

Supplementary Information

Synthesis of a film-forming europium(III) complex and its organogelation and photoluminescent properties

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Materials

1,3,5-Triacetoacetamidobenzene,¹ 5-amino-1,10-phenanthroline² and 3,4,5-tris(dodecyloxy)benzoic acid³ were prepared following synthetic procedures reported previously. All other chemicals were purchased from Aldrich and used without any further purification. Tetrahydrofuran (THF) was dried over sodium metal and distilled. Other reagent grade solvents were used as received.

Measurement

¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 (300 MHz) and Avance 500 (125MHz) spectrometer. Elemental analyses were performed using a Flash EA 1112 elemental analyzer. FT-IR measurements were made on a PERKIN ELMER Spectrum GX I using KBr pellets. X-ray diffraction patterns were obtained using Bruker Xps GADDS (Cu K α radiation, $\lambda = 1.54 \text{ \AA}$). 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. SEM images were obtained by using a JEOL JSM-6330F microscope. TEM images were taken by using a JEM1010 microscope operating at 80 kV. The organogel was heated at 70 °C and dropped on a carbon-coated copper grid which was preheated at the same temperature. The sample was cooled to room temperature and dried.

Synthesis of compound 1

To a solution of 3,4,5-trioctyloxybenzoic acid (2.0 g, 2.96 mmol) in chloroform (100 mL) was added thionyl chloride (0.43 mL, 5.93 mmol). After stirred for 4 h at rt, the solvent and thionyl chloride were removed by evaporation. The crude product was dissolved in THF (100 mL) followed by addition of a solution of 5-amino-1,10-phenanthroline (0.69 g, 3.56 mmol) and triethylamine (0.41 mL, 2.96 mmol) in THF (10 mL). The reaction mixture was stirred overnight at rt. After evaporation of the solvent, the product was isolated by recrystallization in ethanol. Yield: 78%. ¹H NMR (300 MHz, CDCl₃, ppm): δ 9.25 (d, $J = 4.8 \text{ Hz}$, Ar-H, 1H), 9.17 (d, $J = 2.4 \text{ Hz}$, Ar-H, 1H), 8.35-8.24 (overlap, Ar-H, 3H), 8.11 (s, CONH, 1H), 7.72-7.63 (m, Ar-H, 2H), 7.12 (s, Ar-H, 2H), 4.08 (tt, overlap, OCH₂, 6H), 1.88-1.76 (m, OCH₂CH₂, 6H), 1.54-1.26 (m, alkyl chain proton, 54H), 0.89 (t, $J = 3 \text{ Hz}$, CH₃, 9H). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 166.94, 153.48, 150.20, 150.04, 146.54, 144.79, 142.10, 136.07, 131.31, 130.70, 129.04, 128.34, 124.96, 123.58, 122.84, 121.19, 106.45, 73.82, 69.66, 32.12, 32.10, 30.55, 29.95, 29.93, 29.89, 29.84, 29.79, 29.67, 29.62, 29.58, 29.55, 26.29, 22.86, 14.28. IR (KBr, cm⁻¹): 3420, 3249, 2920, 2851, 1643, 1585, 1505, 1468, 1424, 1381, 1338, 1231, 1120, 990, 880, 738, 650. Anal. Calcd for C₁₁₀H₁₇₂Cl₃EuN₆O₉: C, 77.51; H, 10.05; N, 4.93. Found: C, 77.77; H, 9.74; N, 4.87.

Synthesis of compound 2

Compound 2 was prepared according to the literature procedure with a minor modification.⁴ To a solution of compound 1 (1.0 g, 1.17 mmol) in hot ethanol (100 mL) was added dropwise a solution of europium(III) chloride hexahydrate (0.21 g, 0.59 mmol) in ethanol (3 mL). The reaction mixture was refluxed for 2h. The precipitate was isolated by filtration, washed with ethanol and dried in vacuo. Yield: 85%. Anal. Calcd for C₁₁₀H₁₇₂Cl₃EuN₆O₉: C, 66.70; H, 8.75; N, 4.24. Found: C, 66.74; H, 8.72; N, 4.21.

Synthesis of compound 3

A solution of 1,3,5-triacetoacetamidobenzene (63.17 mg, 0.17 mmol) in N-methyl-2-pyrrolidone (3 mL) was mixed with a solution of NaOH (21.54 mg, 0.54 mmol) in methanol (3 mL). This mixture was slowly added to a solution of compound **2** (2.0 g, 1.01 mmol) in hot chloroform (100 mL). The reaction mixture was refluxed overnight. After solvent evaporation, the product was dissolved in chloroform and precipitated in methanol. The precipitate was isolated by filtration, washed with methanol and dried in vacuo. The product was obtained as a brown powder. Yield: 74 %. IR (KBr, cm^{-1}): 3392, 3241, 2922, 2852, 1645, 1584, 1523, 1502, 1470, 1426, 1381, 1337, 1231, 1118, 736, 520, 418. Anal. Calcd for $\text{C}_{348}\text{H}_{534}\text{Eu}_3\text{N}_{21}\text{O}_{36}$: C, 69.16; H, 8.91; N, 4.87. Found: C, 68.99; H, 9.10; N, 4.63.

Synthesis of complex 4

2,2,6,6-Tetramethyl-3,5-heptanedione (0.09 mL, 0.43 mmol) and NaOH (17.62 mg, 0.44 mmol) were dissolved in methanol (3 mL). This solution was added dropwise to a solution of compound **3** (859 mg, 0.14 mmol) in chloroform (100 mL). The reaction mixture was refluxed overnight. After solvent evaporation, the resulting product was dissolved in chloroform and precipitated in methanol. The precipitate was isolated by filtration, washed with methanol and dried in vacuo. The product was obtained as a yellow powder. Yield: 88%. IR (KBr, cm^{-1}): 3423, 3246, 2922, 2852, 1644, 1583, 1526, 1502, 1468, 1424, 1380, 1338, 1232, 1120, 740, 536, 415. Anal. Calcd for $\text{C}_{381}\text{H}_{588}\text{Eu}_3\text{N}_{21}\text{O}_{39}$: C, 69.94; H, 9.06; N, 4.50. Found: C, 69.99; H, 9.11; N, 4.53.

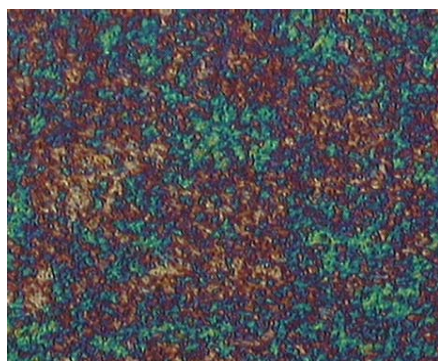


Fig. S1 POM image of complex **4** at 124 °C on cooling.

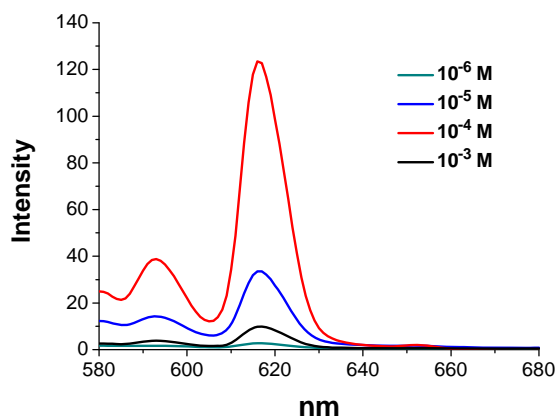


Fig. S2 Emission spectra of complex **4** in toluene with various concentrations obtained at 25 °C ($\lambda_{\text{ex}} = 310$ nm).

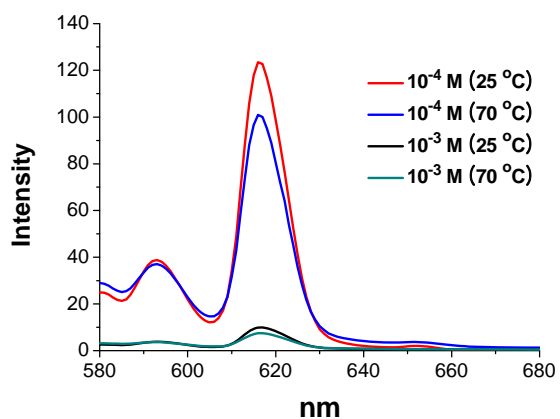


Fig. S3 Emission spectra of complex **4** in toluene obtained at 25 and 70 °C ($\lambda_{\text{ex}} = 310$ nm).

References

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