Electronic supplementary information

for

Diastereoselective formation of luminescent dinuclear lanthanide(III) helicates with enantiomerically pure tartaric acid derived $bis(\beta$ -diketonate) ligands

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Characterization data for compounds 2_3M_2 (M = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb) and 3_3M_2 (M = La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Yb).

2₃M₂ (M = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb).

Complexes of 3R, 4R-bis-(3-phenyl-oxopropanoyl)-2, 2-dimethyldioxolan **2**-H₂ (0.12 mmol) are prepared as described before.

2₃**La**₂: Yield: 61 mg (0.039 mmol, 99 %). - IR (KBr): \tilde{v} (cm⁻¹) = 3060, 2986, 2931, 1601, 1566, 1511, 1482, 1435, 1398, 1306, 1269, 1208, 1158, 1087, 957, 855, 778, 694, 550. - UV (CH₂Cl₂): λ_{max} (nm) = 336, 249. - positive ESI MS: $m/z = 739 [M+Na+H]^{2+}$. - Analysis calcd. for C₆₉H₆₀O₁₈La₂ · 5 H₂O (1545.11): C 53.54, H 4.57; found: C 53.69, H 4.43.

2₃**Ce**₂: Yield: 62 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3060, 2984, 2927, 1599, 1560, 1513, 1482, 1383, 1273, 1208, 1086, 960, 853, 756, 694, 620, 506. - UV (CH₂Cl₂): λ_{max} (nm) = 331, 250. - positive ESI MS: m/z = 1457 [M+H]⁺; negativ ESI MS: m/z = 1493 [M+Cl]⁻. - Analysis calcd. for C₆₉H₆₀O₁₈Ce₂ · 5 H₂O (1547.54): C 53.55, H 4.56; found: C 53.87, H 4.95.

2₃**Pr**₂: Yield: 59 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3060, 2987, 2931, 1599, 1565, 1513, 1482, 1455, 1410, 1337, 1306, 1272, 1209, 1156, 1087, 959, 853, 778,

696. - UV (CH₂Cl₂): λ_{max} (nm) = 330, 249. - negative FAB MS: m/z = 1493 [M+Cl]⁻, 925 [M-2-Pr]⁻. - Analysis calcd. for C₆₉H₆₀O₁₈Pr₂ · 2 H₂O (1495.07): C 55.43, H 4.31; C 55.63, H 4.67.

2₃Nd₂: Yield: 61 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3060, 2989, 2929, 2854, 1600, 1567, 1514, 1483, 1453, 1407, 1307, 1273, 1210, 1158, 1088, 960, 856, 780, 695, 618. - UV (CH₂Cl₂): λ_{max} (nm) = 332, 250. - positive ESI MS: $m/z = 1465 [M+H]^+$. - Analysis calcd. for C₆₉H₆₀O₁₈Nd₂ · 2 H₂O (1501.74): C 55.19, H 4.30; found: C 55.17, H 4.59.

2₃**Sm**₂: Yield: 62 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3061, 2986, 2930, 1602, 1565, 1516, 1480, 1458, 1411, 1339, 1272, 1157, 1086, 962, 854, 775, 697, 620, 509. - UV (CH₂Cl₂): λ_{max} (nm) = 333, 249. - negative ESI MS: m/z = 1512 [M+Cl]⁻. - Analysis calcd. for C₆₉H₆₀O₁₈Sm₂ · 3 H₂O (1532.07): C 54.09, H 4.34; found: C 53.96, H 4.28.

2₃**Eu**₂: Yield: 60 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3060, 2986, 2931, 1602, 1566, 1515, 1482, 1458, 1409, 1271, 1211, 1157, 1087, 962, 854, 774, 695, 618, 514. - UV (CH₂Cl₂): λ_{max} (nm) = 332, 252. - positive ESI MS: m/z = 1503 [M+Na]⁺. - Analysis calcd. for C₆₉H₆₀O₁₈Eu₂ · H₂O (1499.16): C 53.08, H 4.07; found: C 53.16, H 4.06.

2₃**Gd**₂: Yield: 63 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3060, 2986, 2932, 1599, 1566, 1515, 1482, 1458, 1415, 1274, 1209, 1154, 1086, 852, 775, 696, 620, 497. - UV (CH₂Cl₂): λ_{max} (nm) = 329, 249. - positive ESI MS: m/z = 1494 [M+H]⁺. - Analysis calcd. for C₆₉H₆₀O₁₈Gd₂ · 4 H₂O (1563.79): C 53.00, H 4.38; found: C 53.24, H 4.23.

2₃Tb₂: Yield: 63 mg (0.040 mmol, quant.). - IR (KBr): ∇ (cm⁻¹) = 3061, 2987, 2929, 1603, 1566, 1521, 1481, 1417, 1340, 1272, 1157, 1088, 963, 856, 777, 696, 621, 513. - UV (CH₂Cl₂): λ_{max} (nm) = 331, 252. - positive ESI MS: m/z = 1495 [M+H]⁺. - Analysis calcd. for C₆₉H₆₀O₁₈Tb₂ · 3 H₂O (1549.12): C 53.50, H 4.29; found: C 53.54, H 4.46.

2₃**D**y₂: Yield: 60 mg (0.039 mmol, 96 %). - IR (KBr): \tilde{v} (cm⁻¹) = 3061, 2986, 2927, 1600, 1568, 1515, 1483, 1454, 1410, 1340, 1308, 1274, 1210, 1157, 1089, 962, 855, 779, 696,

620. - UV (CH₂Cl₂): λ_{max} (nm) = 331, 251. - positive ESI MS: $m/z = 1502 [M+H]^+$. - Analysis calcd. for C₆₉H₆₀O₁₈Dy₂ · 3 H₂O (1556.27): C 53.25, H 4.27; found: C 53.18, H 4.64.

2₃**Ho**₂: Yield: 61 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3062, 2987, 2927, 1600, 1567, 1515, 1483, 1455, 1412, 1340, 1309, 1275, 1210, 1157, 1090, 963, 855, 778, 696. - UV (CH₂Cl₂): λ_{max} (nm) = 330, 250. - positive ESI MS: $m/z = 1507 [M+H]^+$. - Analysis calcd. for C₆₉H₆₀O₁₈Ho₂ · H₂O (1525.10): C 54.34, H 4.10; found: C 54.39 H 4.28.

2₃**Er**₂: Yield: 64 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3062, 2987, 2932, 1602, 1568, 1517, 1483, 1456, 1411, 1341, 1308, 1277, 1211, 1158, 1091, 965, 856, 777, 697, 622, 558, 522. - UV (CH₂Cl₂): λ_{max} (nm) = 329, 250. - positive ESI MS: m/z = 1511 [M+H]⁺; negative ESI MS: m/z = 1547 [M+Cl]⁻, 1581 [M+2H₂O+Cl]⁻. - Analysis calcd. for C₆₉H₆₀O₁₈Er₂ · 3 H₂O (1565.79): C 52.93, H 4.25; found: C 52.67, H 4.22.

2₃Yb₂: Yield: 62 mg (0.040 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 3060, 2985, 2925, 1604, 1567, 1517, 1483, 1456, 1411, 1276, 1209, 1157, 1089, 964, 856, 777, 695, 622. - UV (CH₂Cl₂): λ_{max} (nm) = 329, 250. - positive ESI MS: m/z = 1523 [M+H]⁺. - Analysis calcd. for C₆₉H₆₀O₁₈Yb₂ · 2 H₂O (1559.34): C 53.15, H 4.14; found: C 53.12, H 4.60.

3₃M₂ (M = La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Yb).

Complexes of 3R, 4R-bis-(3-(4-bromophenyl)-oxopropanoyl)-2, 2-dimethyldioxolan $3-H_2$ (0.09 mmol) are prepared as described before.

3₃La₂: Yield: 58 mg (0.029 mmol, 98 %). - IR (KBr): \tilde{v} (cm⁻¹) = 2985, 2933, 1590, 1512, 1477, 1411, 1379, 1265, 1212, 1158, 1073, 1007, 959, 851, 792, 751. - UV (CH₂Cl₂): λ_{max} (nm) = 342, 267. - negative FAB MS: m/z = 1238 [M–L–La]⁻; positive ESI MS: m/z = 2023 [M+4H₂O+Na]⁺. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈La₂ · 3 H₂O (1982.46): C 41.80, H 3.05; found: C 41.74, H 3.05.

3₃Ce₂: Yield: 58 mg (0.029 mmol, 98 %). - IR (KBr): \tilde{v} (cm⁻¹) = 2986, 2933, 1588, 1553, 1513, 1475, 1411, 1378, 1367, 1212, 1157, 1092, 1008, 962, 848, 791, 750, 542. - UV (CH₂Cl₂): λ_{max} (nm) = 339, 267. - positive ESI MS: m/z = 988 [M+2Na]²⁺; negative FAB

MS: $m/z = 1825 [M^+-Ce^{3+}+Cl]^-$, 1274 $[M-L-Ce+Cl]^-$ 1241 $[M-L-Cl]^-$, 925 $[M-L-Ce-4Br]^-$. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Ce₂ · 3 H₂O (1984.89): C 41.75, H 3.05; found: C 41.76, H 2.85.

3₃**Pr**₂: Yield: 57 mg (0.029 mmol, 58 %). - IR (KBr): ∇ (cm⁻¹) = 2986, 2934, 1590, 1556, 1513, 1477, 1418, 1379, 1265, 1091, 1008, 849, 789, 752. - UV (CH₂Cl₂): λ_{max} (nm) = 365 (sh), 340, 267. - negative FAB MS: *m*/*z* = 1967 [M+H₂O+OH]⁻. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Pr₂ · 3 H₂O (1986.46): C 41.72, H 3.04; found: C 41.50 H 3.00.

3₃Nd₂: Yield: 59 mg (0.030 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 2984, 2933, 1596, 1555, 1514, 1476, 1416, 1378, 1338, 1265, 1212, 1162, 1075, 1006, 962, 848, 785, 555. - UV (CH₂Cl₂): λ_{max} (nm) = 360 (sh), 339, 267. - positive ESI MS: m/z = 1995 [M+H₂O+K]⁺; negative FAB MS: m/z = 1793 [M–Nd+2H]⁻, 1244 [M–L–Nd]⁻. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Nd₂ · 3 H₂O (1993.13): C 41.58, H 3.03; found: C 41.48, H 3.08.

3₃Sm₂: Yield: 59 mg (0.029 mmol, 98 %). - IR (KBr): \tilde{v} (cm⁻¹) = 2985, 2933, 1591, 1557, 1514, 1477, 1417, 1379, 1338, 1266, 1212, 1158, 1073, 1008, 962, 848, 783, 752, 536. - UV (CH₂Cl₂): λ_{max} (nm) = 365 (sh), 339, 269. - positive ESI MS: m/z = 2013 [M+2H₂O+Na]⁺; negative FAB MS: m/z = 1801 [M-Sm+2H]⁻, 1402 [M-L]⁻, 1249 [M-L-Sm]⁻. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Sm₂ · 5 H₂O (2041.48): C 40.60, H 3.16; found: C 40.62, H 3.24.

3₃Eu₂: Yield: 59 mg (0.029 mmol, 98 %). - IR (KBr): \tilde{v} (cm⁻¹) = 2985, 2933, 1710, 1692, 1670, 1660, 1556, 1513, 1477, 1418, 1379, 1265, 1209, 1072, 1007, 963, 850, 783, 744, 537. - UV (CH₂Cl₂): λ_{max} (nm)= 334, 266. – positive ESI MS: $m/z = 1977 [M+Na]^+$. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Eu₂ · 3 H₂O (2008.57): C 41.26, H 3.01; found: C 41.24 H 3.06.

3₃Tb₂: Yield: 59 mg (0.029 mmol, 98 %). - IR (KBr): \tilde{v} (cm⁻¹) = 2985, 2934, 1591, 1557, 1514, 1478, 1418, 1379, 1267, 1211, 1157, 1072, 1008, 848, 790. - UV (CH₂Cl₂): λ_{max} (nm)= 336, 268. - negative ESI MS: m/z = 2039 [M+2H₂O+Cl]⁻. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Tb₂ · 2 H₂O (2004.48): 41.35, H 2.92; found: 41.32 H 2.93.

3₃**Dy**₂: Yield: 60 mg (0.030 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 2985, 2934, 1599, 1557, 1515, 1477, 1418, 1380, 1268, 1212, 1158, 1072, 1007, 965, 848, 780, 754. - UV (CH₂Cl₂): λ_{max} (nm) = 365 (sh), 338, 268. - positive ESI MS: m/z = 1976 [M]⁺. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Dy₂ · 2 H₂O (2011.63): C 41.20, H 2.91; found: C 41.27, H 2.95.

3₃Ho₂: Yield: 60 mg (0.030 mmol, quant.). - IR (KBr): \tilde{v} (cm⁻¹) = 2984, 2933, 1600, 1556, 1513, 1416, 11377, 1264, 1212, 1163, 1092, 1004, 963, 850, 784, 751. - UV (CH₂Cl₂): λ_{max} (nm) = 364 (sh), 337, 268. - positive ESI MS: $m/z = 2016 [M+2H_2O]^+$. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Ho₂ · 2 H₂O (2016.49): C 41.10, H 2.90; found: C 40.51, H 2.82.

3₃**Er**₂: Yield: 59 mg (0.029 mmol, 98 %). - IR (KBr): \tilde{v} (cm⁻¹) = 2985, 2932, 2871, 1593, 1558, 1515, 1478, 1423, 1381, 1340, 1272, 1211, 1158, 1094, 1073, 966, 849, 782. - UV (CH₂Cl₂): λ_{max} (nm) = 363 (sh), 337, 267. - positive ESI MS: $m/z = 2021 [M+2H_2O+H]^+$. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Er₂ · 3 H₂O (2039.17): C 40.64, H 2.97; found: C 40.77, H 2.77.

3₃Yb₂: Yield: 60 mg (0.029 mmol, 98 %). - IR (KBr): \tilde{v} (cm⁻¹)= 2985, 2932, 1593, 1558, 1516, 1478, 1420, 1379, 1271, 1211, 1158, 1092, 1072, 1007, 965, 847, 785, 541. - UV (CH₂Cl₂): λ_{max} (nm)= 366 (sh), 336, 268. - positive ESI MS: $m/z = 2056 [M+2H_2O+Na]^+$, 2037 [M+H₂O+Na]⁺. - Analysis calcd. for C₆₉H₅₄Br₆O₁₈Yb₂ · 3 H₂O (2050.73): C 40.06, H 3.02; found: C 39.99 H 2.94.

Fig. S1 Room temperature luminescence spectra of the ligand **3**-H₂ in solid state, $\lambda_{em} = 494$ nm, $\lambda_{ex} = 409$ nm. Black line: excitation spectrum, gray line: emission spectrum.



Table S1 Ligand excitation and emission maxima λ_{max} /nm for the complexes L_3Ln_2

	L = 1		L = 2		L = 3	
	Exc.	Em.	Exc.	Em.	Exc.	Em.
free ligand					409 (weak: 285, 360, 446)	494 (weak: 450, 476, 525)
$\mathbf{L}_3 \mathrm{Eu}_2$	280, 338, 400	—	379	420	330, 375	_
L_3Tb_2	272, 328	400	340	430	290, 347	~ 440
L_3Ho_2					340	410, 430