Electronic supplementary information

4,7-DI-*n*-BUTOXY-1,10-PHENANTHROLINE-2,9-DICARBOXAMIDE: A TETRADENTATE LIGAND FEATURING EXCELLENT SOLUBILITY IN NONPOLAR MEDIA

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S1. Starting materials and instrumentation

1-Iodobutane (Aldrich), SeO_2 (Aldrich), triethylamine (Acros), potassium carbonate (Khimmed), *n*-heptane (Panreac), cyclohexane (Panreac), 1,4-dioxane (Panreac), H_2O_2 (Aldrich), chloroform (Khimmed), ethyl acetate (Khimmed), THF (Khimmed), 1,2-dimethoxyethane (Aldrich), $SOCl_2$ (Merck), diethyl ether (Khimmed), $La(NO_3)_3(H_2O)_6$ (Dalchem), and acetonitrile (Panreac) were used as purchased without further purification. DMF (Komponent-Reaktiv) was dried by refluxing over phosphorus pentoxide and distilled prior to use. 2,9-Dimethyl-1,10-phenanthroline-4,7(1H,10H)-dione [1] and *N*-ethyl-4-*n*-hexylaniline [2] were prepared according to the procedures described earlier. Silica Gel 60 (Merck, 60 Å, 70–230 mesh) was used for column chromatography.

NMR spectra were recorded using Bruker Avance 400, Bruker Avance 500 and Bruker Avance 600 spectrometers. Chemical shifts were measured relative to the residual ^{1}H and ^{13}C resonances of the solvents: $CDCl_3$—7.24 (^{1}H) and 77.0 (^{13}C); $(CD_3)_2SO$—2.49 (^{1}H) and 39.5 (^{13}C); toluene-d_8—2.09 (for methyl, ^{1}H) and 20.4 (for methyl, ^{13}C). Chemical shifts are given in ppm and coupling constants—in Hz. Infrared spectra were registered with a Bruker Tensor 37 FTIR-spectrometer. Elemental analyses were performed in the Laboratory of Microanalysis of INEOS RAS.

S2. Preparation of *N,N'*-diethyl-*N,N'*-di-4-*n*-hexylphenyl-4,7-di-*n*-buthoxy-1,10-phenanthroline-2,9-dicarboxamide (2) and its $La(NO_3)_3$ complex (8)

2,9-Dimethyl-4,7-di-n-buthoxy-1,10-phenanthroline (3)

2,9-Dimethyl-1,10-phenanthroline-4,7(1H,10H)-dione (**1**) (16.04 g, 66.8 mmol), K_2CO_3 (36.8 g, 0.27 mol), dry DMF (300 mL), 1-iodobutane (24.6 g, 0.134 mol), and TEBAC (23 mg, 0.1 mmol) were sequentially placed in a 500-mL two-neck flask equipped with an overpressure valve. The suspension was heated to 80 °C and stirred overnight. After cooling to room temperature, the dark-colored suspension was slowly poured into 1 L of water under vigorous stirring. The resulting pale-brown amorphous precipitate was filtered off, washed twice with 100 mL of H_2O, and dried in a vacuum desiccator for 3 days. The target compound was extracted with cyclohexane by the Soxhlet technique and recrystallized from a heptane–cyclohexane mixture (1:1) to yield 17.9 g (76%) of pure product **2** as a light-beige microcrystalline powder. Mp: 212–214 °C. Calc. for $C_{22}H_{28}N_2O_2$ (%): C, 74.97; H, 8.01; N, 7.95. Found (%): C, 74.80; H, 7.88; N, 8.13. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.06 (s, 2H, CH_{Ar}), 6.81 (s, 2H, CH_{Het}), 4.17 (t, ^3J = 6.35, 4H, OCH_2), 2.84 (s, 6H, CH_3), 1.90 (m, 4H, OCH$_2$CH_2), 1.57 (m, 4H, CH_2CH$_3$), 1.01 (t, ^3J = 7.45, 6H, CH$_2$CH_3). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 161.76, 160.07, 145.49, 119.42, 117.89, 103.3, 68.13 (OCH_2), 30.94, 26.33, 19.26 (CH_2CH$_3$), 13.77 (CH$_2$$CH_3$).

4,7-Di-n-buthoxy-1,10-phenanthroline-2,9-dicarboxaldehyde (5)

SeO_2 (7.84 g, 70 mmol) was added to a mixture of dioxane-1,4 (200 mL) and H_2O (6 mL) in a 500-mL flask equipped with a condenser. The suspension was heated to 50 °C under stirring until complete homogenization. 2,9-Dimethyl-4,7-di-*n*-buthoxy-1,10-phenanthroline (**4**) (9.96 g, 28.3 mmol) was added and

the reaction mixture was stirred under reflux for 2 h, during which it turned red and then black. The hot suspension was passed through a Celite® pad and the clear solution was evaporated, affording a reddish residue. Flash chromatography (silica gel, MeOH/$CHCl_3$ (1:10)) and recrystallization of the solid from toluene gave two portions of yellow crystals of **5** with the overall yield 8.4 g (78%). Mp: 224–226 °C. Calc. for $C_{22}H_{24}N_2O_4$ (%): C, 69.46; H, 6.36; N, 7.36. Found (%): C, 69.24; H, 6.37; N, 7.41. IR (KBr, ν/cm^{-1}): 1707 (vs, C=O). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 10.42 (s, 2H, C(O)*H*), 8.34 (s, 2H, CH_{Ar}), 7.66 (s, 2H, CH_{Het}), 4.34 (t, ^3J = 6.35, 4H, OCH_2), 1.97 (m, 4H, OCH_2CH_2), 1.6 (m, 4H, CH_2CH_3), 1.04 (t, ^3J = 7.45, 6H, CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 193.82 (*C*(O)H), 162.97, 153.81, 146.51, 123.72, 121.68, 100.07, 69.24 (O*C*H_2), 30.77 (OCH_2CH_2), 19.24 (CH_2CH_3), 13.77 (CH_2CH_3).

4,7-Di-n-buthoxy-1,10-phenanthroline-2,9-dicarboxylic acid (6)

30% H_2O_2 (0.22 mL, 2.2 mmol) was added dropwise to a suspension of 4,7-di-*n*-buthoxy-1,10-phenanthroline-2,9-dicarboxaldehyde (**5**) (0.3 g, 0.79 mmol) in ethanol (10 mL) in a 50-mL flask. The reaction mixture was stirred for 15 h at room temperature. The solvents were evacuated on a rotary evaporator and the yellow residue was thoroughly triturated in 30 mL of H_2O. The precipitate was filtered off, washed with H_2O (2×10 mL) and dried in a vacuum desiccator under P_2O_5. The yield of a light-yellow amorphous powder of monohydrate **5**·H_2O was 0.32 g (99%). Mp: 172–174 °C. Calc. for $C_{22}H_{26}N_2O_7$ (%): C, 61.39; H, 6.09; N, 6.51. Found (%): C, 61.09; H, 6.16; N, 6.59. IR (KBr, ν/cm^{-1}): 3432, 3257, 3078 (br., OH), 1720 (s, C=O). ^{1}H NMR (600 MHz, $(CD_3)_2SO$), δ: 8.28 (s, 2H, CH_{Ar}), 7.85 (s, 2H, CH_{Het}), 4.44 (t, ^3J = 6.35, 4H, OCH_2), 1.91 (m, 4H, OCH_2CH_2), 1.57 (m, 4H, CH_2CH_3), 1.01 (t, ^3J = 7.45, 6H, CH_2CH_3). ^{13}C NMR (150 MHz, $(CD_3)_2SO$), δ: 165.43 (*C*(O)OH), 162.72, 149.48, 144.06, 121.97, 120.54, 103.74, 69.04 (O*C*H_2), 30.23 (OCH_2CH_2), 18.60 (CH_2CH_3), 13.53 (CH_2CH_3).

4,7-Di-n-buthoxy-N,N'-diethyl-N,N'-bis(4-n-hexylphenyl)-1,10-phenanthroline-2,9-dicarboxamide (2)

4,7-Di-*n*-buthoxy-1,10-phenanthroline-2,9-dicarboxylic acid (**6**) (0.62 g, 1.5 mmol) and a drop of DMF were sequentially added to 15 mL of thionyl chloride in a 50-mL Schlenk flask under argon, and the reaction mixture was stirred for 24 h at room temperature. Evaporation of volatiles under reduced pressure gave a light-green microcrystalline powder of dichloroanhydride **7** which was immediately used at the next stage as follows.

A solution of dichloroanhydride **7** in 20 mL of dry THF was added dropwise to a mixture of *N*-ethyl-4-*n*-hexylaniline (0.68 g, 3.3 mmol), trimethylamine (0.5 mL, 3.6 mmol), and 10 mL of THF in a 50-mL Schlenk flask, and the reaction mixture was left overnight under stirring at ambient temperature. The volatiles were removed on a rotary evaporator and the residue was redissolved in 40 mL of 1,2-dimethoxiethane. The white precipitate of ammonium salt was filtered off, and the filtrate was evaporated to afford a viscose oil. Extraction with 30 mL of hot heptane and subsequent chromatographic purification on silica gel (ethyl acetate/heptane (1:3)) gave after drying *in vacuo* 0.76 g (64%) of diamide **2** as a honey-like pale-brown substance. IR (KBr, ν/cm^{-1}): 1650 (s, C=O). ^{1}H NMR (400 MHz, toluene-d_8, 19 °C), δ: 7.92 (br. s, 2H), 7.41 (br. s, 4H), 7.15 (br. s, 2H), 6.92 (br. s, 4H), 4.16 (br. m, 4H), 3.53 (br. m, 4H), 2.20 (br. m, 4H), 1.70–0.75 (m, 42H). ^{1}H NMR (600 MHz, toluene-d_8, 80°C), δ: 7.98 (s, 2H, CH_{Ar}), 7.40 (d, ^3J = 8.11, 4H, $C_6H_2H_2$), 7.27 (s, 2H, CH_{Het}), 6.97 (d, ^3J = 8.11, 4H, $C_6H_2H_2$), 4.18 (q, ^3J = 7.0, 4H, NCH_2), 3.73 (t, ^3J = 6.35, 4H, OCH_2), 2.31 (t, 4H, $C_6H_4CH_2$), 1.57 (m, 4H), 1.44 (t, ^3J = 7 Гц, 6H, NCH_2CH_3), 1.34 (m, 12H), 1.34 (m, 12H), 1.10 (m, 12H), 0.86 (t, ^3J = 7.45, 6H), 0.80 (t, ^3J = 7.0, 6H). ^{13}C NMR (150 MHz, toluene-d_8, 80 °C), δ: 168.97 (*C*(O)N), 162.22, 156.32, 146.4, 141.67, 141.54, 129.17, 121.54, 119.71, 103.75, 68.66 (O*C*H_2), 45.93(br., N*C*H_2), 35.78, 32.06, 31.43, 31.31, 29.2, 22.9, 19.63, 14.14, 13.95 (br.), 13.85.

***Complex 2·La(NO$_3$)$_3$* (8)**

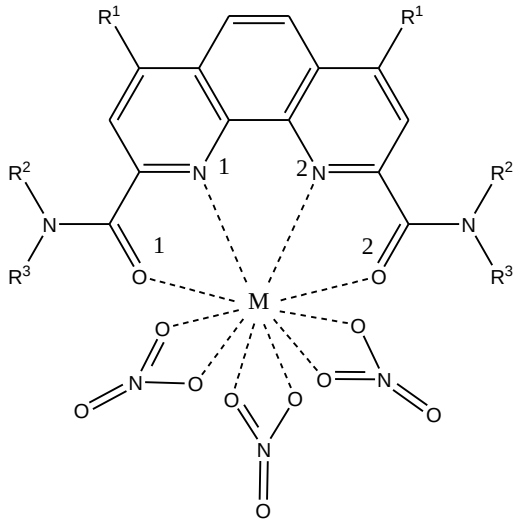
A mixture of 4,7-di-*n*-buthoxy-*N*,*N'*-diethyl-*N*,*N'*-bis(4-*n*-hexylphenyl)-1,10-phenanthroline-2,9-dicarboxamide (**6**) (0.2 g, 0.25 mmol) and $La(NO_3)_3(H_2O)_6$ (0.11 g, 0.25 mmol) in 5 mL of dry acetonitrile was stirred under reflux for 2 h. The solvent was removed under reduced pressure to afford a pale-yellow amorphous powder, which was triturated in 5 mL of Et_2O, filtered off, and dried under vacuum. The yield of

pure complex **8** was 0.26 g (93%). It was redissolved in 0.5 mL of hot acetonitrile and the solution was left overnight, affording the polyhedral single crystals suitable for X-ray crystallography. Calc. for $C_{50}H_{66}LaN_7O_{13}$ (%): C, 54.01; H, 5.98; N, 8.82. Found (%): C, 54.14; H, 6.1; N, 8.81. IR (KBr, ν/cm^{-1}): 1615 (s, C=O), 1467 (vs, NO_3, ν_{as}), 1274 (vs, NO_3, ν_s). ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.03 (s, 2H, CH_{Ar}), 7.31 (d, ^3J = 7.89, 4H, $C_6H_2H_2$), 7.24 (d, ^3J = 7.89, 4H, $C_6H_2H_2$), 6.42 (s, 2H, CH_{Het}), 4.14 (q, ^3J = 7.23, 4H, NCH_2), 3.55 (t, ^3J = 6.36, 4H, OCH_2), 2.61 (t, 4H, ^3J = 7.9, $C_6H_4CH_2$), 1.70 (m, 4H), 1.57 (m, 4H), 1.50–1.20 (m, 22H), 0.95 (t, ^3J = 7.24, 6H), 0.88 (t, ^3J = 6.8, 6H). ^{13}C NMR (150 MHz, $CDCl_3$), δ: 168.09 (*C*(O)N), 162.43, 151.59, 145.22, 144.57, 138.75, 130.26, 127.96, 121.97, 121.16, 106.28, 69.26, 48.94, 35.55, 31.62, 30.28, 29.03, 22.54, 19.07, 14.03, 13.59, 11.71.

S3. X-ray analysis of 8

Crystal data for **8**: $C_{50}H_{66}N_7O_{13}La$, M = 1112.00, monoclinic, space group P21/n, a = 15.8667(6), b = 19.7650(7), c = 17.4932(6) Å, β = 106.5340(7)º, V = 5259.1(3) Å3, d_{calc} = 1.404 g/cm3, Z = 4, MoKα radiation (λ = 0.71073 Å), μ = 8.80 cm-1, T = 120(2) K, $2\theta_{max}$ = 58°, R_1 = 0.0339 for 11528 reflections with $I > 2\sigma(I)$, and wR_2 = 0.0833 for all 13975 unique reflections (R_{int} = 0.0417). Crystal data were collected with a Bruker SMART APEX II diffractometer; the SHELX program package [3] was used throughout the calculations; CCDC reference number 1909560 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

Table S1. Selected bond lengths (Å) and angles (deg.) in the lanthanide complexes with PDCA ligands



Distances (Å) and angles (deg.)	Complexes				
	M = Nd, R^1 = H, R^2 = Et, R^3 = 4-EtC_6H_4 [4]	**M = Gd, R^1 = H, R^2 = Et, R^3 = 4-EtC_6H_4 [4]**	**M = Eu, R^1 = Cl, R^2 = Et, R^3 = Ph [5]**	**M = La, R^1 = OC_5H_{11}, R^2 = Et, R^3 = Ph [5]**	**M = La, R^1 = OC_4H_9, R^2 = Et, R^3 = 4-$C_6H_{11}C_6H_4$ (8)**
M–O1	2.510(6)	2.485(5)	2.400(3)	2.572(2)	2.5689(15)
M–O2	2.389(6)	2.373(4)	2.428(4)	2.559(2)	2.5314(15)
M–N1	2.599(6)	2.541(6)	2.632(3)	2.712(3)	2.6899(18)
M–N2	2.636(7)	2.572(6)	2.588(4)	2.716(3)	2.6990(17)
M–O(NO3)	2.517(6)–2.600(6)	2.462(5)–2.697(6)	2.495(3)–2.533(4)	2.570(3)–2.627(2)	2.5661(18)–2.6484(17)
O1–M–O2	153.7(2)	153.1(2)	157.0(1)	169.71(7)	168.54(5)

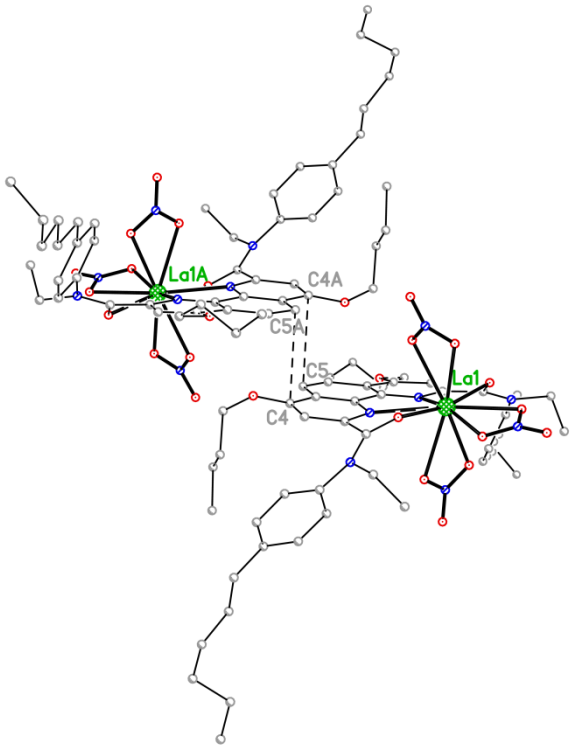


Figure S1. Centrosymmetric stacking dimers in the crystal of **8**.

In crystals, the molecules of complex **8** form centrosymmetric stacking-dimers (Fig. S1) with insignificant overlapping of aromatic systems of the phenanthroline ligands. The shortest interatomic distance in the dimer is C(4)–C(5A)$_{1-x,-y,2-z}$ 3.374(3) Å, the interplane distance is 3.48 Å, and the distance between centroids is 5.75 Å. The formation of analogous stacking dimers was detected in the case of all the previously described related complexes [4, 5].

References

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