Spontaneous enrichment of one-handed helix by dissolution of quasiracemic crystals of a tetranuclear single helical complex

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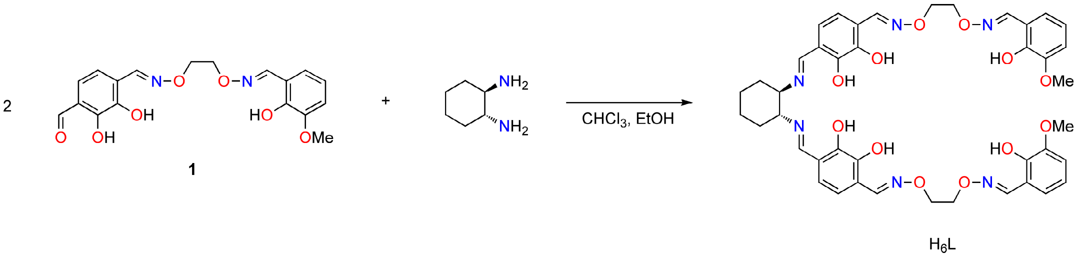
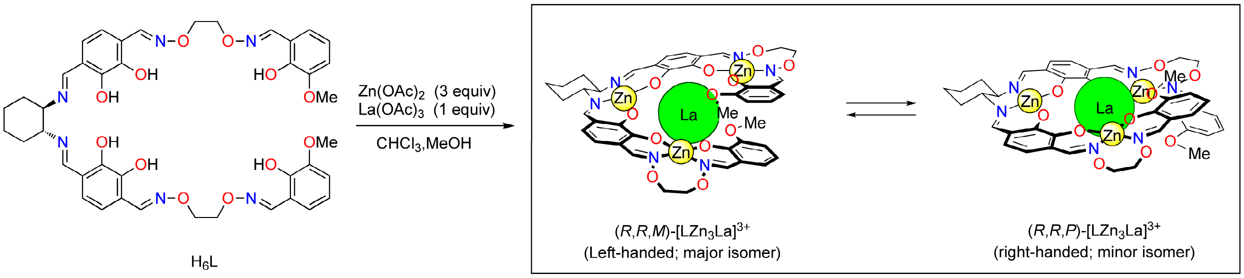
Supporting Information

Synthetic procedure for [$LZn_3La(OAc)_3$]

Synthesis of Ligand H_6L. A solution of *R*,*R*-cyclohexanediamine (17.8 mg, 0.156 mmol) in a small amount of ethanol/chloroform was added to a solution of aldehyde **1**[1] (129.8 mg, 0.312 mmol) in ethanol/chloroform (1:1, 10 mL) and the solution was heated for 3 h at 60 °C. After the solution was cooled to room temperature, the solvent was removed under reduced pressure and the crude product was purified by GPC (Japan Analytical Industry, LC908 equipped with JAIGEL 1H-2H columns; eluent, chloroform) to give H_6L (94 mg, 73%) as yellow solid, mp 91–92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.46-1.52 (m, 2H), 1.70-1.78 (m, 2H), 1.91 (d, J = 9.1 Hz, 2H), 1.98 (d, J = 13.8 Hz, 2H), 3.32-3.38 (m, 2H), 3.90 (s, 6H), 4.47-4.49 (m, 8H), 6.64 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H), 6.79-6.86 (m, 4H), 6.89 (dd, J = 7.4, 2.1 Hz, 2H), 8.197 (s, 2H), 8.201 (s, 2H), 8.24 (s, 2H), 9.38 (s, 2H), 9.74 (s, 2H), 13.64 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.03, 32.89, 56.19, 72.08, 73.08, 73.11, 113.57, 116.48, 117.93, 118.55, 118.74, 119.45, 121.66, 122.42, 146.04, 147.11, 148.16, 151.07, 151.40, 151.96, 164.49. Anal. Calcd for $C_{42}H_{46}N_6O_{12}$•$0.5H_2O$: C, 60.35; H, 5.67; N,10.05. Found: C, 60.19; H, 5.60; N, 9.82.



Synthesis of [$LZn_3La(OAc)_3$]. Solutions of H_6L (8.26 mg, 0.010 mmol) in chloroform, zinc(II) acetate dihydrate (6.58 mg, 0.030 mmol) in methanol, and lanthanum(III) acetate sesquihydrate (3.44 mg, 0.010 mmol) were mixed and the solvent was evaporated under reduced pressure. The residue was recrystallized from chloroform/methanol/ether to give [$LZn_3La(OAc)_3$] (8.84 mg, 55%) as yellow crystals; ^{1}H NMR (600 MHz, $CDCl_3/CD_3OD$, 1:1, 303 K) major isomer (*R*,*R*,*M*): δ 1.54-1.57 (m, 4H), 1.74 (s, 9H), 2.08-2.12 (brm, 2H), 2.62-2.65 (brm, 2H), 3.59-3.62 (brm, 2H), 3.73 (s, 6H), 4.11 (brd, J = 13 Hz, 2H), 4.17 (brdd, J = 15, 3 Hz, 2H), 4.48-4.52 (m, 2H), 4.99 (brt, J = 12 Hz, 2H), 6.41 (dd, J = 7.9, 1.2 Hz, 2H), 6.51 (t, J = 7.9 Hz, 2H), 6.55 (d, J = 8.4 Hz, 2H), 6.737 (d, J = 8.4 Hz, 2H), 6.84 (dd, J = 7.9, 1.2 Hz, 2H), 7.87 (s, 2H), 8.35 (s, 2H), 8.43 (s, 2H); minor isomer (*R*,*R*,*P*): δ 1.54-1.57 (m, 4H), 1.74 (s, 9H), 2.08-2.12 (brm, 2H), 2.62-2.65 (brm, 2H), 3.50-3.53 (brm, 2H), 3.78 (s, 6H), 4.13 (brd, J = 13 Hz, 2H), 4.20 (brdd, J = 15, 3 Hz, 2H), 4.48-4.52 (m, 2H), 4.92 (brt, J = 12 Hz, 2H), 6.42 (dd, J = 8.0, 1.1 Hz, 2H), 6.53 (t, J = 8.0 Hz, 2H), 6.55 (d, J = 8.3 Hz, 2H), 6.744 (d, J = 8.3 Hz, 2H), 6.87 (dd, J = 8.0, 1.1 Hz, 2H), 7.86 (s, 2H), 8.36 (s, 2H), 8.43 (s, 2H). Anal. Calcd for $C_{51}H_{55}Cl_6LaN_6O_{19}Zn_3$ (= [$LZn_3La(OAc)_3(MeOH)$]•$2CHCl_3$): C, 38.19; H, 3.46; N, 5.24. Found: C, 38.65; H, 3.42; N, 5.28.



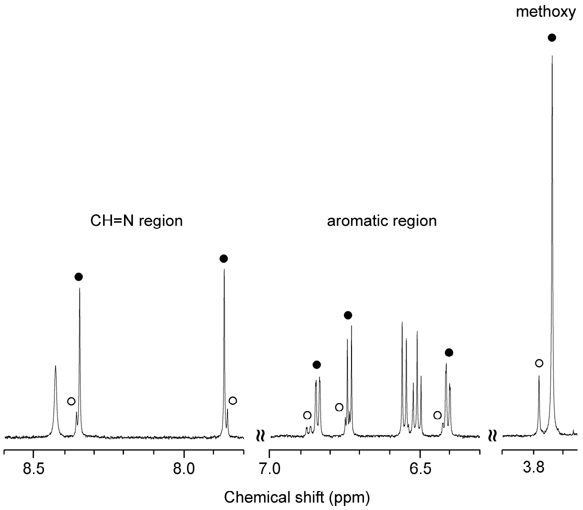


Figure S1. Part of the ^{1}H NMR spectrum of [$LZn_3La(OAc)_3$] in $CDCl_3/CD_3OD$ (1:1) at 600 MHz. Filled and open circles denote the signals of major (*R*,*R*,*M*) and minor (*R*,*R*,*P*) isomers, respectively.

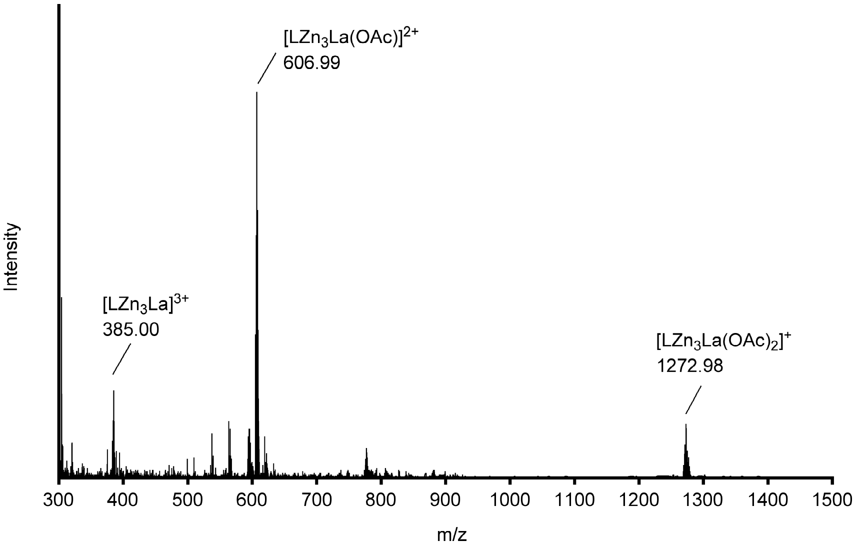


Figure S2. ESI-mass spectrum of [$LZn_3La(OAc)_3$].

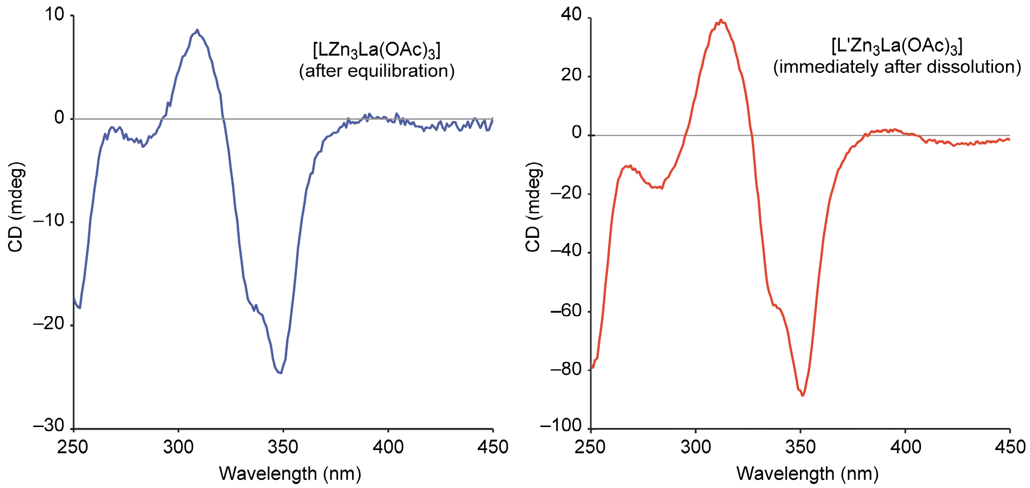


Figure S3. CD spectra of [LZn$_3$La(OAc)$_3$] in this study (0.006 mM) and (*M*)-[L'Zn$_3$La(OAc)$_3$][2] (0.012 mM) in chloroform/methanol (1:1).

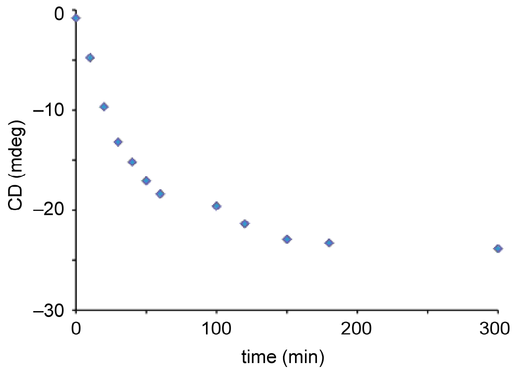


Figure S4. Change in the CD spectra of [LZn$_3$La(OAc)$_3$] in this study (0.006 mM) in chloroform/methanol (1:1).

References

[1] S. Akine, T. Taniguchi, T. Saiki, T. Nabeshima, *J. Am. Chem. Soc.*, 2005, **127**, 540-541

[2] S. Akine, T. Matsumoto, T. Nabeshima, *Chem. Commun.*, 2008, 4604-4606.