

Supporting Information

Synthesis of A Chiral Metallo-capsule Composed of Concave Molecules and Chirogenesis upon Fullerene Binding

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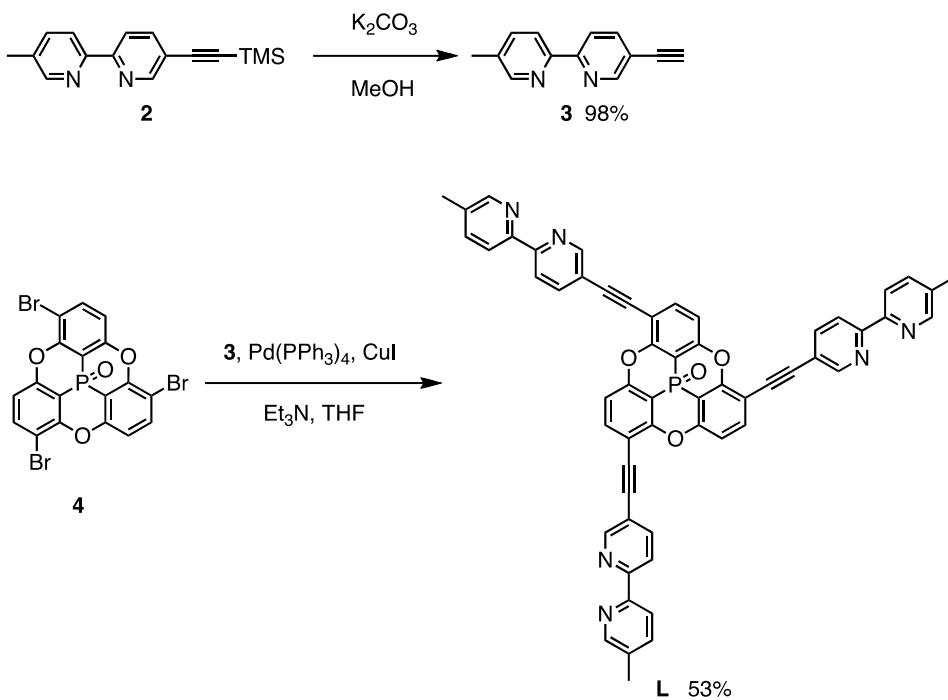
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(1) General

All chemicals employed were of reagent grade, and used without further purification. All reactions were carried out under an atmosphere of dinitrogen. Chromatography was carried out using SiO₂-60N (0.063–0.212 mm; Kanto), while preparative chiral resolution was achieved using a JAI LC-9201 chromatograph equipped with DAICEL CHIRALPAK IA columns using hexane/CHCl₃(1:1, v/v) as the eluent. Melting points were determined on a Yanaco melting point apparatus and are uncorrected. ¹H, ¹³C, and ³¹P NMR spectra were recorded on a Bruker AVANCE400 (400 MHz) spectrometer. Deuterated solvents were purchased from Cambridge Isotope Laboratories or Aldrich and used as received. In the NMR measurements, tetramethylsilane was used as the internal standard (0 ppm) for ¹H and ¹³C NMR measurements, while 85% phosphoric acid was used as the external standard (0 ppm) for the ³¹P NMR spectroscopy. ESI-TOF mass spectra were recorded on a Waters UPLC/Synapt G2 HDMS spectrometer. UV-vis absorption spectra were recorded on a JASCO Ubest V-660 spectrophotometer. Circular dichroism spectra were recorded on a JASCO J-720W spectrometer, while the specific rotation ([α]_D) was measured on a JASCO DIP-1000 spectrometer. Fluorescence spectra were recorded on a JASCO FP-8600 spectrometer, and absolute quantum yields were recorded using a Hamamatsu Photonics absolute PL quantum yield measurement system C9920-02.

(2) Synthetic Procedure

Ligand **L** was synthesized according to Scheme S1. Tribromophosphangulene **4**^{S1} and 5-methyl-5'-(trimethylsilylethynyl)bipyridine **2**^{S2} were synthesized according to literature procedures.



Scheme S1

Synthesis of L

A suspension of *rac*-4 (202 mg, 0.362 mmol), **3** (277 mg, 1.45 mmol), CuI (6.1 mg, 0.032 mmol), and Pd(PPh₃)₄ (57.9 mg, 0.050 mmol) in THF (8 mL) containing Et₃N (8 mL) was stirred under an argon atmosphere at 80 °C for 16 hours. After evaporation of all volatiles, the crude products were separated by column chromatography on silica gel (chloroform/ethyl acetate, 4:1, v/v) to give a pale yellow powder of *rac*-L (172 mg, 0.192 mmol, 53%). The racemix mixture of *rac*-L was separated by chiral HPLC to afford enantiopure *P*-L and *M*-L. *rac*-L: pale yellow powder, mp > 300 °C; Anal. Calcd for C₅₇H₃₃N₆O₄P·H₂O: C, 74.83; H, 3.86; N, 9.19. Found: C, 74.61; H, 3.80; N, 9.11; ¹H NMR (400 MHz, CDCl₃) δ 2.42 (s, 9H), 7.38 (dd, *J* = 8.7 Hz, *J* = 4.9 Hz, 3H), 7.66 (dd, *J* = 8.2 Hz, *J* = 2.2 Hz, 3H), 7.77 (d, *J* = 8.7 Hz, 3H), 8.01 (dd, *J* = 8.2 Hz, *J* = 2.2 Hz, 3H), 8.35 (d, *J* = 8.2 Hz, 3H), 8.44 (d, *J* = 8.2 Hz, 3H), 8.54 (d, *J* = 2.2 Hz, 3H), 8.89 (d, *J* = 2.2 Hz, 3H); ³¹P NMR (162 MHz, CDCl₃) δ -50.6 (s); ¹³C NMR (100 MHz, CDCl₃) δ 18.45 (s, CH₃), 86.01 (s, C), 92.88 (s, C), 109.71 (d, *J* = 107.2 Hz, C), 111.15 (d, *J* = 6.3 Hz, C), 115.89 (d, *J* = 4.8 Hz, CH), 119.29 (s, C), 120.17 (s, CH), 121.06 (s, CH), 134.02 (s, C), 137.24 (s, CH), 137.60 (s, CH), 139.44 (s, CH), 149.81 (s, CH), 151.78 (s, CH), 152.80 (s, C), 155.58 (s, C), 159.02 (s, C), 159.18 (s, C); ESI MS *m/z* 897.75 [M+H]⁺; [α]_D for *P*-L: -1422 (CHCl₃, *c* = 0.083, 20 °C); [α]_D for *M*-L: +1489 (CHCl₃, *c* = 0.069, 22 °C).

Synthesis of 1

A solution of Zn[B_F₄]₂ (2.5 mM, 4.7 mL, 11.8 μmol) in methanol (2.5 mL) was added to a solution of *rac*-L (8.78 mg, 9.79 μmol) in chloroform (2 mL) before acetonitrile (3 mL) was added. The reaction mixture was stirred at 75 °C for 26 hours. After evaporation of all solvents, the crude product was re-precipitated from acetonitrile/diethyl ether to give a yellow powder of *rac*-1 (11.0 mg, 99%). Single crystals suitable for diffraction analysis were prepared by recrystallization from acetonitrile/acetone. Enantiopure *P*-1 and *M*-1 were synthesized in a similar manner from *P*-L and *M*-L, respectively. *rac*-1: yellow powder, ¹H NMR (600 MHz, CD₃CN) δ 2.33 (s, 36H), 6.58 (dd, *J* = 8.8 Hz, *J* = 4.2 Hz, 12H), 7.78 (d, *J* = 1.6 Hz, 12H), 8.08 (d, *J* = 8.8 Hz, 12H), 8.14 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 12H), 8.23 (d, *J* = 1.6 Hz, 12H), 8.51 (d, *J* = 8.4 Hz, 12H), 8.55 (dd, *J* = 8.6 Hz, *J* = 1.6 Hz, 12H), 8.61 (d, *J* = 8.4 Hz, 12H); ³¹P NMR (243 MHz, CD₃CN) δ -51.1 (s); ¹³C NMR (150 MHz, CD₃CN) δ 17.69 (s, CH₃), 88.37 (s, C), 90.59 (s, C), 109.62 (d, *J* = 110.2 Hz, C), 115.52 (s, CH), 117.33 (s, CH), 121.79 (s, C), 123.56 (s, CH), 123.84 (s, CH), 136.86 (s, CH), 139.30 (s, C), 142.24 (s, CH), 143.07 (s, CH), 145.96 (s, C), 148.63 (s, CH), 149.16 (s, C), 150.67 (s, CH), 159.27 (s, C), 159.52 (s, C); ESI-MS calcd for C₂₂₈H₁₃₂N₂₄O₁₆BF₄P₄Zn₄ [L₄Zn₄ BF₄]⁷⁺: 562.092, found: 562.082; Crystallographic data of [(BF₄)₂(acetone)₃⊂1][BF₄]₆(acetone)₉: Trigonal space group *P*3₁/*c*, *γ* = 0.800 Å (Synchrotron radiation source), *T* = 100 K, *a* = 27.825(4) Å, *c* = 44.321(8) Å, *V* = 29717(7) Å³, *Z* = 4, *F*(000) = 10496, collected/unique 39465/7540 (*R*_{int} = 0.055), *R*₁(*I* > 2 σ(*I*)) = 0.1393, *wR*₂(all data) = 0.4107, GOF = 1.471, CCDC 1445414. ¹H, ¹³C, and ³¹P NMR spectra are shown in SI Appendix Fig. S5, S6, and S7, respectively. ESI MS is shown in SI Appendix Fig. S8.

Synthesis of G₆₀-incorporated 1

A solution of C₆₀ (12.0 mg, 16.7 μmol) in carbon disulfide (3 mL) and a solution of Zn[B_F₄]₂ (12.4 mg, 34.1 μmol) in methanol (2.5 mL) were added to a chloroform solution (4 mL) of *rac*-L (20.0 mg, 22.3 μmol), before acetonitrile (3 mL) was added. The reaction mixture was stirred at 75 °C for 16 hours. After evaporation of all solvents, the crude product was successively washed with toluene and

chloroform. The residue was re-precipitated from acetonitrile/diethyl ether to give a brown powder of *rac*-**1** (20.5 mg, 70%). *rac*-[C₆₀⊂**1**]: brown powder; ¹H NMR (600 MHz, CD₃CN) δ 2.33 (s, 36H), 6.40 (dd, *J* = 9.0 Hz, *J* = 4.2 Hz, 12H), 7.69 (d, *J* = 1.6 Hz, 12H), 7.89 (d, *J* = 8.8 Hz, 12H), 7.97 (d, *J* = 1.6 Hz, 12H), 8.16 (dd, *J* = 8.8 Hz, *J* = 1.6 Hz, 12H), 8.56 (d, *J* = 8.4 Hz, 12H), 8.65 (dd, *J* = 8.6 Hz, *J* = 1.6 Hz, 12H), 8.73 (d, *J* = 8.4 Hz, 12H); ³¹P NMR (243 MHz, CD₃CN) δ -53.0 (s); ¹³C NMR (150 MHz, CD₃CN) δ 17.71 (s, CH₃), 89.00 (s, C), 90.91 (s, C), 109.35 (d, *J* = 105.7 Hz, C), 111.18 (d, *J* = 5.7 Hz, CH), 116.47 (s, CH), 122.02 (s, C), 124.26 (s, CH), 124.70 (s, CH), 137.19 (s, CH), 139.65 (s, C), 140.31 (s, C), 142.37 (s, CH), 143.25 (s, CH), 145.78 (s, C), 148.12 (s, CH), 148.66 (s, C), 150.09 (s, CH), 159.44 (s, C), 159.90 (s, C); ESI-MS calcd for C₂₈₈H₁₃₂N₂₄O₁₆P₄Zn₄ [C₆₀⊂**1**]⁸⁺: 571.190, found: 571.205;; Anal. Calcd for C₂₈₈H₁₃₂N₂₄O₁₆B₈F₃₂P₄Zn₄·16H₂O: C, 62.30; H, 2.98; N, 6.05. Found: C, 61.61; H, 3.01; N, 6.15. ¹H, ¹³C, and ³¹P NMR spectra were shown in SI Appendix Fig. S10, S11, and S12, respectively. Enantiopure C₆₀-incorporated container **1** was similarly prepared and isolated.

(3) Compound Data

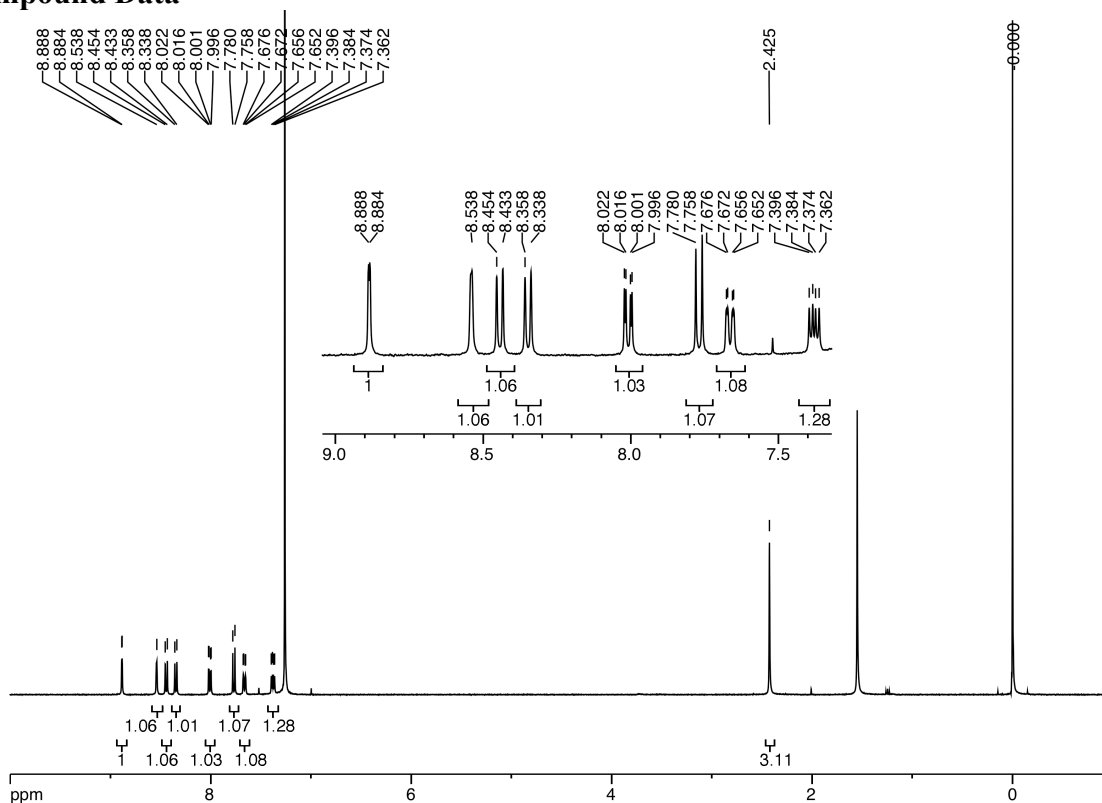


Fig. S1. ¹H NMR spectrum of *rac-L* (400 MHz, CDCl₃).

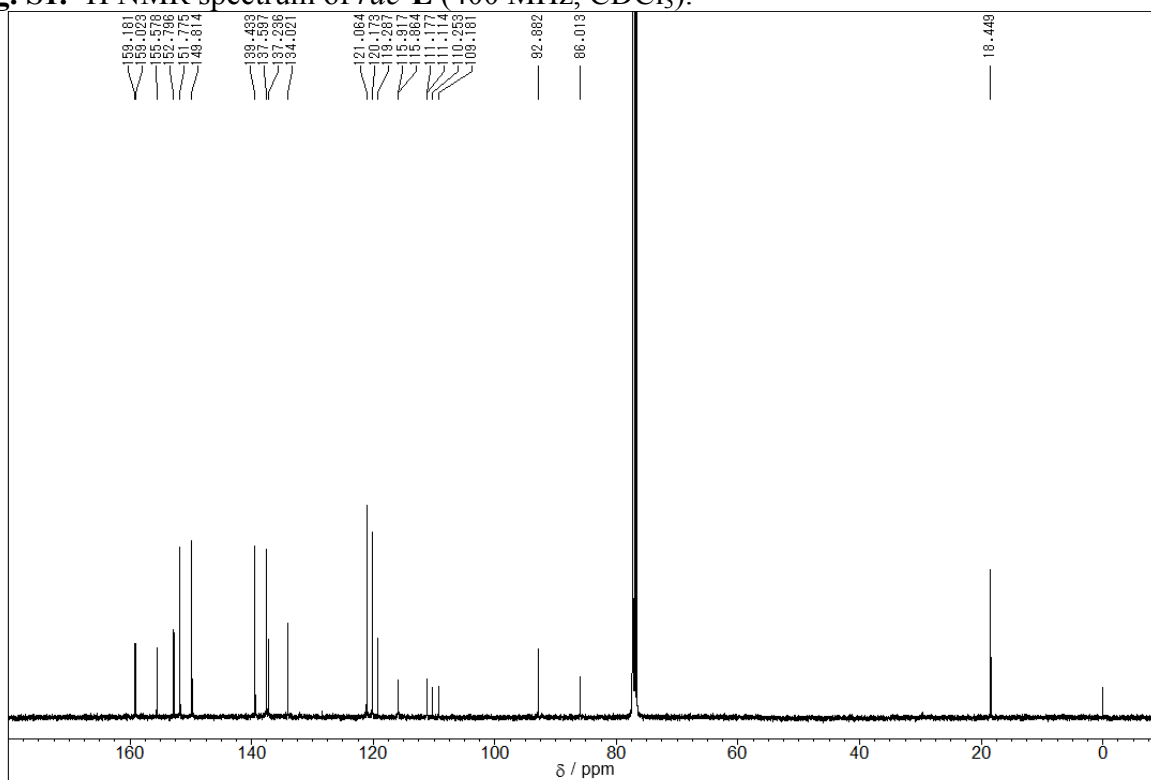


Fig. S2. ¹³C NMR spectrum of *rac-L* (100 MHz, CDCl₃).

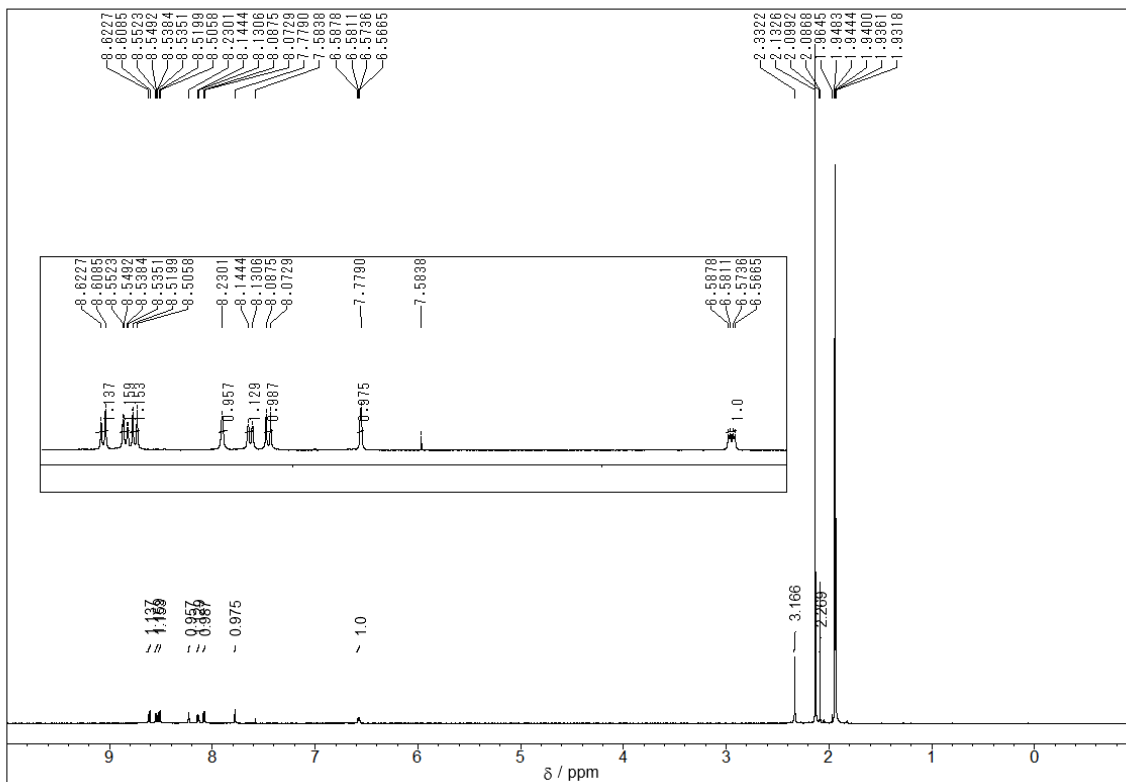


Fig. S3. ¹H NMR spectrum of *rac*-1 (600 MHz, CH₃CN).

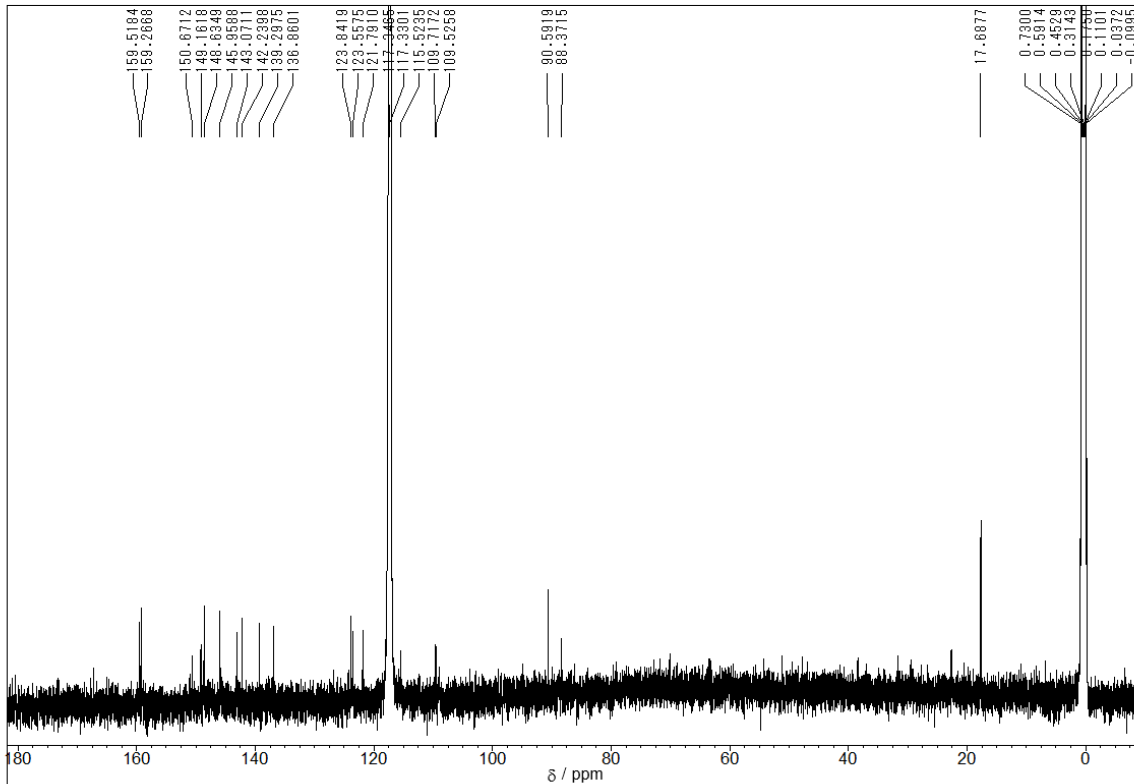


Fig. S4. ¹³C NMR spectrum of *rac*-1 (150 MHz, CH₃CN).

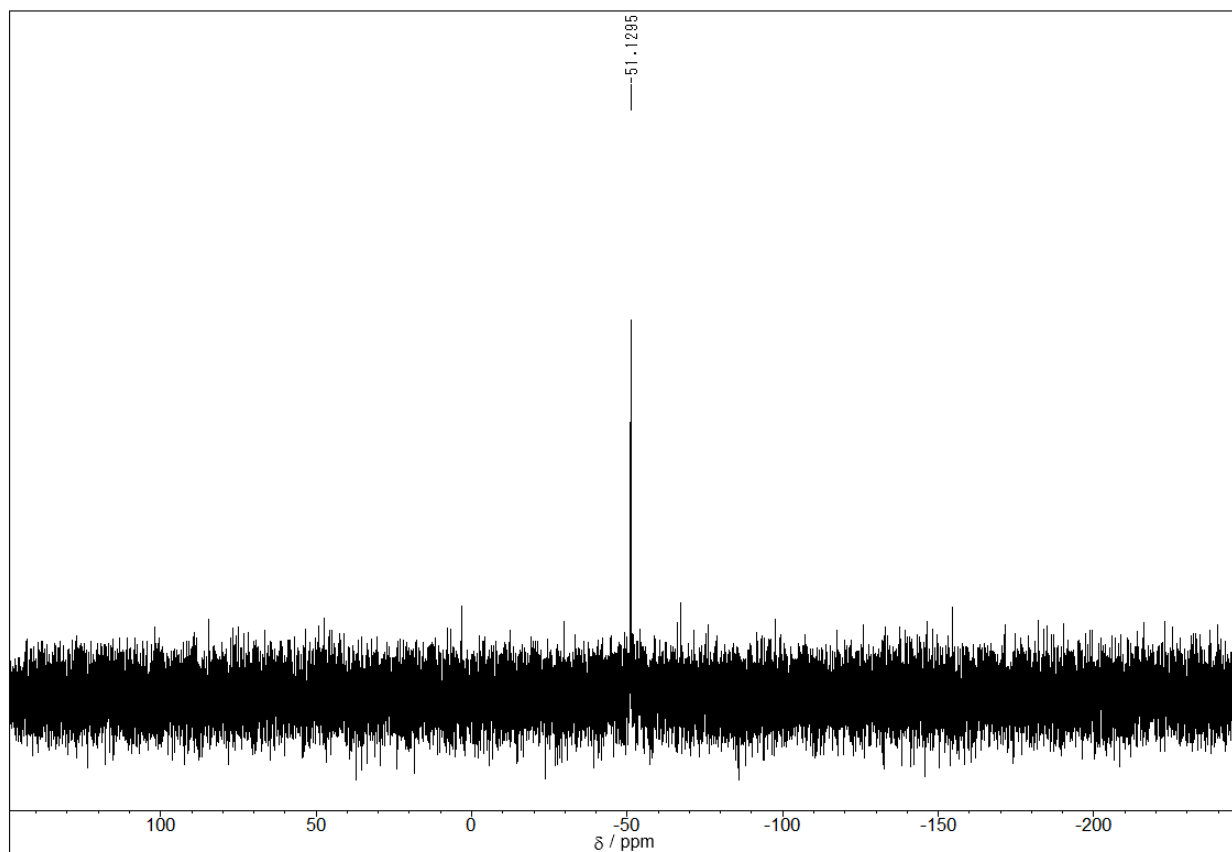


Fig. S5. ^{31}P NMR spectrum of *rac-1* (243 MHz, CH_3CN).

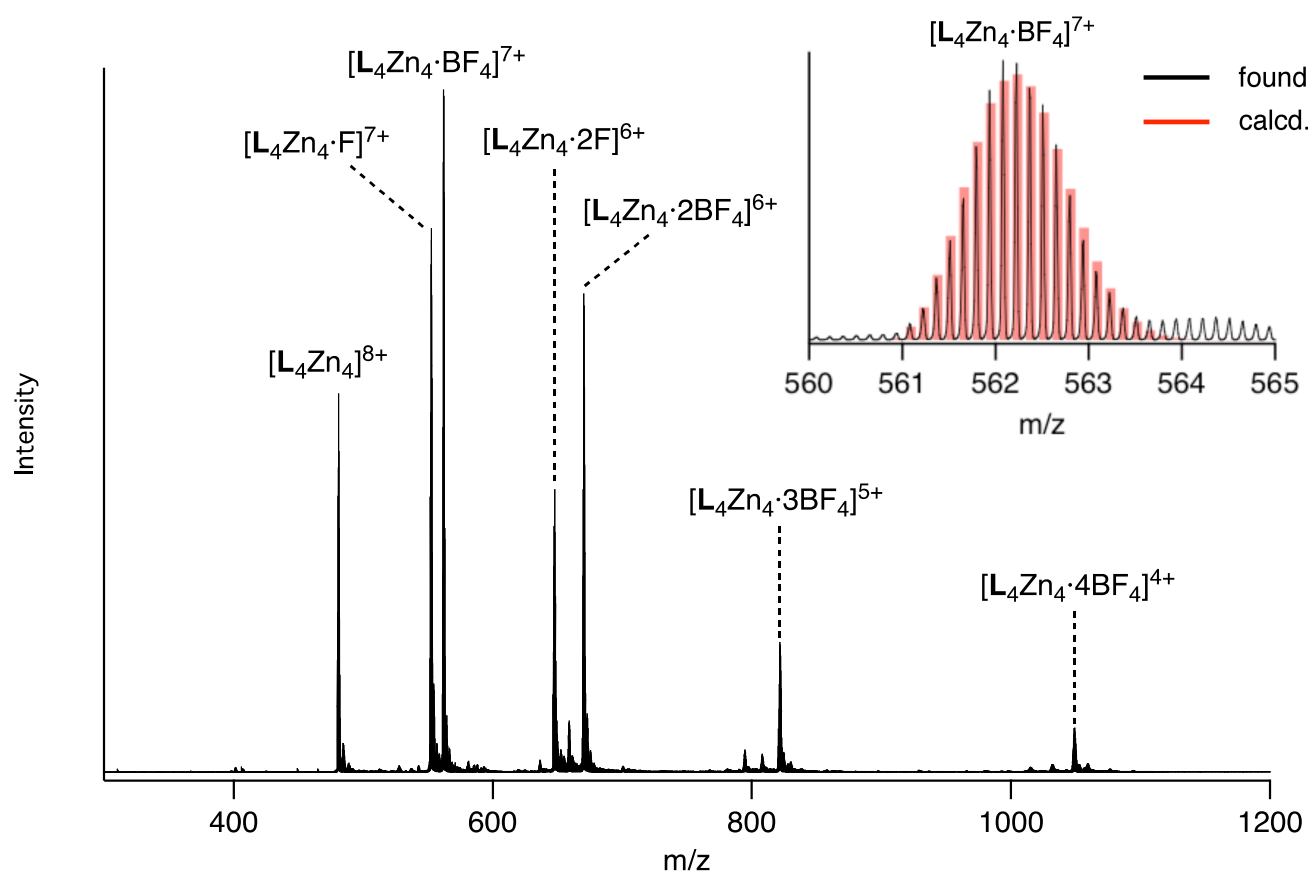


Fig. S6. ESI-mass spectrum of *rac-1* ($[\text{L}_4\text{Zn}_4](\text{BF}_4)_8$).



Fig. S7. ^1H NMR spectrum of *rac*-[$\text{C}_{60}\text{C}1$] (600 MHz, CD_3CN).

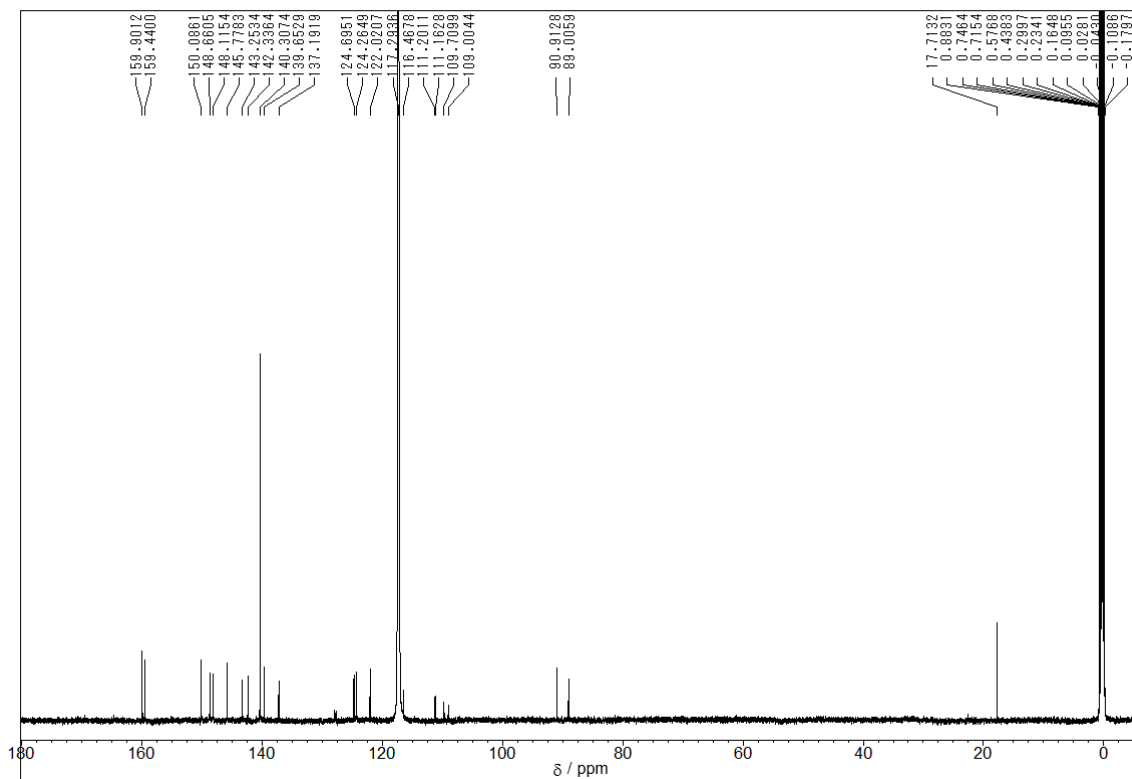


Fig. S8. ^{13}C NMR spectrum of *rac*-[$\text{C}_{60}\text{C}1$] (150 MHz, CD_3CN).

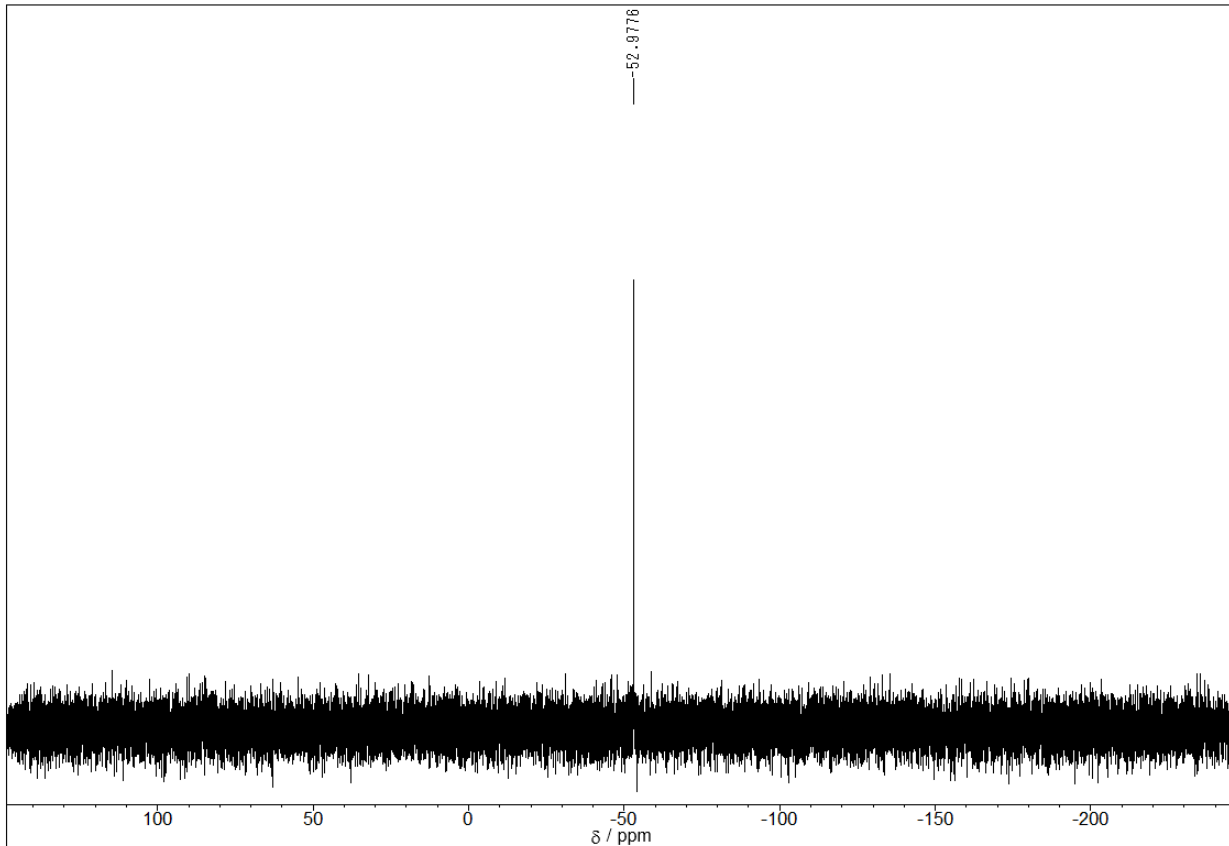


Fig. S9. ^{31}P NMR spectrum of *rac*-[C₆₀C1] (243 MHz, CH₃CN).

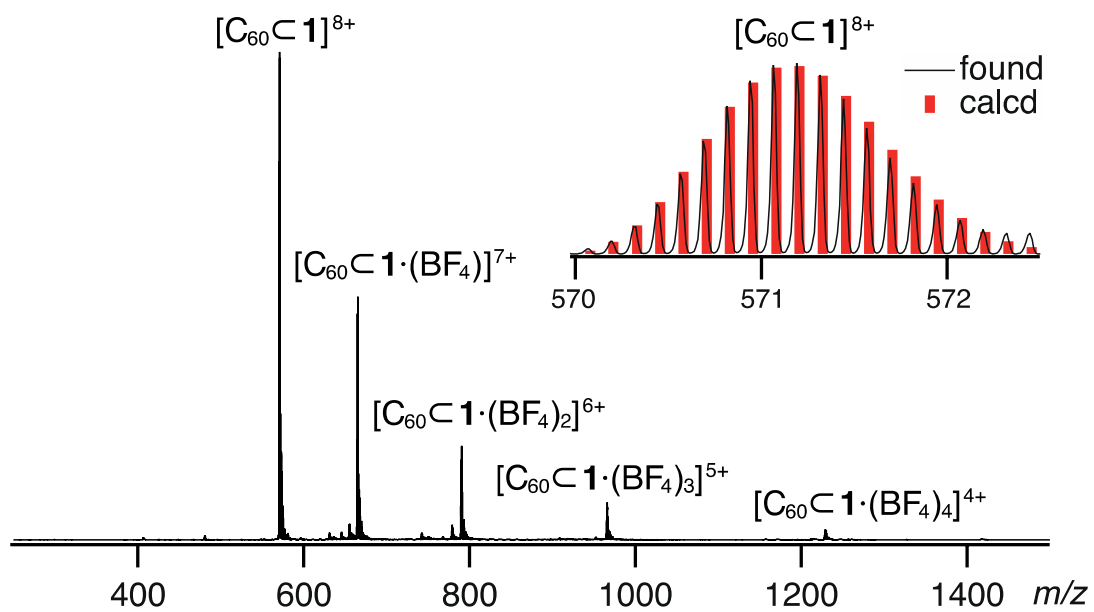


Fig. 10. ESI-mass spectrum of [C₆₀C1][BF₄]₈ (= [C₆₀C1L₄Zn₄][BF₄]₈).

(4) NMR Spectral Titration

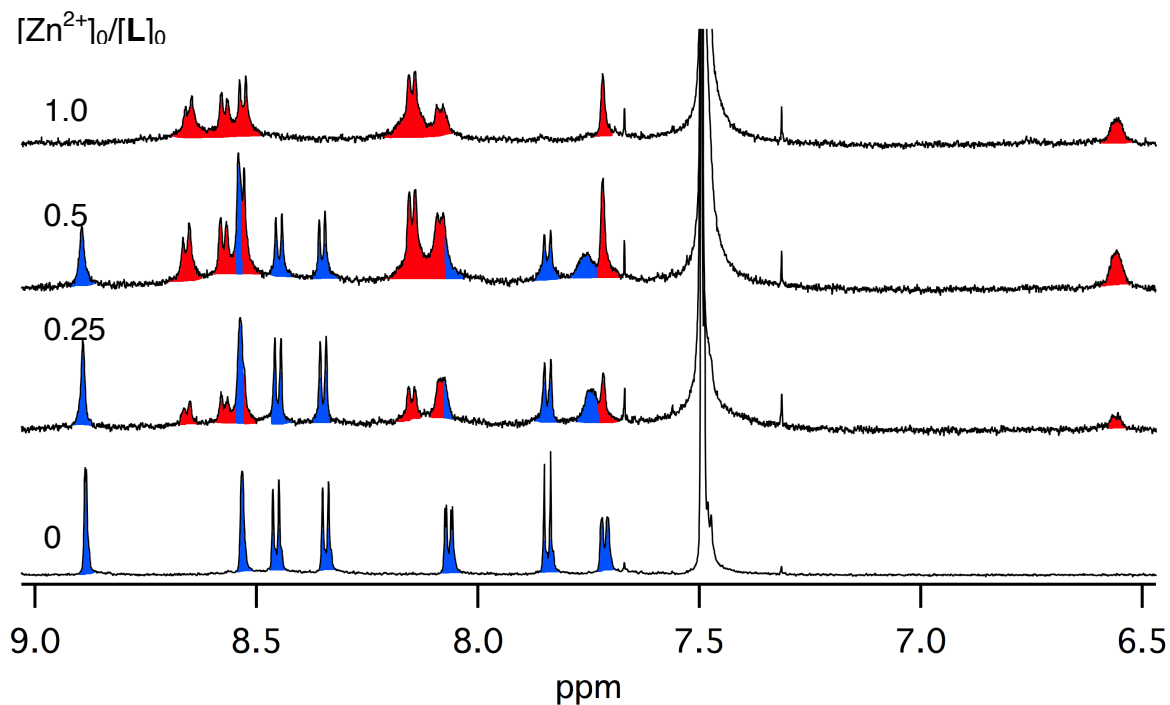


Fig. S11. ¹H NMR spectral titration of *rac-L* with Zn(ClO₄)₂ (600 MHz, CD₃CN/CDCl₃ (1:1, v/v)). Measurements were performed after heating at 75 °C for 12 hours. The blue peaks denote the signals of *rac-L* and the red ones denote the signals of *rac-1*. In the presence of 1.0 eq. of Zn(ClO₄)₂, *rac-1* was formed quantitatively.

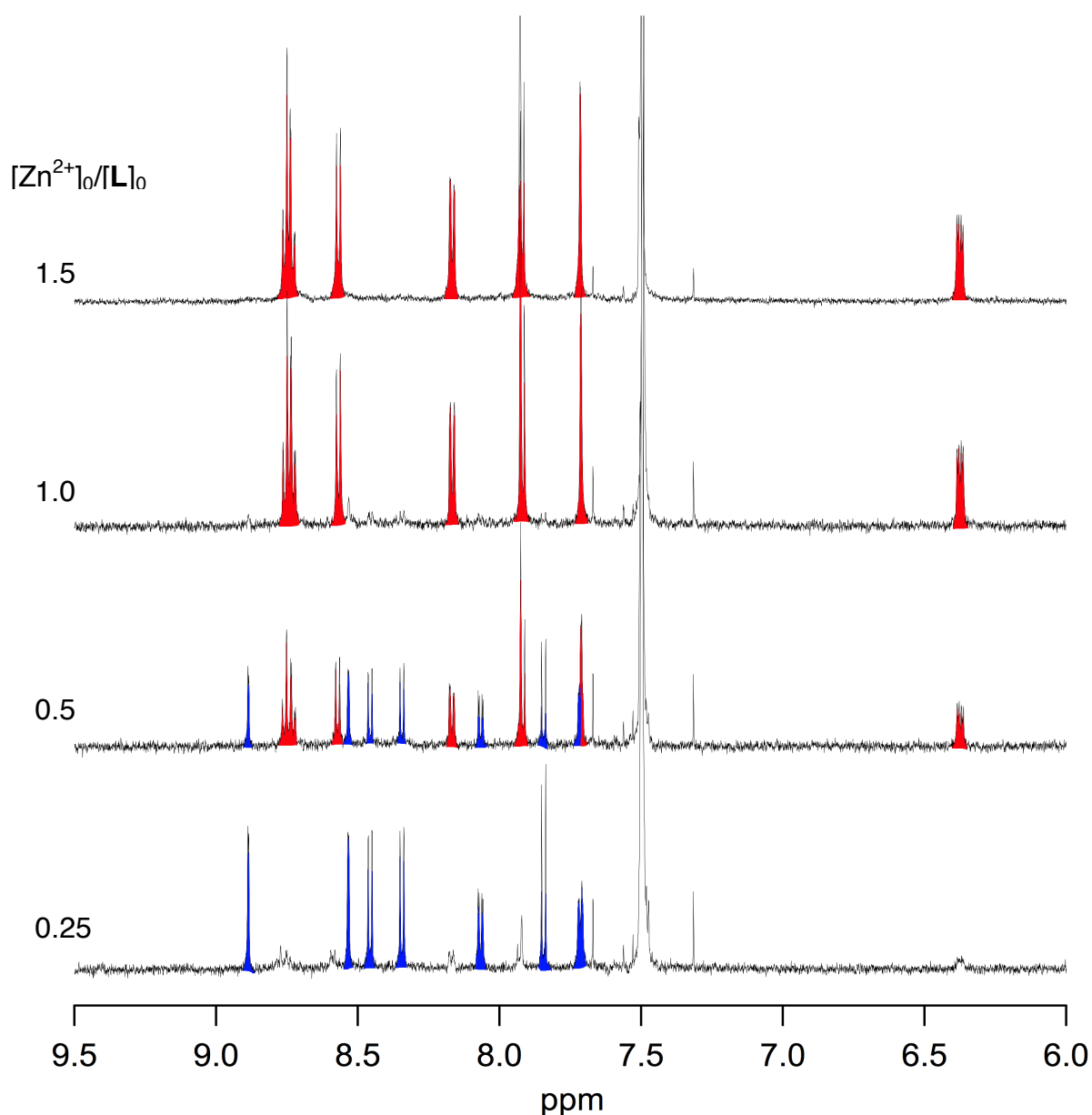


Fig. S12. ^1H NMR spectral titration of *rac*-L with $\text{Zn}(\text{ClO}_4)_2$ in the presence of 3.6 eq. of C_{60} (600 MHz, $\text{CD}_3\text{CN}/\text{CDCl}_3$ (1:1, v/v)). Measurements were performed after heating at 75 °C for 12 hours. The blue peaks denote the signals of *rac*-L and the red ones denote the signals of *rac*-[C₆₀ ⊂ 1]. In the presence of 1.0 eq. of $\text{Zn}(\text{ClO}_4)_2$, *rac*-[C₆₀ ⊂ 1] was formed quantitatively.

(5) DOSY Spectra

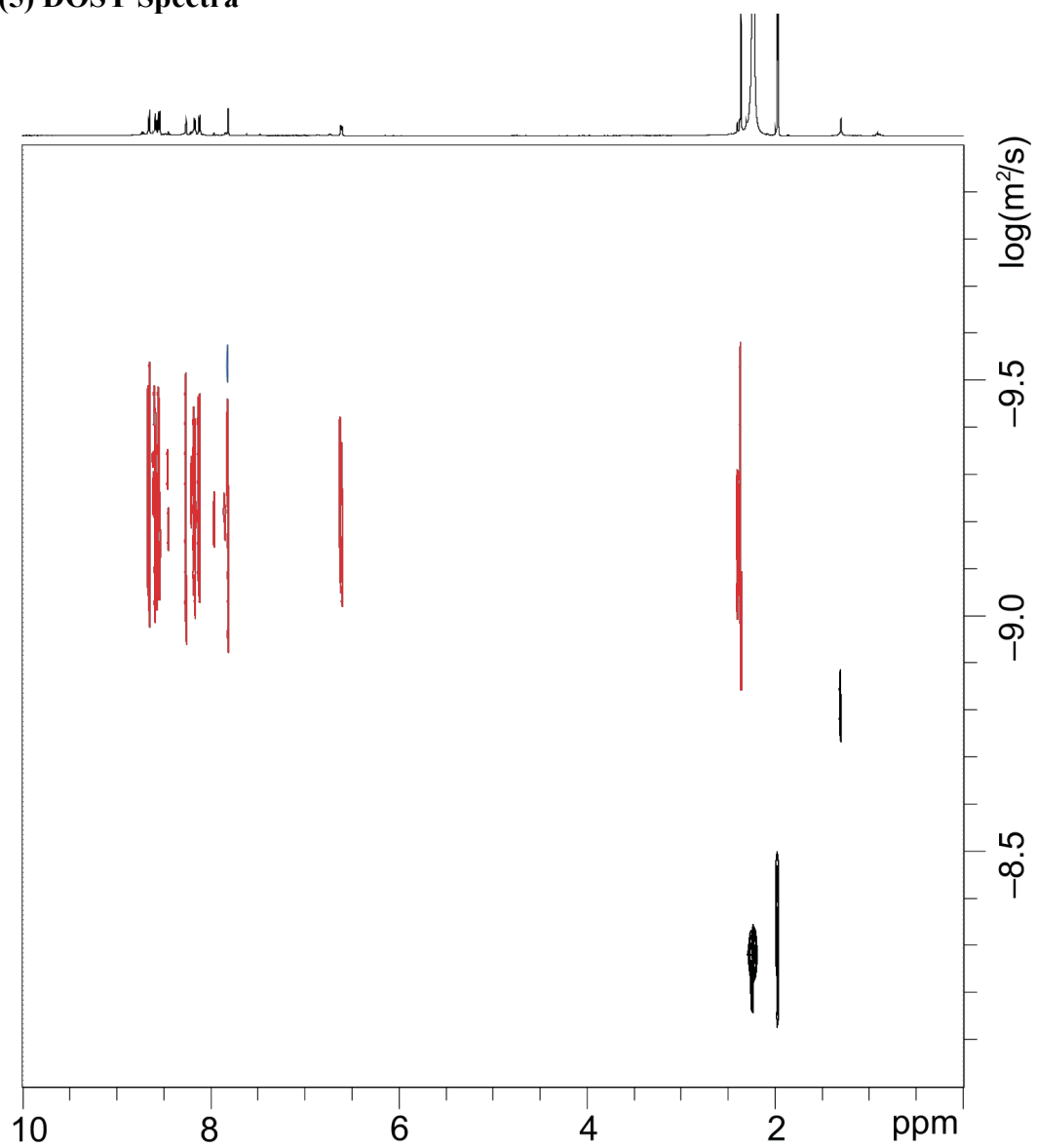


Fig. S13. DOSY spectrum of *rac-1* (600 MHz, CH_3CN). Red peaks denote the signals of *rac-1*. The calculated diffusion constant (D): $6.45 \times 10^{-10} \text{ m}^2\text{s}^{-1}$.

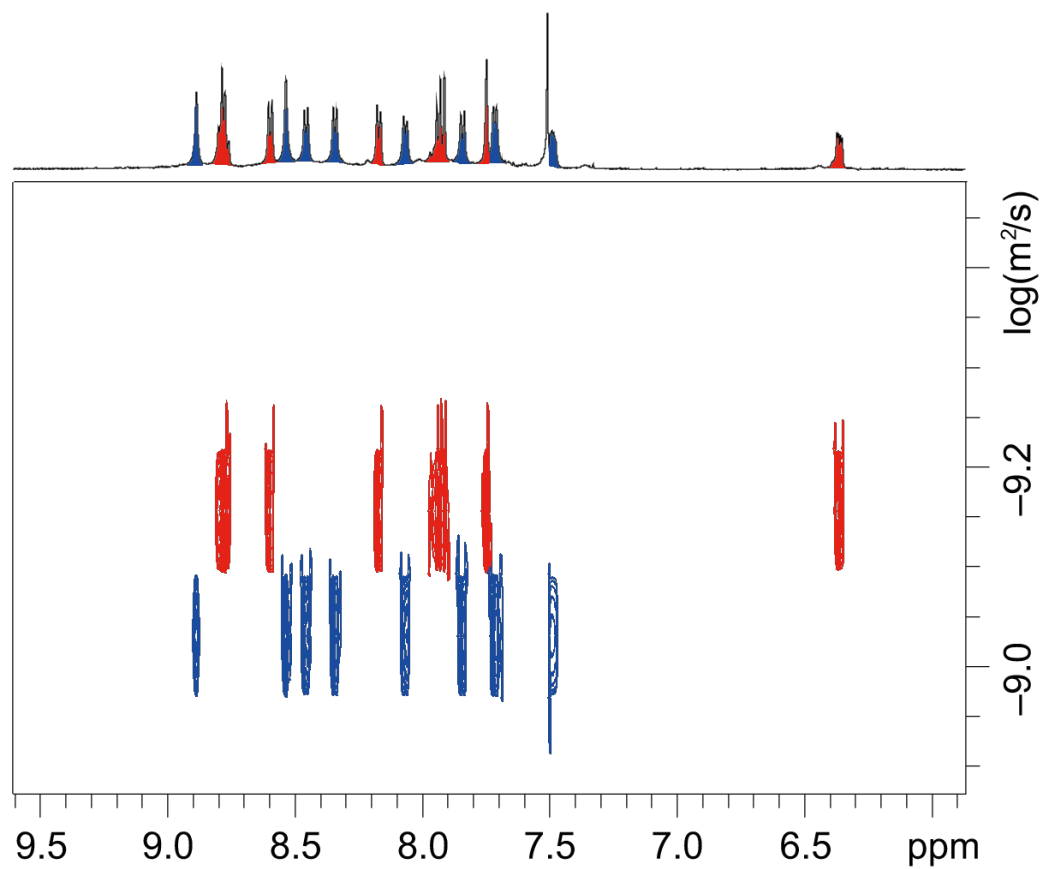


Fig. S14. DOSY spectrum of *rac*-**L** and *rac*-[C₆₀C**1**] (600 MHz, CH₃CN). Blue and red peaks denote the signals of *rac*-**1** and *rac*-[C₆₀C**1**], respectively. The calculated diffusion constant (D) for *rac*-**L**: $8.90 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, D for -[C₆₀C**1**]: $6.56 \times 10^{-10} \text{ m}^2\text{s}^{-1}$.

(6) UV-vis Absorption and Circular Dichroism Spectra

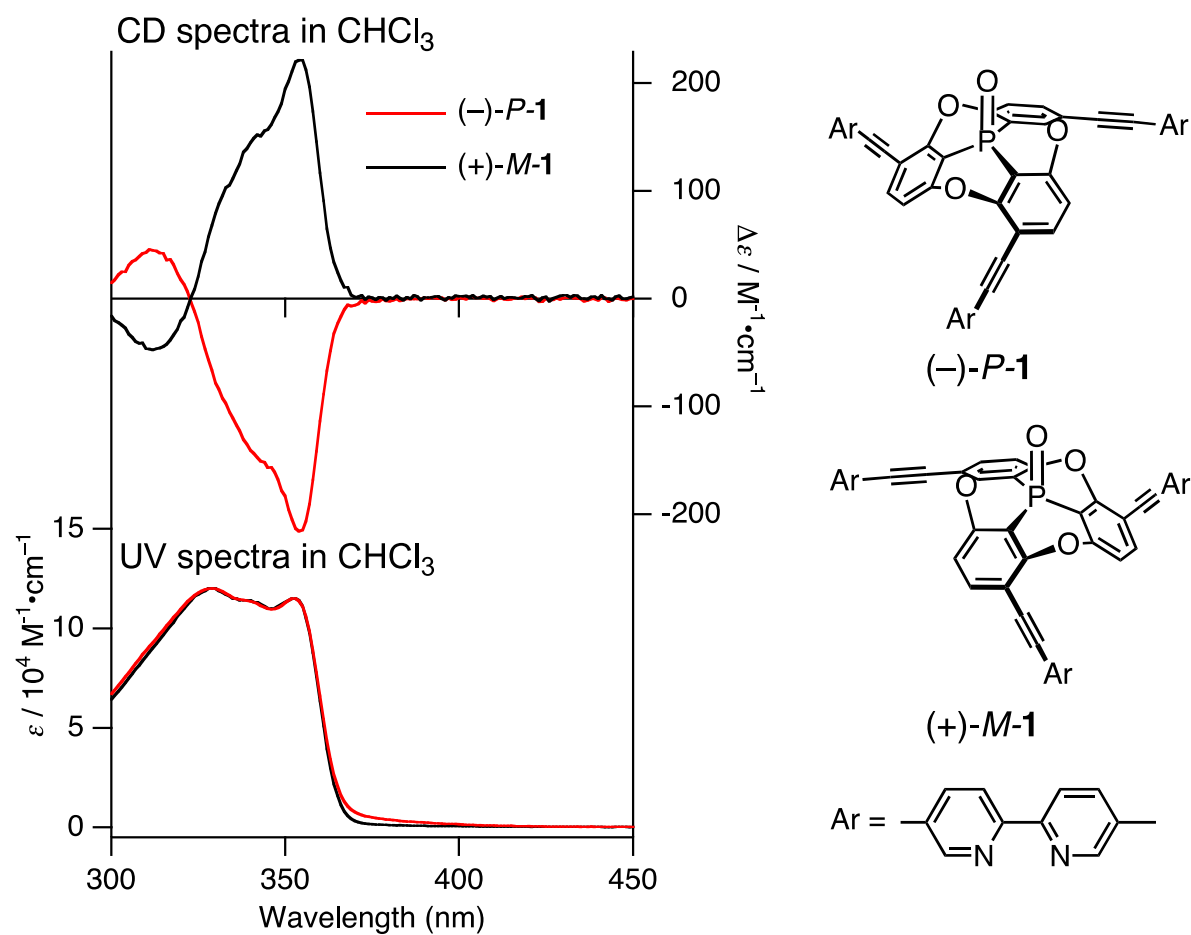


Fig. S15. UV-vis and CD spectra of *P-L* and *M-L* (CHCl_3 , $4.0 \mu\text{M}$).

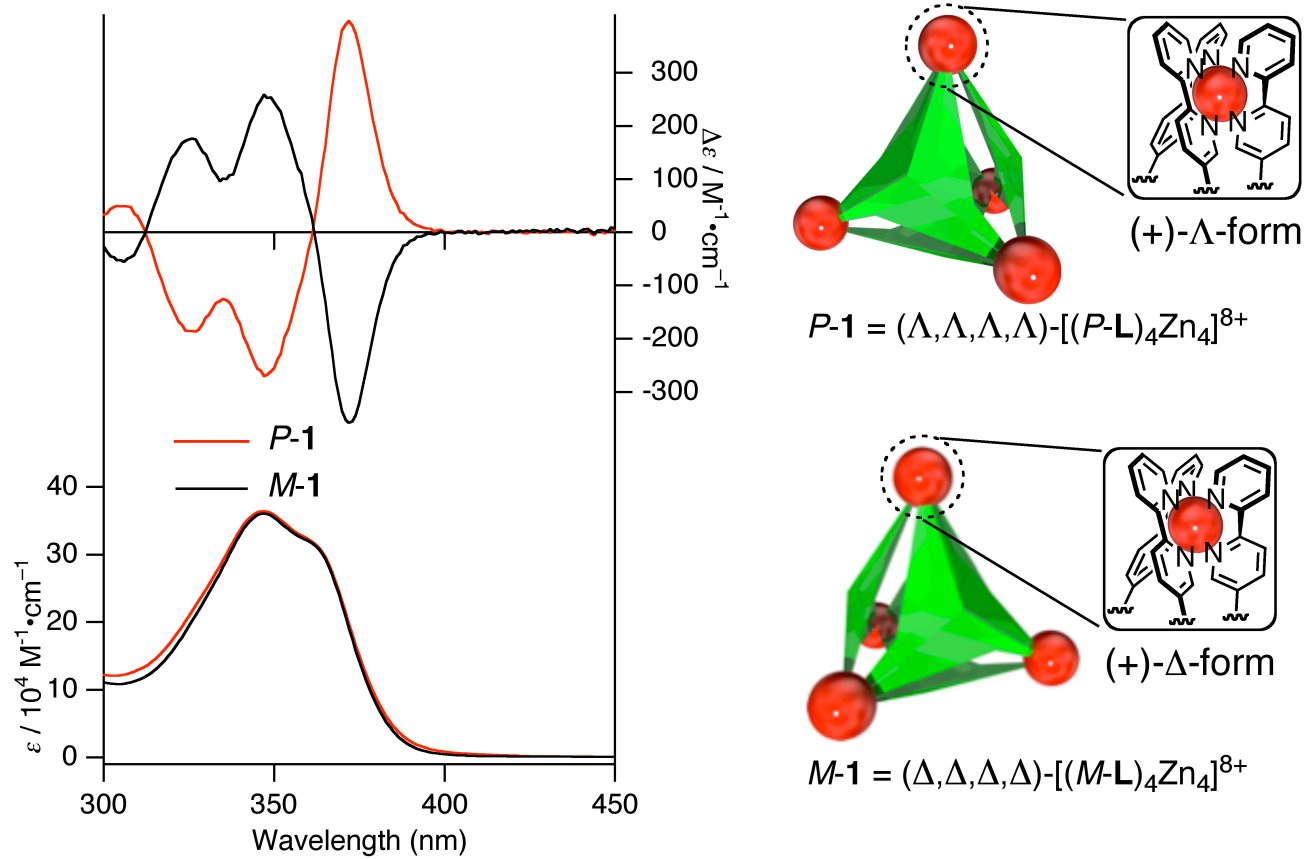


Fig. S16. UV-vis and CD spectra of *P-1* and *M-1* (CH₃CN, 2.5 μ M).

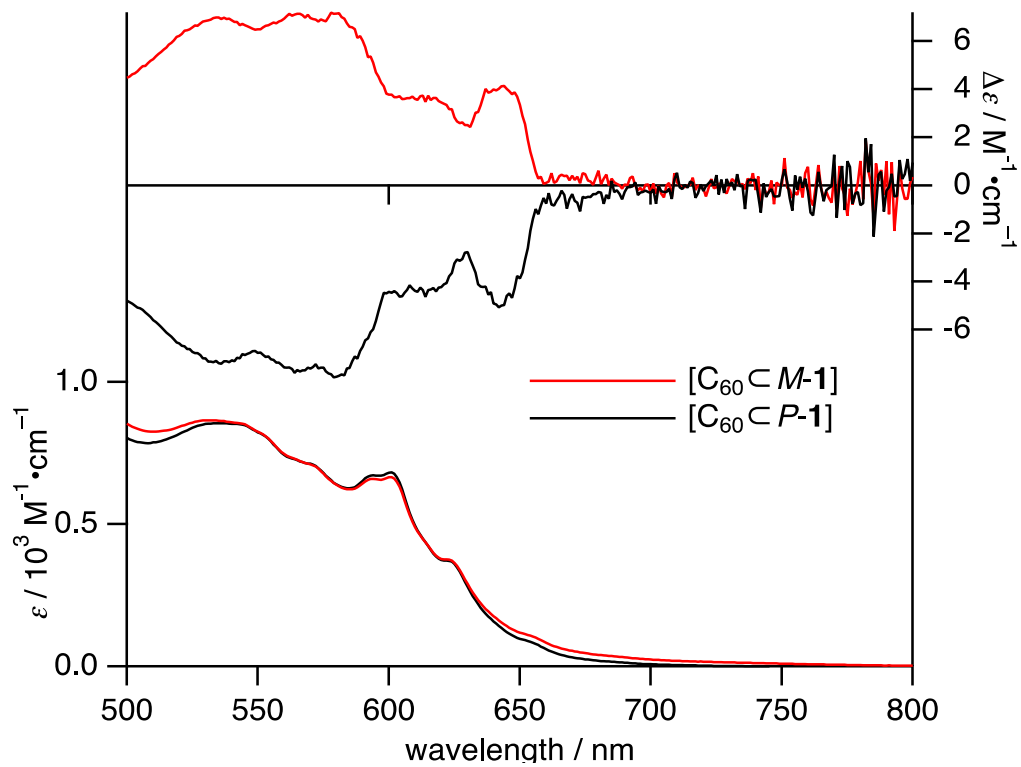


Fig. S17. UV-vis and CD spectra of P - $[C_{60}C1]$ and M - $[C_{60}C1]$ (CH_3CN , $50 \mu M$).

(7) Guest Encapsulation

Containers **1** incorporating other guest, C₇₀, **G1**, and **G2**, were also prepared in a very small scale and the ESI MS of the crude products confirmed the formation (SI Appendix Fig. S14 S15 and S16)

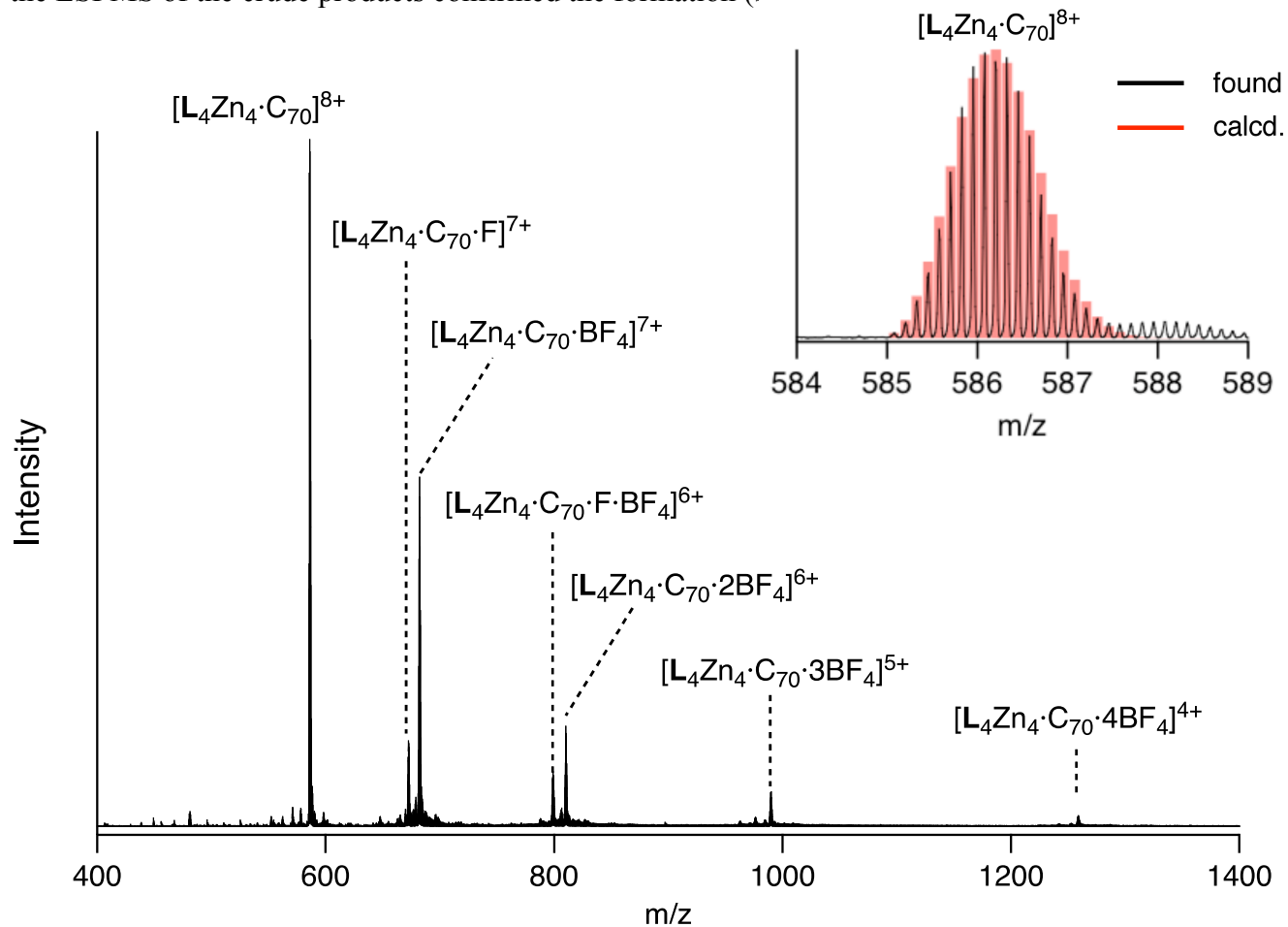


Fig. S18. ESI-mass spectrum of *rac*-[C₇₀C**1**] ([C₇₀C L₄Zn₄](BF₄)₈).

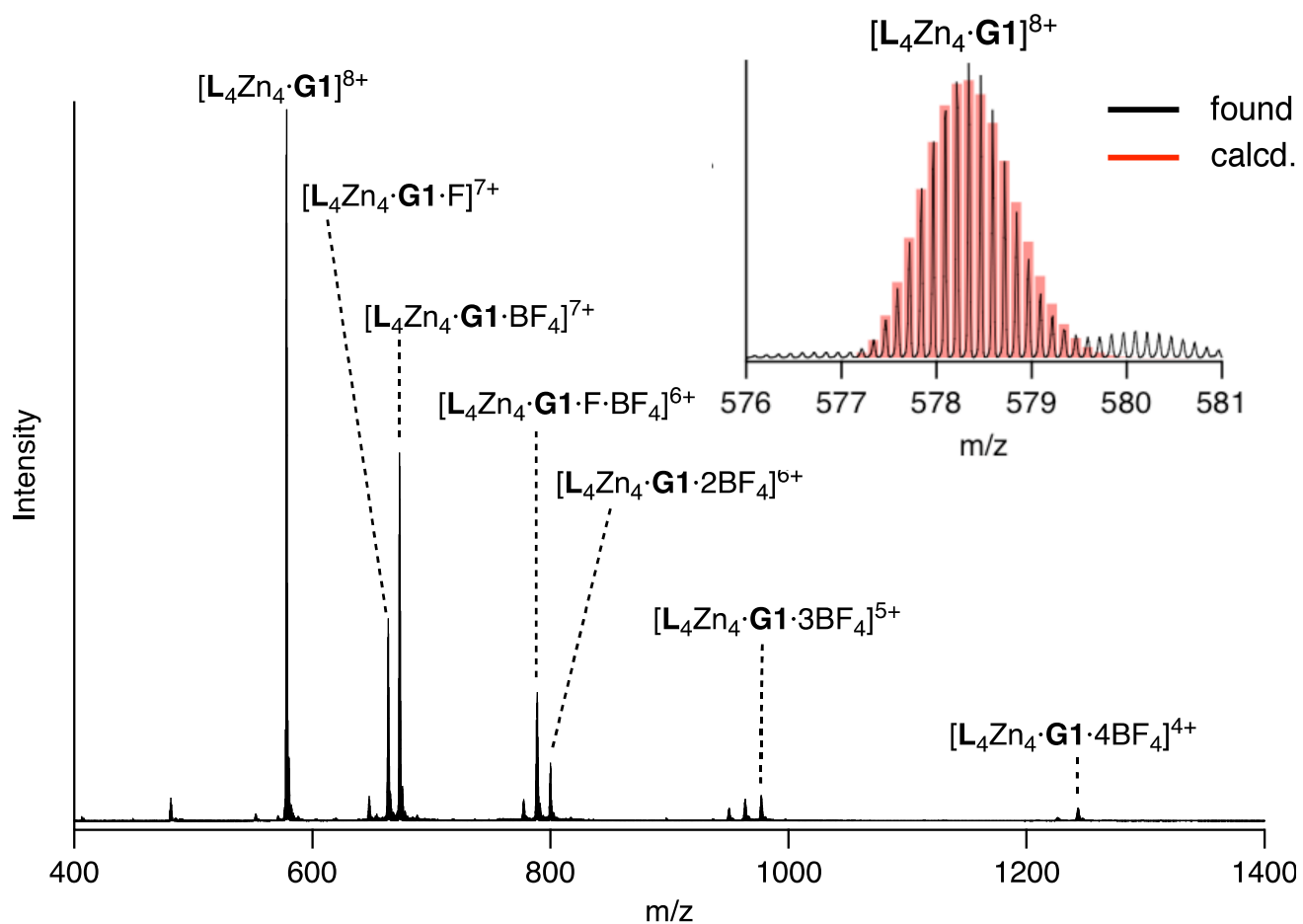


Fig. S19. ESI-mass spectrum of *rac*-[G1C1] ($[G1C1L_4Zn_4](BF_4)_8$).

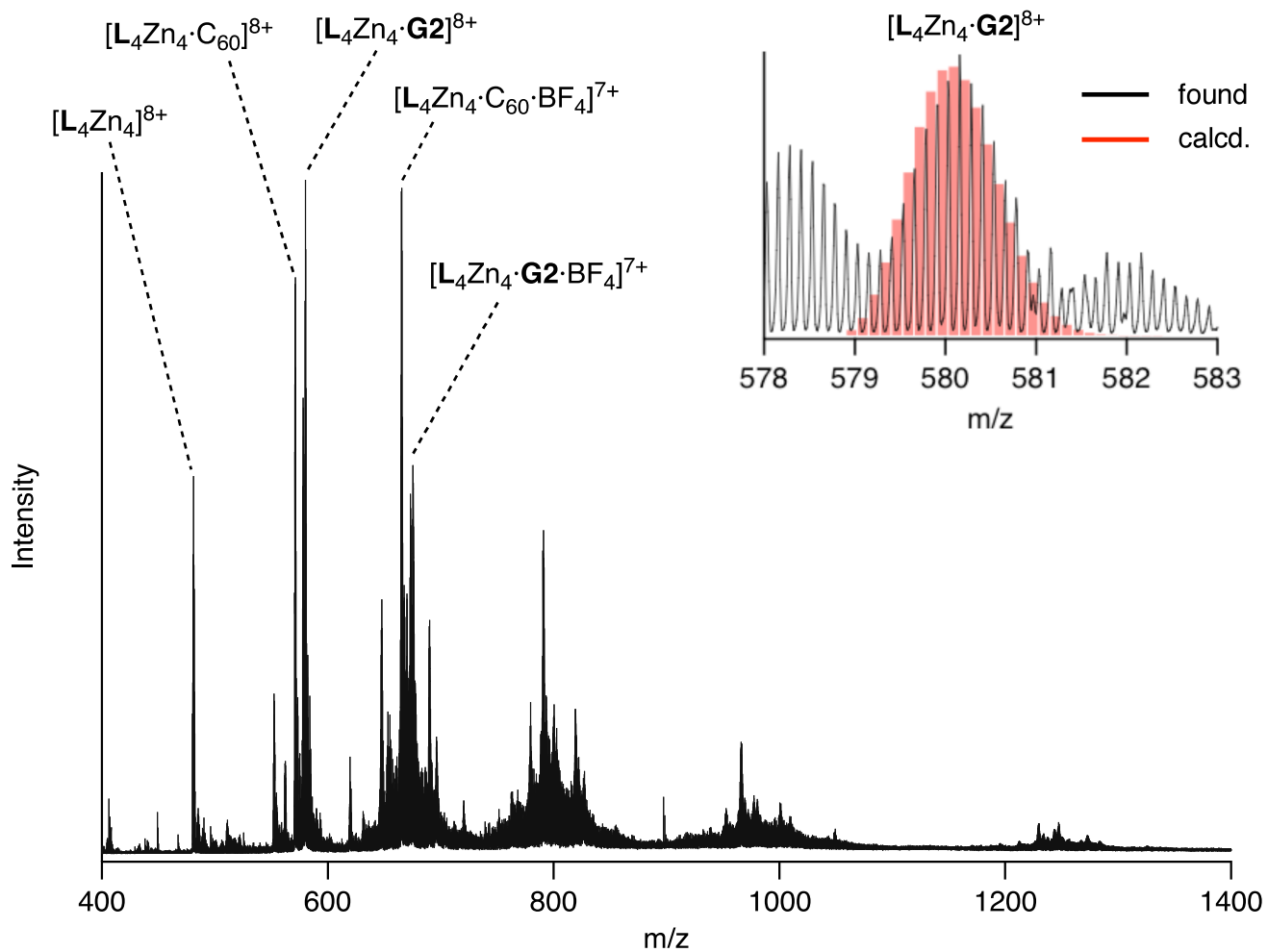


Fig. S20. ESI-mass spectrum of *rac*-[G2C1] ($[G2C L_4Zn_4](BF_4)_8$). $[C_{60}C1]$ would be formed by the reaction with very small amount of C_{60} incorporated in G2 as a starting material.

(8) X-ray Crystallographic Analysis

X-ray diffraction intensities were collected on a CCD diffractometer at 100 K using 0.800 Å synchrotron radiation (RIKEN Spring-8). The structure was solved by the direct method of SIR92 and refined using the SHELXL-2014 program.^{1,2} All of the positional parameters and thermal parameters of non-hydrogen atoms were anisotropically refined on F^2 by the full-matrix least-squares method. Hydrogen atoms were placed at the calculated positions and refined riding on their corresponding carbon atoms. The crystallographic data for **1** was deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 1445414. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk).

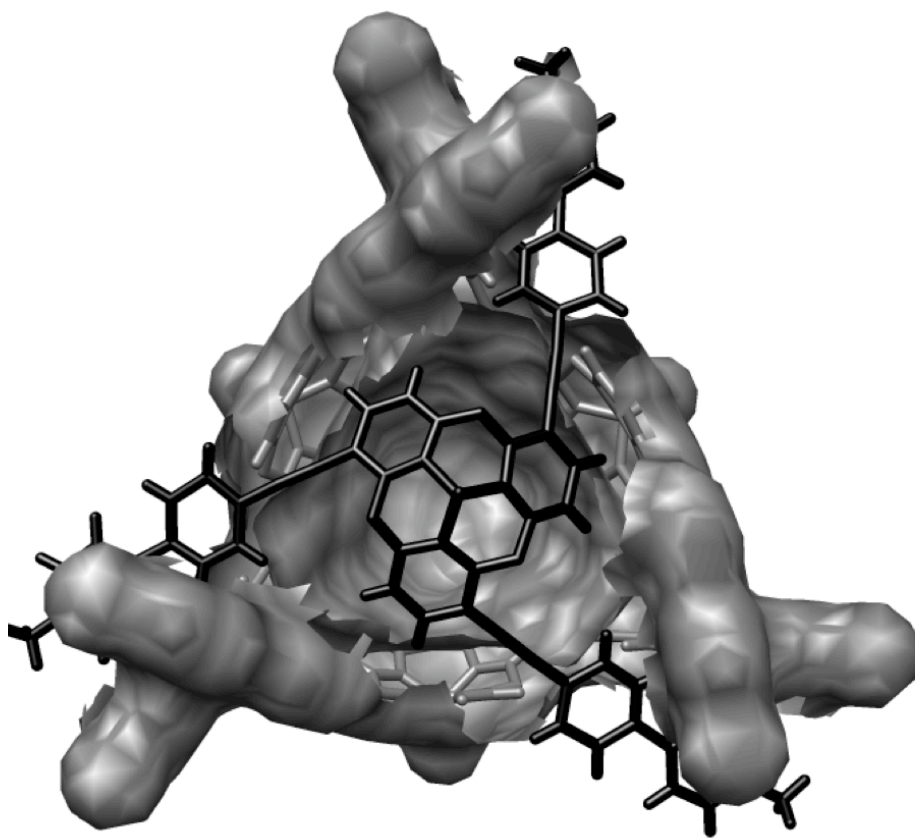


Fig. S21. Electrostatic surface of the crystal structure of **1**; the surface of one ligand is omitted for clarity. Inside counter anions and solvent molecules are omitted for clarity.

References

- (S1) M. Yamamura, T. Saito, T Nabeshima, *J. Am. Chem. Soc.* **2014**, *136*, 14299–14306.
(S2) A. Lützen, M. Hapke, H. Staats, J. Bunzen, *Eur. J. Org. Chem.* **2003**, 3948-3957.