A molecular leverage for helicity control and helix inversion

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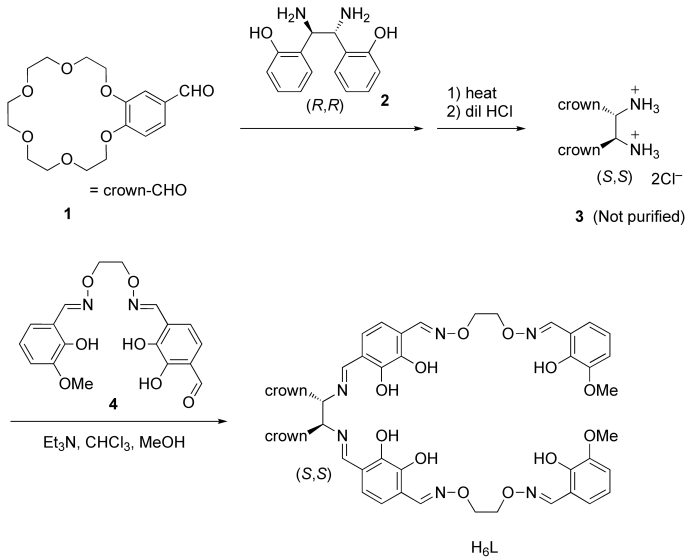
Supporting Information

Synthesis of tetranuclear complex [$LZn_3La(OAc)_3$]. A solution of diamine (*R*,*R*)-**2** (32.6 mg, 0.13 mmol) and 4-formylbenzo-18-crown-6 (**1**) [1] (101 mg, 0.30 mmol) in ethanol (0.45 mL) was stirred at room temperature for 1 h and then heated at 50 °C for 3 h. The solution was concentrated to dryness to give yellow oil, to which concentrated hydrochloric acid (0.17 mL) and methanol (0.35 mL) was added. The solution was stirred at room temperature for 2 h and the solvent was removed under reduced pressure. The residue and aldehyde **4** [2] (88 mg, 0.23 mmol) were dissolved in chloroform/methanol (4 mL) and then triethylamine (0.1 mL) was added. After the solution was stirred at 55 °C for 2 h, 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, chloroform as eluent) to afford H_6L (47.5 mg, 25%) as yellow oil, which was used for the complexation without purification. A solution of the ligand H_6L (47.5 mg, 0.034 mmol) in chloroform was mixed with a solution of zinc(II) acetate dihydrate (22.5 mg 0.10 mmol) and lanthanum(III) acetate sesquihydrate (11.7 mg, 0.034 mmol) in aqueous methanol and the resulting solution was concentrated to dryness. The crude complex was purified by recrystallization from methanol/ether to yield [$LZn_3La(OAc)_3$] (30.6 mg, 47%) as yellow powder, ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$, 1:1) *P*-isomer: δ 3.61–5.22 (m, 48H), 6.42–6.55 (m, 12H), 6.80–6.94 (m, 12H), 7.89 (s, 2H), 7.97 (s, 2H), 8.35 (s, 2H); *M*-isomer: δ 3.61–5.22 (m, 48H), 6.42–6.55 (m, 12H), 6.80–6.94 (m, 12H), 7.89 (s, 2H), 8.14 (s, 2H), 8.37 (s, 2H). ESI-MS *m*/*z* 1839.7 for $[LZn_3La(OAc)_2]^+$, 890.3 for $[LZn_3La(OAc)]^{2+}$. Anal. Calcd for $C_{76}H_{87}LaN_6O_{30}Zn_3 \cdot 3H_2O \cdot 2CHCl_3$: C, 42.73; H, 4.37; N, 3.83. Found: C, 42.35; H, 4.74; N, 3.59.



[1] D'Souza, F.; Chitta, R.; Gadde, S.; McCarty, A. L.; Karr, P. A.; Zandler, M. E.; Sandanayaka, A. S. D.; Araki, Y.; Ito, O. *J. Phys. Chem. B* **2006**, *110*, 5905–5913.

[2] (a) Akine, S.; Taniguchi, T.; Saiki, T.; Nabeshima, T. *J. Am. Chem. Soc.* **2005**, *127*, 540-541; (b) Akine, S.; Matsumoto, T.; Sairenji, S.; Nabeshima, T. *Supramol. Chem.* **2011**, *23*, 106-112.

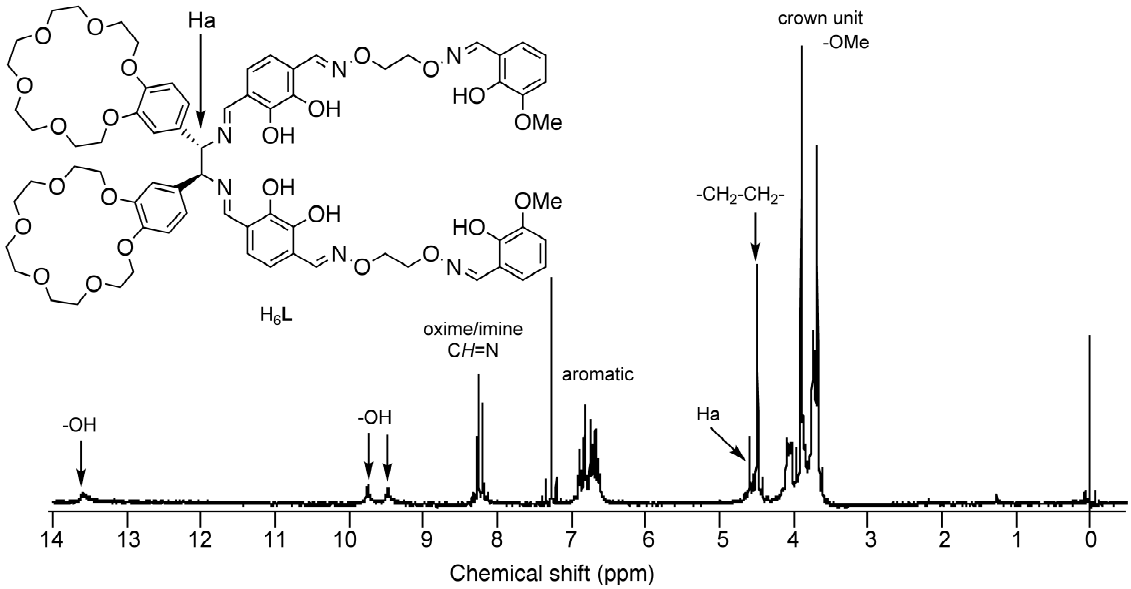


Figure S1. ^{1}H NMR spectrum of H_6L in $CDCl_3$ (400 MHz, $CDCl_3$).

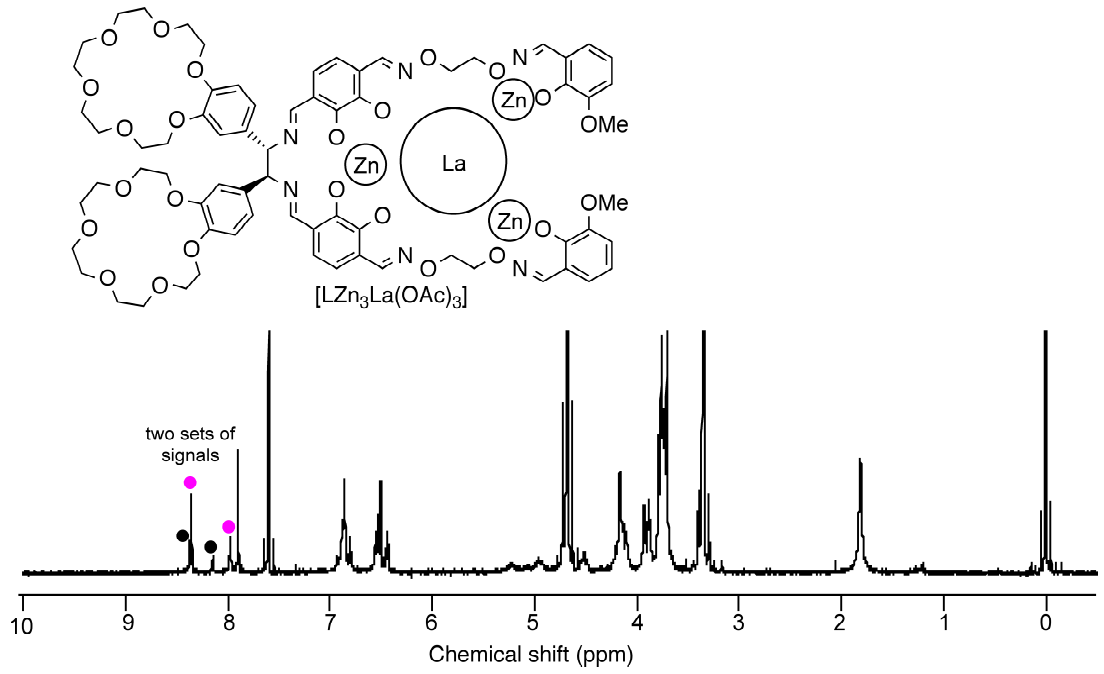


Figure S2. ^{1}H NMR spectrum of $[LZn_3La(OAc)_3]$ in $CDCl_3/CD_3OD$ (1:1) (400 MHz).

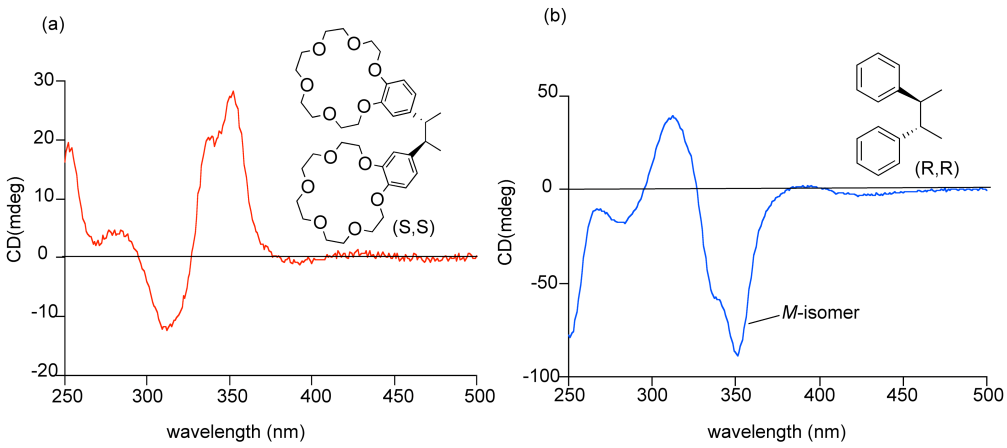


Figure S3. Comparison of the CD spectra of (a) $[LZn_3La(OAc)_3]$ and (b) $[L'Zn_3La(OAc)_3]$ in chloroform/methanol (1:1) showing that the preferred isomer of $[LZn_3La(OAc)_3]$ is *P* isomer.

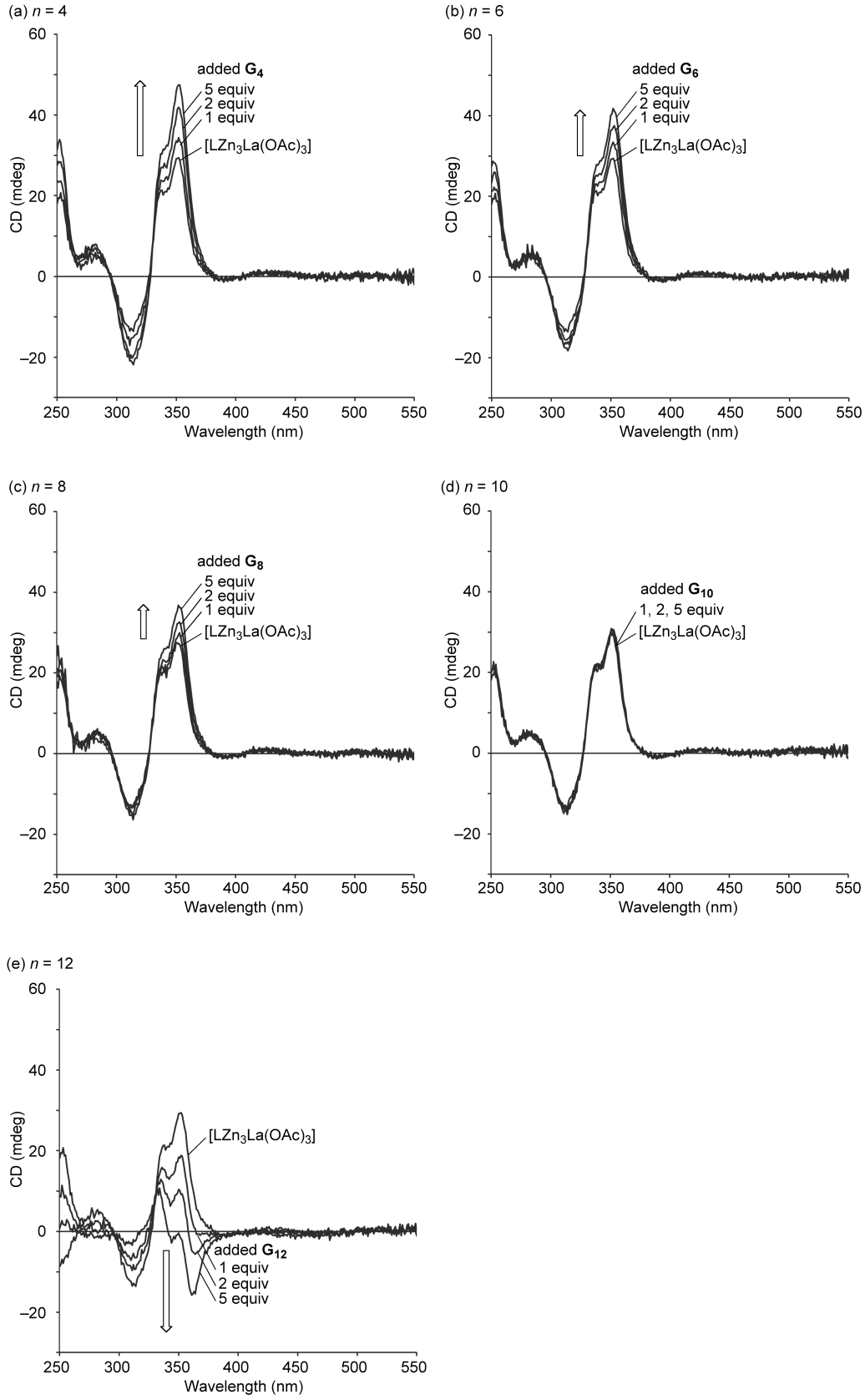


Figure S4. CD spectral changes of $[LZn_3La(OAc)_3]$ upon the addition of $\mathbf{G}_n$ in chloroform/methanol (1:1), 0.02 mM concentration. (a) $n = 4$; (b) $n = 6$; (c) $n = 8$; (d) $n = 10$; (e) $n = 12$.