

**Metallomesogens with extended bent tridentate receptors: columnar and cubic mesomorphism tuned by the size of the lanthanide metal ions.**

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**Supporting Information**

**Synthesis of 2,6-bis-[1-ethyl-5-(3,4,5-tris(dodecyloxy)-benzoate)-benzimidazol-2-yl]pyridine**

**(L3).** A catalytic quantity of 4-diméthylaminopyridine and 2,6-bis-(1-éthyl-5-hydroxy-benzimidazol-2-yl)pyridine<sup>8</sup> (0.20 g, 0.5 mmol) were refluxed for 6 h with a solution of 3,4,5-tri(dodecyloxy)-benzoic acid (0.68 g, 1.0 mmol) and 1-(3-diméthylaminopropyl)-3-éthylcarbodiimide hydrochloride (EDCI, 0.29 g, 1. mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml). The resulting mixture was washed with water (100 ml water), the organic layer separated, dried (Na<sub>2</sub>SO<sub>4</sub>) and evaporated to dryness. The crude residue was purified by column chromatography (silicagel; CH<sub>2</sub>Cl<sub>2</sub>/MeOH 99.5:0.5→99:1) to give 600 mg (0.35 mmol, yield 70%) of L3 as a yellow solid. Anal. Calcd. for C<sub>109</sub>H<sub>173</sub>N<sub>5</sub>O<sub>10</sub>: C, 76.40; H, 10.18; N, 4.09. Found: C, 76.06; H, 10.17; N 3.94. <sup>1</sup>H NMR in CDCl<sub>3</sub>: δ/ppm 0.82-0.86 (18H, m), 1.23-1.40 (114H, m), 1.69-1.86 (12H, m), 4.04 (12H, t, *J*<sup>3</sup>=6.3 Hz), 4.76 (4H, q, *J*<sup>3</sup>=7.2 Hz), 7.18 (2H, dd, *J*<sup>3</sup>=9.0 Hz, *J*<sup>4</sup>=2.1 Hz), 7.43 (4H, s), 7.48 (2H, d, *J*<sup>3</sup>=9.0 Hz), 7.64 (2H, d, *J*<sup>4</sup>=2.1 Hz), 8.05 (1H, t, *J*<sup>3</sup>=8.1 Hz), 8.32 (2H, d, *J*<sup>3</sup>=7.8 Hz). <sup>13</sup>C NMR in CDCl<sub>3</sub>: δ/ppm 14.33, 15.70 (primary C); 22.90, 26.30, 29.52, 29.57, 29.61, 29.79, 29.85, 29.91, 29.95, 30.56, 32.13, 40.24, 69.48, 73.80 (secondary C); 108.80, 110.68, 113.31, 118.43, 126.14, 138.46 (tertiary C); 124.23, 134.14, 143.13, 143.40, 147.20, 150.03, 151.05, 153.18, 165.84 (quaternary C). ESI-MS (MeOH): 1736.6 ([M+Na]<sup>+</sup>).

The derivative **2,6-bis-[1-ethyl-5-(3,4,5-tris(butyloxy)-benzoate)-benzimidazol-2-yl]pyridine (L3-C4)** was obtained with the same procedure by using 3,4,5-tri(butyloxy)-benzoic acid. Anal Calcd for C<sub>61</sub>H<sub>77</sub>N<sub>5</sub>O<sub>10</sub>: C, 70.43; H, 7.46; N, 6.73 . Found: C, 70.14; H, 7.57; N, 6.50. <sup>1</sup>H NMR in CDCl<sub>3</sub>: δ/ppm 0.92-0.99 (18H, m), 1.38 (6H, t, *J*<sup>3</sup>=7.2 Hz), 1.45-1.58 (12H, m), 1.68-1.85 (12H, m), 4.05 (12H, t, *J*<sup>3</sup>=6.3 Hz), 4.78 (4H, q, *J*<sup>3</sup>=7.2 Hz), 7.19 (2H, dd, *J*<sup>3</sup>=8.7 Hz, *J*<sup>4</sup>=2.1 Hz), 7.45 (4H, s), 7.48 (2H, d, *J*<sup>3</sup>=8.7 Hz), 7.64 (2H, d, *J*<sup>4</sup>=2.1 Hz), 8.05 (1H, t, *J*<sup>3</sup>=7.8 Hz), 8.33 (2H, d, *J*<sup>3</sup>=7.8 Hz). <sup>13</sup>C NMR in CDCl<sub>3</sub>: 14.06, 14.09, 15.70 (primary C); 19.35, 19.48, 31.54, 32.54, 40.24, 69.16, 73.41 (secondary C); 108.79, 110.69, 113.30, 118.42, 126.12, 138.46 (tertiary C); 124.26,

134.15 , 143.13, 143.40, 147.19, 150.03, 151.06, 153.20, 165.85 (quaternary C). ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 9:1): 1062.5 ([M+Na]<sup>+</sup>), 2102.9 ([2M+Na]<sup>+</sup>).

**Preparation of 2,6-bis[ethyl-6-(4-dodecyloxybenzoic ester) benzimidazol-2-yl]pyridine (L4).**

A dimethylformamide solution (20 ml) of dodecyloxybenzoic acid (153.6 mg, 0.5 mmol) and carbonyldiimidazole (84 mg, 1 mmol) was stirred 1h at room temperature. 2,6-bis(1-ethyl-6-hydroxy-benzimidazol-2-yl)pyridine (100mg, 0.25 mmol)<sup>8</sup> was then added and the resulting pale yellow solution was stirred for 24h at 60°C under an inert atmosphere. The solution was evaporated to dryness, and half saturated aqueous NaCl (15 ml) was added. The resulting suspension was extracted with dichloromethane (3 x 30mL). The combined organic layer was washed with water (3 x 30 mL), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated. The crude residue was purified by column chromatography (silicagel; CH<sub>2</sub>Cl<sub>2</sub>/THF 95:5) to give 125 mg (0.13 mmol, yield 52%) of L4. Anal. Calcd. for C<sub>61</sub>N<sub>5</sub>H<sub>77</sub>O<sub>6</sub>: C, 75.04; H, 7.95; N, 7.17. Found: C, 75.06; H, 7.94; N, 7.10. <sup>1</sup>H NMR in CDCl<sub>3</sub>: δ/ppm 8.41 (2H, d, <sup>3</sup>J= 9 Hz), 8.13 (4H, d, <sup>3</sup>J= 9 Hz), 8.01 (2H, d, <sup>3</sup>J= 9 Hz), 7.90 (1H, t, <sup>3</sup>J= 8 Hz), 7.37 (2H, s), 7.19 (2H, d, <sup>3</sup>J= 9 Hz), 6.96 (4H, d, <sup>3</sup>J= 9 Hz), 4.76 (4H, q, <sup>3</sup>J= 7 Hz), 4.02 (4H, t, <sup>3</sup>J= 6 Hz), 1.80 (6H, q, <sup>3</sup>J= 8 Hz), 1.47 (8H, m), 1.24 (36H, m), 0.85 (6H, t, <sup>3</sup>J= 6 Hz). <sup>13</sup>C NMR in CDCl<sub>3</sub>: δ/ppm 14.23, 15.47, 15.48 (primary C); 22.86, 24.12, 24.32, 24.69, 25.45, 25.72, 29.36, 30.75, 41.68, 64.53, 71.69 (secondary C); 104.02, 114.557, 117.87, 120.86, 121.64, 126.08 (tertiary C); 136.18, 138.57, 147.98, 149.73, 150.57, 163.84, 165.60 (quaternary C). EI-MS: 975.6 ([M]<sup>+</sup>).

**Preparation of [Zn(L1)(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>·0.3H<sub>2</sub>O and [Zn(L1)(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>·DMF (1).** The dropwise addition of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.88g, 2.96 mmol) in dichloromethane/ethanol (10 ml) into a dichloromethane solution of L1 (1g, 2.96 mmol) gave a white precipitate [Zn(L1)(NO<sub>3</sub>)<sub>2</sub>]<sup>+</sup>·0.3H<sub>2</sub>O which was filtered

and washed with hexane (10 ml) and dried under vacuum (1.83 g, 2.84 mmol, yield 96%).  
Anal. Calcd. for  $C_{21}N_7H_{17.6}O_{6.3}Zn$ : C, 47.14; H, 3.33; N, 18.32. Found: C, 47.02; H, 3.35; N, 18.66.  
 $^1H$  NMR in DMF-d<sub>7</sub>:  $\delta$ /ppm 8.71 (1H, t,  $^3J=8$  Hz), 8.50 (2H, d,  $^3J=8$  Hz), 7.70 (2H, d,  $^3J=9$  Hz), 7.14 (6H, m), 4.34 (6H, s).  $^{13}C$  NMR in DMSO-d<sub>6</sub>:  $\delta$ /ppm 33.65 (primary C); 112.65, 118.81, 124.94, 125.30, 125.76, 137.76 (tertiary C); 139.68, 144.03, 148.44 (quaternary C). Conductivity:  $\Lambda$ (DMF,  $10^{-3}M$ )=155.7  $\Omega^{-1} \cdot M^{-1} \cdot cm^2$  (27°C). Suitable crystals of  $[Zn(L1)(NO_3)_2] \cdot DMF$  (**1**) for X-ray diffraction were obtained by recrystallization in a dimethylformamide/diethylether.

**Preparation of  $[Zn(L2)(NO_3)_2] \cdot 3H_2O$  (**2**).** L2 (40 mg, 0.041 mmol) in dichloromethane (2 ml) was added a solution of  $Zn(NO_3)_2 \cdot 6H_2O$  (10.4 mg, 0.041 mmol) in acetonitrile (2 ml). The yellow resulting solution was stirred overnight and dichloromethane was then evaporated. Diffusion of diethylether provided 35 mg of  $[Zn(L2)(NO_3)_2] \cdot 3H_2O$  (**2**, 0.029 mmol, yield 70%) as yellow microcrystals. Anal. Calcd for  $C_{61}N_7H_{83}O_{15}Zn$ : C, 60.06; H, 6.85; N, 8.03. Found: C, 60.06; H, 6.60; N, 7.99.  $^1H$  NMR in  $CDCl_3$ :  $\delta$ /ppm 8.22 (1H, t,  $^3J=8$  Hz), 8.12 (4H, d,  $^3J=9$  Hz), 8.05 (2H, d,  $^3J=9$  Hz), 7.88 (2H, s), 7.36 (2H, d,  $^3J=9$  Hz), 7.14 (2H, d,  $^3J=9$  Hz), 7.34 (4H, d,  $^3J=9$  Hz), 4.34 (4H, m), 4.00 (4H, t,  $^3J=6$  Hz), 1.80 (6H, q,  $^3J=8$  Hz), 1.49 (8H, m), 1.24 (36H, m), 0.85 (6H, t,  $^3J=6$  Hz).  $^{13}C$  NMR in  $CDCl_3$ :  $\delta$ /ppm 14.35, 15.47 (primary C); 22.91, 26.21, 29.35, 29.58, 29.63, 29.80, 29.83, 29.86, 29.89, 32.13, 66.09, 68.56 (secondary C); 111.16, 113.10, 114.57, 121.19, 121.68, 122.80 (tertiary C); 132.68, 134.33, 139.11, 142.82, 149.25, 163.93, 165.39 (quaternary C). Conductivity:  $\Lambda$ (DMF,  $10^{-3}M$ )=118.5  $\Omega^{-1} \cdot M^{-1} \cdot cm^2$  (27°C). TGA: at 240°C, weight loss of two water molecules (calc: 35 uma, found: 36 uma).

**Preparation of  $[Zn(L4)(NO_3)_2] \cdot 3H_2O$  (**3**).**  $Zn(NO_3)_2 \cdot 6H_2O$  (15.2 mg, 0.05 mmol) in acetonitrile (2 ml) was added to L4 (50 mg, 0.05 mmol) in dichloromethane (2 ml). After 10 mn stirring at room temperature, a white precipitate was formed. The suspension was filtered and the white residual

solid dried. Recrystallisation in THF/diethylether gave 48.8 mg of  $[\text{Zn}(\text{L4})(\text{NO}_3)_2] \cdot 3\text{H}_2\text{O}$  (**3**, 0.04 mmol, yield 80%) as a yellow microcrystalline powder. Anal. Calcd. for  $\text{C}_{61}\text{N}_7\text{H}_{83}\text{O}_{15}\text{Zn}$ : C, 60.06; H, 6.85; N, 8.03. Found: C, 60.12; H, 6.52; N, 8.00.  $^1\text{H}$  NMR in  $\text{CDCl}_3$ :  $\delta$ /ppm 8.26 (1H, t,  $^3J = 9$  Hz), 8.16 (2H, d,  $^3J = 9$  Hz), 8.11 (4H, d,  $^3J = 9$  Hz), 8.05 (2H, d,  $^3J = 9$  Hz), 7.43 (2H, s), 7.29 (2H, d,  $^3J = 9$  Hz), 6.94 (4H, d,  $^3J = 9$  Hz), 4.54 (4H, m), 4.02 (4H, t,  $^3J = 6$  Hz),  $\delta$  1.80 (8H, m), 1.59 (6H, t,  $^3J = 6.5$  Hz), 1.45 (2H, m), 1.24 (36H, m), 0.85 (6H, t,  $^3J = 6$  Hz).  $^{13}\text{C}$  NMR in  $\text{CDCl}_3$ :  $\delta$ /ppm 14.33, 15.49 (primary C); 22.91, 26.21, 29.35, 29.58, 29.63, 29.80, 29.83, 29.86, 29.89, 32.13, 66.09, 68.56 (secondary C); 111.16, 113.10, 114.57, 121.19, 121.68, 122.80, (tertiary C); 132.68, 134.33, 139.11, 142.82, 149.25, 163.93, 165.39 (quaternary C). Conductivity:  $\Lambda(\text{DMF}, 10^{-3}\text{M}) = 121.1 \Omega^{-1} \cdot \text{M}^{-1} \cdot \text{cm}^2$  (27°C).

**Preparation of  $[\text{Zn}(\text{L3})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$  (**4**).**  $\text{L}^3$  (0.050 g,  $2.92 \cdot 10^{-5}$  mol) in  $\text{CH}_2\text{Cl}_2$  (5 ml) was added to  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.009 g,  $3.02 \cdot 10^{-5}$  mol) in  $\text{CH}_3\text{CN}$  (5 ml). The solution was refluxed for 12 hours and the  $\text{CH}_2\text{Cl}_2$  was evaporated. The resulting white precipitate was filtered, washed with  $\text{CH}_3\text{CN}$  and dried to give 0.047 g of  $[\text{Zn}(\text{L3})(\text{NO}_3)_2] \cdot \text{H}_2\text{O}$  (**4**,  $2.46 \cdot 10^{-5}$  mol, yield = 84 %). Anal. Calcd. for  $\text{C}_{109}\text{H}_{175}\text{N}_7\text{O}_{17}\text{Zn}$ : C, 68.15; H, 9.18; N, 5.10. Found: C, 68.36; H, 9.11; N, 5.07.  $^1\text{H}$  NMR in  $\text{CDCl}_3$ :  $\delta$ /ppm 0.84 (18H, t,  $J^3 = 9.0$  Hz), 1.15-1.40 (96H, m), 1.40-1.56 (12H, m), 1.62 (6H, t,  $J^3 = 6.0$  Hz), 1.70-1.92 (12H, m), 4.07 (12H, t,  $J^3 = 6.0$  Hz), 4.40-4.50 (4H, br), 7.19-7.23 (2H, br), 7.41-7.44 (6H, m), 7.90-7.96 (2H, br), 8.08 (2H, d,  $J^3 = 7.8$  Hz), 8.27 (1H, t,  $J^3 = 7.5$  Hz). ESI-MS ( $\text{CH}_2\text{Cl}_2$ ):  $([\text{M}-\text{NO}_3]^+) = 1839.1$ .

**Preparation of  $[\text{Ln}(\text{L3})(\text{NO}_3)_3]$  (**Ln = Eu, 5; Ln = Dy, 6; Ln = Lu, 7**).**  $\text{L}^3$  ( $0.10 \text{ g}, 5.84 \cdot 10^{-5} \text{ mol}$ ) in dichloromethane (5 ml) was added to  $\text{Ln}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  (**Ln = Eu,  $x = 2.6$ ; Ln = Dy,  $x = 2.5$ ; Ln = Lu,  $x = 3.7$** ) in acetonitrile (5 ml). After 1 h. stirring at RT, the dichloromethane was evaporated and

the white precipitate was filtered, washed with CH<sub>3</sub>CN and dried to give 80 % of [Ln(L3)(NO<sub>3</sub>)<sub>3</sub>] (Ln = Eu, **5**; Ln = Dy, **6**; Ln = Lu, **7**).

**5**: Anal. Calcd. for C<sub>109</sub>H<sub>173</sub>N<sub>8</sub>O<sub>19</sub>Eu: C, 63.81; H, 8.50; N, 5.46. Found: C, 64.13; H, 8.72; N, 5.18.

<sup>1</sup>H NMR in CDCl<sub>3</sub>: δ/ppm : 1.30-2.20 (144H, m); 4.00-4.40 (12H, m), 5.46 (4H, s), 5.88 (2H, s), 6.92 (1H, s), 7.44 (4H, s), 7.77 (2H, m), 9.06 (2H, s), 18.18 (2H, s).

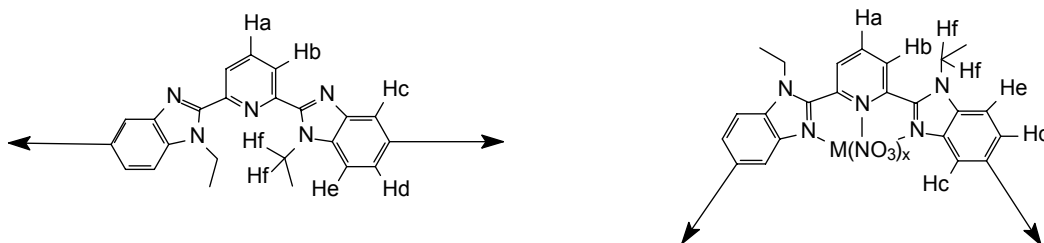
**6**: Anal. Calcd. for C<sub>109</sub>H<sub>173</sub>N<sub>8</sub>O<sub>19</sub>Dy: C, 63.49; H, 8.46; N, 5.43. Found: C, 63.32; H, 8.50; N, 5.30.

<sup>1</sup>H NMR in CDCl<sub>3</sub>: δ/ppm -20.0 (10H, br), -18.1 (5H, br), -9.4 (8H, br), -5.0 (4H, br), -2.0-2.0 (144H, m)

**7**: Anal. Calcd. for C<sub>109</sub>H<sub>173</sub>N<sub>8</sub>O<sub>19</sub>Lu: C, 63.11; H, 8.41; N, 5.40. Found: C, 63.03; H, 8.41; N, 5.40.

<sup>1</sup>H NMR in CDCl<sub>3</sub>: δ/ppm 0.81-0.85 (18H, m), 1.15-1.40 (96H, m), 1.41-1.60 (12H, m), 1.65 (6H, t,  $J^3 = 7.2$  Hz), 1.70-1.90 (12H, m), 4.00-4.10 (12H, m), 4.40-4.55 (4H, large), 7.23 (2H, dd,  $J^3 = 9.0$  Hz,  $J^4 = 1.8$  Hz), 7.43 (4H, s), 7.45 (2H, d,  $J^3 = 9.0$  Hz), 8.09 (2H, d,  $J^3 = 8.4$  Hz), 8.12 (2H, d,  $J^4 = 2.1$  Hz), 8.35 (1H, t,  $J^3 = 8.1$  Hz).

The aromatic parts of the  $^1\text{H}$  NMR spectra of the ligand L3 and complexes **4**, **5** and **7** are shown below in order to demonstrate the meridional complexation of the tridentate binding unit to the metal ions in solution.<sup>8</sup>



Composé	Ha [ppm]	Hb [ppm]	Hc [ppm]	Hd [ppm]	He [ppm]	Hf [ppm]
L3	8.05	8.32	7.64	7.18	7.48	4.76
Zn(L3)(NO <sub>3</sub> ) <sub>2</sub>	8.27	8.08	7.19	7.21	7.43	4.45
Lu(L3)(NO <sub>3</sub> ) <sub>3</sub>	8.35	8.09	8.12	7.24	7.46	4.47
Eu(L3)(NO <sub>3</sub> ) <sub>3</sub>	6.92	5.88	18.18	9.06	7.77	5.46