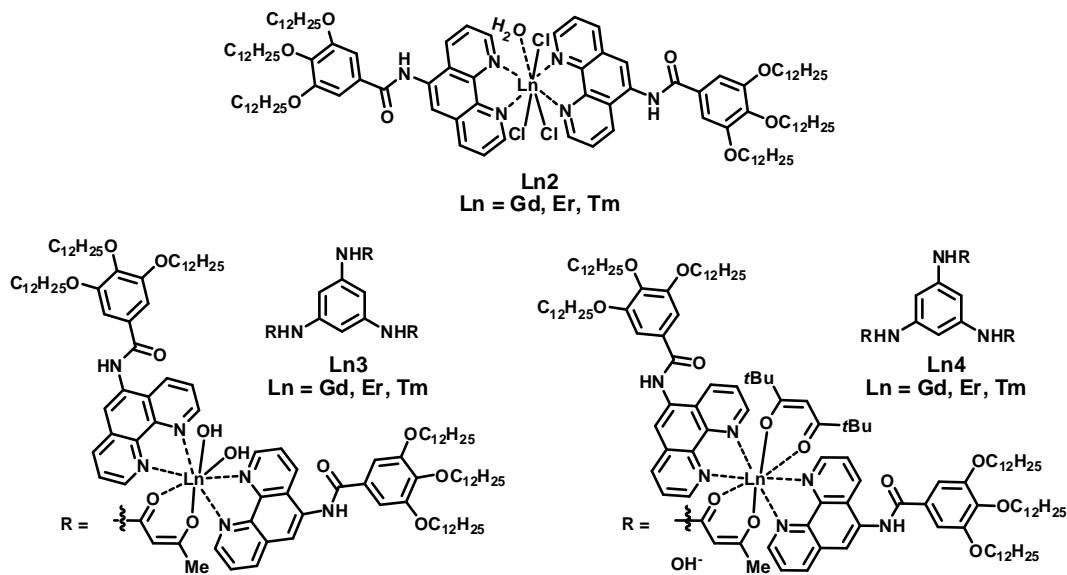
All reactions were performed in flame-dried glassware under a positive pressure of nitrogen unless otherwise noted. All reagents used were purchased commercially and were used as received unless otherwise noted. Air-and moisture-sensitive liquids were transferred by syringe or stainless steel cannula. 1,3,5-Triacetoacetamidobenzene was prepared by following reported procedures.<sup>1</sup> *N*-(3,4,5-tris(dodecyloxy)phenyl)-1,10-phenanthrolin-5-amine and europium(III) complexes such as **Eu2**, **Eu3** and **Eu4** were

synthesized by following the same procedure described for **1**, **2**, **3**, and **4** respectively in previous paper.<sup>2</sup> Terbium(III) complexes such as **Tb2**, **Tb3**, and **Tb4** were synthesized by following the same procedure described in previous paper.<sup>3</sup> Ethylene glycol dimethylacrylate (EGDMA) was purified by passing through a column filled with aluminum oxide (Aldrich) to remove the inhibitor. Tetrahydrofuran (THF) was dried over sodium metal and distilled.

## Instrumentation

Elemental analyses were performed using a Flash EA 1112 elemental analyzer. Fourier transform infrared (FT-IR) measurements were made on a PERKIN ELMER Spectrum GX I using KBr pellets. Thermogravimetric analyses (TGA) were performed on a TA modulated TGA2050 with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen. Differential scanning calorimetry (DSC) measurements were made on a TA modulated DSC Q10 with a scanning rate of 1 or  $10\text{ }^{\circ}\text{C min}^{-1}$  under nitrogen. Small-angle X-ray scattering (SAXS) patterns were obtained using Bruker Nanostar with monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54\text{ \AA}$ , 40 kV, 35 mA). Optical textures of the mesophases were observed with a Leica DM LP equipped with a Mettler Toledo FP 82HT heating stage and a Mettler Toledo FP 90 central process controller. UV–Vis spectra were obtained with the use of a Sinco S-3150 spectrometer. Fluorescence measurements were performed on a Shimadzu RF-5301PC spectrofluorometer. Near-infrared emission spectra were measured with the Peltier-cooled Hamamatsu H9170-75 photomultiplier system.

## Synthesis of Lanthanide(III) Complexes



**Figure S1.** Chemical structures of **Ln2**, **Ln3**, and **Ln4** complexes incorporated with Gd(III), Er(III), and Tm(III) ions.

### *Synthesis of erbium(III) complexes*

#### (a) **Er2**

To a solution of *N*-(3,4,5-tris(dodecyloxy)phenyl)-1,10-phenanthrolin-5-amine (1.0 g, 1.17 mmol) in hot ethanol was added dropwise a solution of Er(III) chloride hexahydrate (0.22 g, 0.59 mmol) in ethanol (1 mL). The reaction mixture was stirred at 80 °C for 2 h. Then, a precipitate was filtered off, washed with ethanol and dried in vacuum. Yield: 89%. IR (KBr,  $\text{cm}^{-1}$ ): 3083, 2922, 2852, 1641, 1574, 1527, 1496, 1468, 1426, 1384, 1336, 1233, 1114, 735, 541, 419. Anal. Calcd for  $\text{C}_{110}\text{H}_{172}\text{Cl}_3\text{ErN}_6\text{O}_9$ : C, 66.18; H, 8.68; N, 4.21. Found: C, 66.18; H, 8.60; N, 4.22.

(b) **Er3**

A solution of 1,3,5-triacetoacetamidobenzene (50.70 mg, 0.14 mmol) dissolved in *N*-methyl-2-pyrrolidone (NMP) (10 mL) was mixed with a solution of sodium hydroxide (17.29 mg, 0.43 mmol) in methanol (1 mL). This mixture was slowly added to a solution of **Er2** (808.84 mg, 0.41 mmol) in chloroform (50 mL) at 70 °C. The reaction mixture was stirred at 70 °C for 12 h. After cooling down to rt, the solution was condensed under reduced pressure. The resulting product was redissolved in chloroform and precipitated in cold methanol. The precipitate was filtered off, washed with methanol, and dried in vacuum. The product was obtained as an orange solid. Yield: 83 %. IR (KBr,  $\text{cm}^{-1}$ ): 3248, 2922, 2852, 1646, 1583, 1524, 1500, 1468, 1425, 1380, 1337, 1231, 1118, 738, 524, 415. Anal. Calcd for  $\text{C}_{348}\text{H}_{534}\text{Er}_3\text{N}_{21}\text{O}_{36}$ : C, 68.63; H, 8.84; N, 4.83. Found: C, 68.75; H, 8.83; N, 4.76.

(c) **Er4**

2,2,6,6-Tetramethyl-3,5-heptanedione (0.08 mL, 0.38 mmol) and sodium hydroxide (15.64 mg, 0.39 mmol) were dissolved in methanol (1 mL). This solution was added dropwise to a solution of **Er3** (780.60 mg, 0.13 mmol) in chloroform (50 mL). The reaction mixture was stirred at 70 °C for 12 h. After cooling down to rt, the solution was condensed under reduced pressure. The resulting product was redissolved in chloroform and precipitated in cold methanol. The precipitate was filtered off, washed with methanol and dried in vacuum. The product was obtained as an orange powder. Yield: 91%. IR (KBr,  $\text{cm}^{-1}$ ): 3251, 2921, 2851, 1645, 1583, 1526, 1504, 1468, 1425, 1380, 1338, 1231, 1120, 738, 536, 412. Anal. Calcd for  $\text{C}_{381}\text{H}_{588}\text{Er}_3\text{N}_{21}\text{O}_{39}$ : C, 69.45; H, 9.00; N, 4.46. Found: C, 69.11; H, 8.93; N, 4.42.

*Synthesis of gadolinium(III) and thulium(III) complexes*

Gd(III) complexes (**Gd2**, **Gd3**, and **Gd4**) and Tm(III) complexes (**Tm2**, **Tm3**, and **Tm4**) were prepared by the same procedures to erbium(III) complexes (**Er2**, **Er3**, and **Er4**) except using Gd(III) chloride hexahydrate and Tm(III) chloride hexahydrate instead of Er(III) chloride hexahydrate.

(a) **Gd2**

Yield: 87%. IR (KBr,  $\text{cm}^{-1}$ ): 3174, 2922, 2852, 1642, 1578, 1527, 1498, 1468, 1427, 1386, 1338, 1236, 1115, 734, 544, 419. Anal. Calcd for  $\text{C}_{110}\text{H}_{172}\text{Cl}_3\text{GdN}_6\text{O}_9$ : C, 66.52; H, 8.73; N, 4.23. Found: C, 66.26; H, 8.67; N, 3.93.

(b) **Gd3**

Yield: 84%. IR (KBr,  $\text{cm}^{-1}$ ): 3248, 2921, 2851, 1644, 1583, 1525, 1504, 1469, 1425, 1381, 1338, 1231, 1119, 739, 527, 411. Anal. Calcd for  $\text{C}_{348}\text{H}_{534}\text{Gd}_3\text{N}_{21}\text{O}_{36}$ : C, 68.97; H, 8.88; N, 4.85. Found: C, 68.93; H, 8.93; N, 4.70.

(c) **Gd4**

Yield: 92%. IR (KBr,  $\text{cm}^{-1}$ ): 3248, 2921, 2851, 1644, 1584, 1526, 1504, 1469, 1424, 1380, 1338, 1231, 1119, 738, 536, 412. Anal. Calcd for  $\text{C}_{381}\text{H}_{588}\text{Gd}_3\text{N}_{21}\text{O}_{39}$ : C, 69.77; H, 9.04; N, 4.48. Found: C, 69.68; H, 9.13; N, 4.49.

(g) **Tm2**

Yield: 82%. IR (KBr,  $\text{cm}^{-1}$ ): 3233, 2922, 2852, 1645, 1579, 1526, 1497, 1468, 1426, 1384, 1337, 1233, 1116, 735, 542, 418. Anal. Calcd for  $\text{C}_{110}\text{H}_{172}\text{Cl}_3\text{TmN}_6\text{O}_9$ : C, 66.13; H, 8.68; N, 4.21. Found: C, 66.15; H, 8.68; N, 4.15.

**(h) Tm3**

Yield: 85%. IR (KBr,  $\text{cm}^{-1}$ ): 3248, 2922, 2852, 1645, 1583, 1524, 1502, 1468, 1426, 1381, 1337, 1232, 1118, 738, 524, 415. Anal. Calcd for  $\text{C}_{348}\text{H}_{534}\text{Tm}_3\text{N}_{21}\text{O}_{36}$ : C, 68.58; H, 8.83; N, 4.83. Found: C, 68.52; H, 8.80; N, 4.63.

**(i) Tm4**

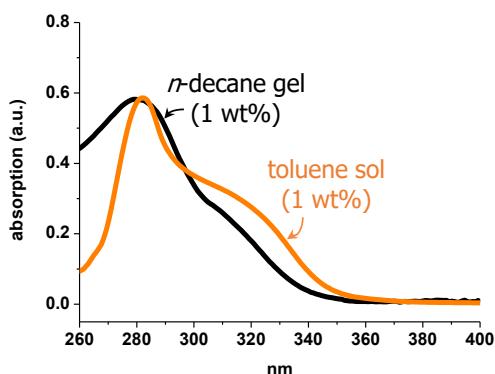
Yield: 89%. IR (KBr,  $\text{cm}^{-1}$ ): 3249, 2921, 2851, 1645, 1583, 1526, 1505, 1468, 1425, 1380, 1338, 1231, 1120, 738, 531, 411. Anal. Calcd for  $\text{C}_{381}\text{H}_{588}\text{Tm}_3\text{N}_{21}\text{O}_{39}$ : C, 69.40; H, 8.99; N, 4.46. Found: C, 69.65; H, 8.94; N, 4.43.

## Organogelation of Lanthanide(III) Complexes

### Organogelation

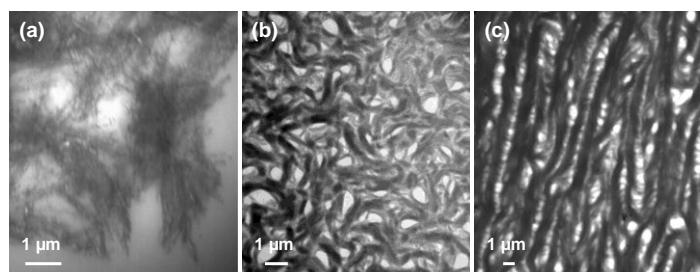
**Gd2** was dissolved in *n*-decane at 100 °C to give a clear solution with a concentration above CGC, and cooled down to rt for 1 h. **Ln4**-type complexes (**Gd4**, **Er4**, and **Tm4**) were dissolved in *n*-hexane at 60 °C or *n*-decane at 70 °C to give clear solutions with concentrations above CGCs, and cooled down to rt for 1 h. The resultant organogels were formed during cooling and thermally reversible (sol-gel transition temperatures; 60 °C in *n*-hexane, 70 °C in *n*-decane), confirmed by the inversion of vials.

### Absorption spectra of *n*-decane gel (1 wt%) and toluene sol (1 wt%) of **Er4**



**Figure S2.** Absorption spectra of **Er4** in *n*-decane (1 wt%; gel state) and toluene (1 wt%; sol state). Absorption maxima were found to be 276 nm and 282 nm respectively.

### TEM measurement of fibrous networks



**Figure S3.** TEM images of fibrous networks of the dry gels obtained from (a) **Gd2** in *n*-decane (2 wt%; diameters, 70–160 nm), (b) **Gd4** in *n*-hexane (1 wt%; diameters, 0.1–0.4 μm), and (c) **Tm4** in *n*-hexane (1 wt%; diameters, 0.2–1.0 μm) after drying the samples on the carbon-coated copper grids.

## Liquid Crystalline Properties of Lanthanide(III) Complexes

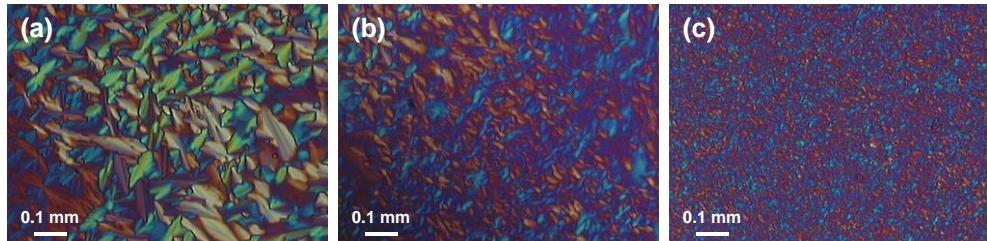
### DSC measurement of thermal properties

**Table S1.** DSC analyses of Eu(III), Tb(III), and Tm(III) complexes. The scanning rates of compounds **Ln2** and **Ln4** were  $10\text{ }^{\circ}\text{C min}^{-1}$  and  $1\text{ }^{\circ}\text{C min}^{-1}$ , respectively.

	Temp., $^{\circ}\text{C}$ ( $\Delta\text{H}$ , $\text{kJ mol}^{-1}$ )	
	2nd heating	2nd cooling
<b>Eu2</b>	Cr 240.13 (63.15) I	I 223 <sup>a</sup> Sm 214.72 (41.28) Cr
<b>Eu4<sup>b</sup></b>	Cr 131.85 (1.74) I	I 124.5 <sup>a</sup> Col <sub>h</sub> 119.02 (2.52) Cr
<b>Tb2</b>	Cr 216.75 (44.25) I	I 216.1 <sup>a</sup> Sm 177.88 (20.55) Cr
<b>Tb4</b>	Cr 92.86 (5.77) I	I 90.4 <sup>a</sup> Col <sub>h</sub> 65.36 (5.39) Cr
<b>Tm2</b>	Cr 234.65 (43.01) I	I 224.6 <sup>a</sup> Sm 204.76 (37.56) Cr
<b>Tm4</b>	Cr 122.45 (76.29) I	I 117.2 <sup>a</sup> Col <sub>h</sub> 103.94 (94.22) Cr

Abbreviations: Cr ) crystalline; Sm ) smectic mesophase; Col<sub>h</sub> ) columnar hexagonal mesophase; I ) isotropic. <sup>a</sup>Determined by POM. <sup>b</sup>from ref. S2 for comparison.

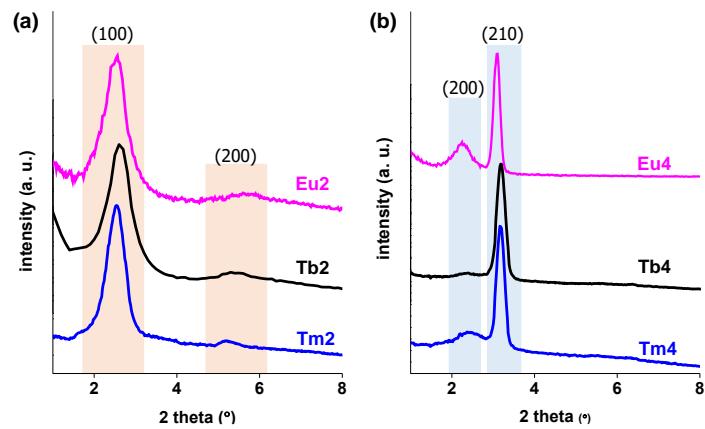
### POM measurement of the development of optical textures



**Figure S4.** Optical textures of (a) **Eu2**, (b) **Tb2**, and (c) **Tb4** developed at  $223\text{ }^{\circ}\text{C}$ ,  $216.1\text{ }^{\circ}\text{C}$ , and  $90.4\text{ }^{\circ}\text{C}$  respectively on cooling.

## SAXS measurement for liquid crystalline structures

Sample preparation: each sample was melted by heating to the isotropic point, and cooled down to the temperatures at which each mesophase appeared. After the optical texture was fully developed when monitored by POM, the sample was quenched to rt with acetone and studied with a small angle X-ray scatterometer.



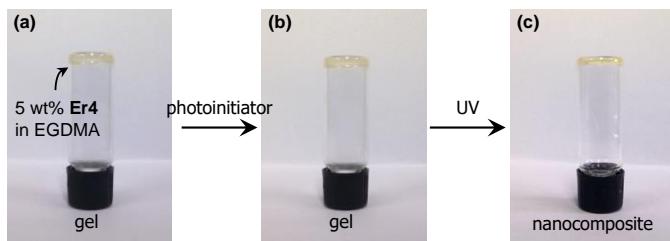
**Figure S5.** SAXS patterns obtained from (a) **Ln2** and (b) **Ln4** compounds in liquid crystalline states. Pink, black, and blue lines correspond to Eu(III), Tb(III), Tm(III) complexes respectively.

## Fabrication of Polymer Composite from Organogel Template

### Film fabrication

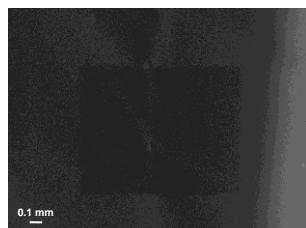
A photoinitiator (2,2-dimethoxy-2-phenylacetophenone, DMPA, total 2 wt%) was dissolved to **Er4** gel in ethylene glycol dimethacrylate (EGDMA) (5 wt%) by brief, gentle heating to 60 °C. The resultant EDGMA gel was formed on a quartz plate by drop-casting and irradiated at rt for 12 h using a high pressure mercury arc lamp (3 mW cm<sup>-2</sup>) equipped with a fan. The lamp was located 20-cm away from the sample. The control film was prepared by the same procedure above only using 2 wt% DMPA in EGDMA without **Er4**.

The same polymerization reaction in an inverted vial provided that the gel state (EGDMA gel, 5 wt%) was maintained while incorporated with photoinitiator (DMPA) and polymerized under UV irradiation, when monitored by the vial inversion method.



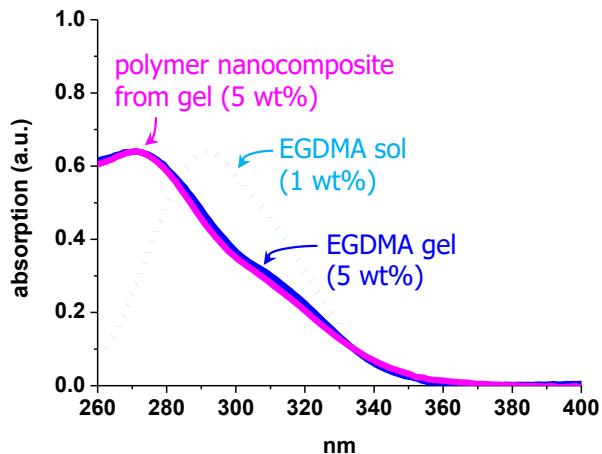
**Figure S6.** Photographs of (a) EGDMA gel (5 wt%) in an inverted vial, (b) after incorporation of photoinitiator (DMPA), and (c) while polymerized under UV irradiation. The gel state was maintained during the processing.

### SEM measurement for the control film



**Figure S7.** SEM image of the surface of the control sample prepared from EGDMA and DMPA (2 wt%) without using **Er4**.

### Absorption spectra of Er4 gel in EGDMA and the nanocomposite from the gel



**Figure S8.** Absorption spectra of **Er4** sol in EGDMA (1 wt%; sky blue), **Er4** gel in EGDMA (5 wt%; blue), and a polymer nanocomposite after the gel-state polymerisation (5 wt%; pink). During the sol-gel transition, the absorption maximum was blue-shifted from 291 (sol) to 271 nm (gel) as the concentration increased from 1 to 5 wt%, and no more changed after polymerisation ( $\lambda_{\text{max}} = 271$  nm).

### References

1. M. J. Jeong, J. H. Park, C. Lee and J. Y. Chang. *Org. Lett.*, 2006, **8**, 2221.
2. H. Kim and J. Y. Chang, *Soft Matter*, 2011, **7**, 7952.
3. H. Kim and J. Y. Chang, *RSC Adv.*, 2013, **3**, 1774.