

Assembly and Disassembly of a Zn₁₀ High-Nuclearity Circular Helicate

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Electronic Supporting Information

Materials and Methods

General. All reactions were performed under a dry nitrogen atmosphere according to standard Schlenk techniques or performed in a glove-box. All solvent used were distilled under nitrogen following standard procedures, and then stored in dried N₂-filled reservoirs which contained 4 Å molecular sieves. Commercially available chemicals were purchased from Aldrich or Acros, and used as received. ¹H, ¹³C, ¹H-¹H COSY and ¹H-¹³C HSQC NMR spectra were collected on a Avance 300 spectrometer. Chemical shifts for ¹H and ¹³C{¹H} spectra were recorded in ppm relative to the residual proton and ¹³C of CDCl₃ (¹H: δ 7.24; ¹³C: δ 77.0). The crystals suitable for structure analysis were mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II or a Bruker AXS SMART-1000 diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71073Å). All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against F² with SHELXL-97.¹ Tables of neutral atom scattering factors, *f'* and *f''*, and absorption coefficients are from a standard source.² All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. The crystal structure of (ZnL)₁₀ contains heavily disordered solvent molecules in the cavity and void spaces. These disordered solvent molecules were not further identified or refined. Instead, a new set of F² (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON program.³ Fluorescence spectra were recorded on a Cary Eclipse Fluorescence spectrophotometer. Elemental analyses and high-resolution MS (HRMS) were performed on a Heraeus CHN-OS Rapid Elemental Analyzer and a HRMS spectrometer (Finnigan/Thermo Quest MAT 95XL), respectively, at the Instruments Center of National Chung Hsing University, Taiwan.

Synthesis of H₂L

A mixture of 2,4-bis(bromomethyl)-1,3,5-triethylbenzene (0.7 g, 1.9 mmol), 2,2'-aminophenyl disulfide (0.8 g, 3.3 mmol), K₂CO₃ (1.0 g, 7.2 mmol), and acetonitrile (50 ml), placed in a 100 ml flask, was refluxed at 85°C for 72 hrs. After cooled down to RT, the yellow precipitates were filtered and washed with CH₃CN (about 100 ml) to remove excess 2,2'-aminophenyl disulfide. The yellow residues were extracted with dichloromethane and distilled water. The combined dichloromethane portions were dried over anhydrous MgSO₄, filtered, and vacuum dried to afford a yellow solid. An open 50 ml flask, containing the yellow solid and excess of NaBH₄ (0.15 g, 4.0 mmol), was placed in an ice-water bath, and

then 25 ml of DMF was added slowly. After the resulting mixture stirred at 4°C for 10 minutes, the water bath was removed and the stirring was continued for another 30 minutes. The yellowish mixture was gradually turned to light-gray clear solution, and then concentrated HCl was added dropwisely to quench excess NaBH₄. After completion, the solution was extracted with dichloromethane and water. The collected dichloromethane fractions were dried over anhydrous MgSO₄, filtered, and vacuum dried to give 0.44 g of light-yellow oil (53% yield). Elem Anal. Calcd (%) for C₂₆H₃₂N₂S₂: C 71.51; H 7.39 ; N 6.42. Found: C 71.50; H 7.39; N 6.06. ¹H NMR (CDCl₃, 300K): δ 7.42 (dd, 2H, C₆H₄), 7.28 (t, 2H, C₆H₄), 7.07 (s, 1H, C₆H₁), 6.81 (dd, 2H, C₆H₄), 6.67 (t, 2H, C₆H₄), 4.24 (s, 4H, NCH₂), 2.74 (m, 6H, CH₂CH₃), 1.26 (m, 9H, CH₂CH₃). ¹³C NMR (CDCl₃, 300K): δ 148.46, 144.09, 143.69, 135.31, 131.63, 129.64, 127.75, 117.19, 111.22, 110.31, 42.11, 26.12, 22.71, 17.19, 16.17.

Synthesis of Hg₂L₂

To a stirring solution containing dithiol (0.27 g, 0.62 mmol) and NEt₃ (0.20 mL, 1.43 mmol) in dried CH₃CN (15 mL), a CH₃CN solution (15 mL) of Hg(NO₃)₂ · H₂O (0.13 g, 0.60 mmol) was added. After the resulting mixture stirred overnight at room temperature, the precipitated solid was collected using Celite 545 and re-dissolved using THF (20 mL). The collected THF solution was dried under vacuum to afford a light-yellow powder (0.26 g, 66%). Brick-like light-yellow crystals (Hg₂L₂·1.5dioxane) suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into THF/1,4-dioxane (v/v 4:1) solution of Hg₂L₂ at 4°C. Elem Anal. Calcd (%) for C₅₂H₆₀Hg₂N₄S₄: C 49.16; H 4.76; N 4.41. Found: C 49.18; H 4.62; N 4.08. ¹H NMR (CDCl₃, 300K): δ 7.37 (d, *J* = 6.6 Hz, 2H, C₆H₄), 7.16 (t, *J* = 7.2 Hz, 2H, C₆H₄), 7.08 (s, 1H, C₆H₁), 6.83 (d, *J* = 7.8 Hz, 2H, C₆H₄), 6.67 (t, *J* = 7.2 Hz, 2H, C₆H₄), 4.32 (s, 2H, NH), 4.26 (s, 4H, NCH₂), 2.68 (m, 6H, CH₂CH₃), 1.25 (m, 9H, CH₂CH₃). ¹³C NMR (CDCl₃, 300K): δ 148.19, 143.99, 143.57, 135.62, 131.67, 128.28, 127.58, 119.25, 117.92, 110.77, 41.94, 26.19, 23.22, 17.16, 16.10. HRMS (ESI) *m/z* calcd: 1271.3168. Found 1271.3151 ([M+H]⁺).

Synthesis of Cd₂L₂

To a stirring solution containing dithiol (0.17 g, 0.39 mmol) and NEt₃ (0.12 mL, 0.86 mmol) in dried CH₃CN (15 mL), a CH₃CN solution (15 mL) of Cd(NO₃)₂ · 4H₂O (0.12 g, 0.39 mmol) was added. After the resulting mixture stirred overnight at room temperature, the precipitated solid was collected using Celite 545 and re-dissolved using DMSO (40 mL). The collected DMSO solution was dried under vacuum to afford a light-yellow powder (0.16 g, 75%). Elem Anal. Calcd (%) for C₅₂H₆₀N₄S₄Cd₂: C 57.08; H 5.53; N 5.12. Found: C 57.14; H 5.32; N 5.01. ¹H NMR (DMSO-d₆, 300K): δ 7.19 (d, 2H, C₆H₄), 6.98 (s, 1H, C₆H₁), 6.90 (t, 2H, C₆H₄), 6.59 (d, 2H, C₆H₄), 6.37 (t, 2H, C₆H₄), 4.84 (s, 2H, NH), 4.10 (s, 4H, NCH₂), 2.68 (m, 6H, CH₂CH₃), 1.23 (m, 9H, CH₂CH₃). ¹³C NMR (DMSO-d₆, 300K): δ 148.67, 143.44, 142.72, 134.48, 132.78, 127.08, 125.66, 124.32, 116.01, 108.72, 42.16, 25.88, 22.05, 17.02, 16.33. HRMS (ESI) *m/z* calcd: 1097.1853. Found: 1097.1841 ([M+H]⁺).

Synthesis of (ZnL)₁₀

To a stirring solution containing dithiol (0.17 g, 0.39 mmol) and NEt₃ (0.12 mL, 0.86 mmol) in dried CH₃CN (15 mL), a CH₃CN solution (15 mL) of ZnCl₂ (0.05 g, 0.39 mmol) was added. After the resulting mixture stirred overnight at room temperature, the precipitated solid was collected using Celite 545 and re-dissolved using CHCl₃ (20 mL). The collected CHCl₃ solution was dried under vacuum to afford a light-yellow powder (0.18 g, 92.5%). Brick-like light-yellow crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into CHCl₃ solution of (ZnL)₁₀ at 4°C. Elem Anal. Calcd (%) for C₂₆₀H₃₀₀N₂₀S₂₀Zn₁₀: C 62.45; H 6.05; N 5.60. Found: C 62.19; H 6.32; N 5.81. ¹H NMR (CDCl₃, 300K): δ 7.86 (d, *J* = 6.6 Hz, 1H, C₆H₄), 7.72 (d, *J* = 7.2 Hz, 1H, C₆H₄), 7.40 (m, 2H, C₆H₄), 6.66 (s, 1H, C₆H₁), 6.20 (t, *J* = 7.2 Hz, 1H, C₆H₄), 5.94 (d, *J* = 10.5 Hz, 1H, NH), 5.86 (m, 2H, C₆H₄), 5.67 (d, *J* = 11.4 Hz, 1H, NH), 5.17 (d, *J* = 7.5 Hz, 1H, C₆H₄), 4.81 (d, *J* = 14.1 Hz, 1H, NCH₂), δ 4.30 (t, *J* = 12.3 Hz, 1H, NCH₂), 3.93 (d, *J* = 11.4 Hz, 1H, NCH₂), 3.63 (t, *J* = 12.3 Hz, 1H, NCH₂), 3.00 (m, 3H, CH₂CH₃), 1.59 (m, 1H, CH₂CH₃), 1.50 (m, 1H, CH₂CH₃), 1.37 (m, 1H, CH₂CH₃), 1.10 (t, *J* = 7.2 Hz, 3H, CH₂CH₃), 0.80 (m, 6H, CH₂CH₃). ¹³C NMR (CDCl₃, 300K): δ 145.56, 143.82, 143.15, 142.34, 141.38, 140.31, 138.71, 133.77, 132.15, 130.17, 130.01, 128.41, 127.99, 125.85, 125.55, 125.14, 124.74, 121.65, 52.00, 48.93, 26.25, 24.77, 24.19, 18.12, 15.54, 13.54.

The studies of fluorescence, absorption and ¹H NMR titrations of (ZnL)₁₀

The salts possessing different anions including Bu₄NCl, Bu₄NBr, Bu₄NI, Bu₄NCIO₄, Bu₄NPF₆, Bu₄NNO₃, Bu₄NHSO₄, and Bu₄NH₂PO₄ were used for the studies of titrations. The fluorescent titrations were performed by incubating 10 μM (ZnL)₁₀ at ambient conditions with varying concentrations of different anions for 10 mins in CHCl₃. The decomposition of (ZnL)₁₀ was monitored by fluorescence spectroscopy (excitation wavelength at 265 nm). For absorption and NMR titrations of (ZnL)₁₀ with H₂PO₄⁻ anions, the procedures used were the same as that used for fluorescence titration. In the case of NMR titrations, 0.1 mM (ZnL)₁₀ and CDCl₃ solvent were used instead.

Fig. S1 Partial ^1H NMR spectra of Zn complex (a), Cd complex (b), Hg complex (c), and H_2L ligand (d). All spectra were obtained from CDCl_3 (*) solution, except the spectrum of Cd complex (in DMSO-d_6).

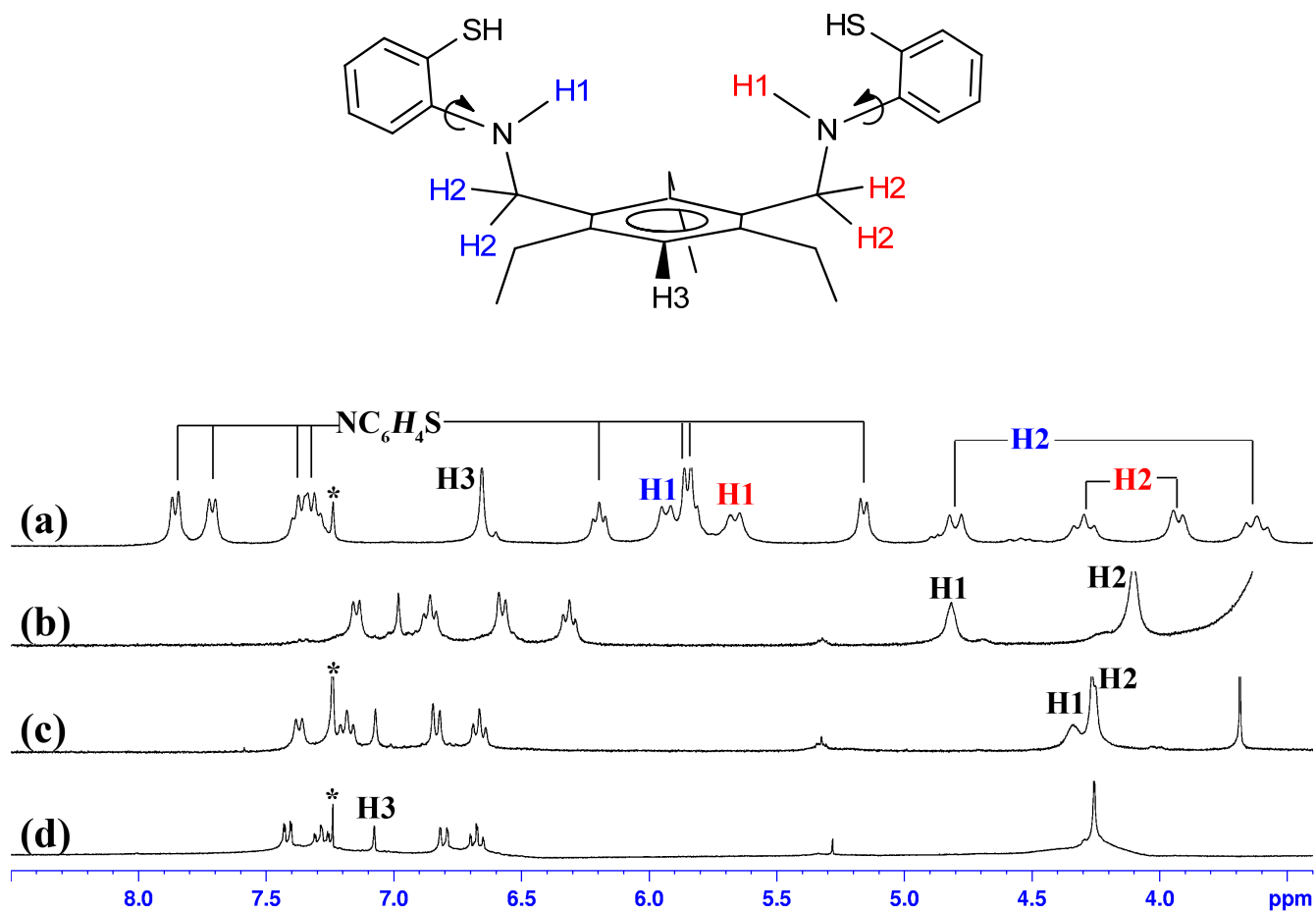


Fig. S2 Ortep drawing of dinuclear complex Hg_2L_2 at 50% probability. All hydrogen atoms and one dioxane molecule outside the complex are omitted for clarity.

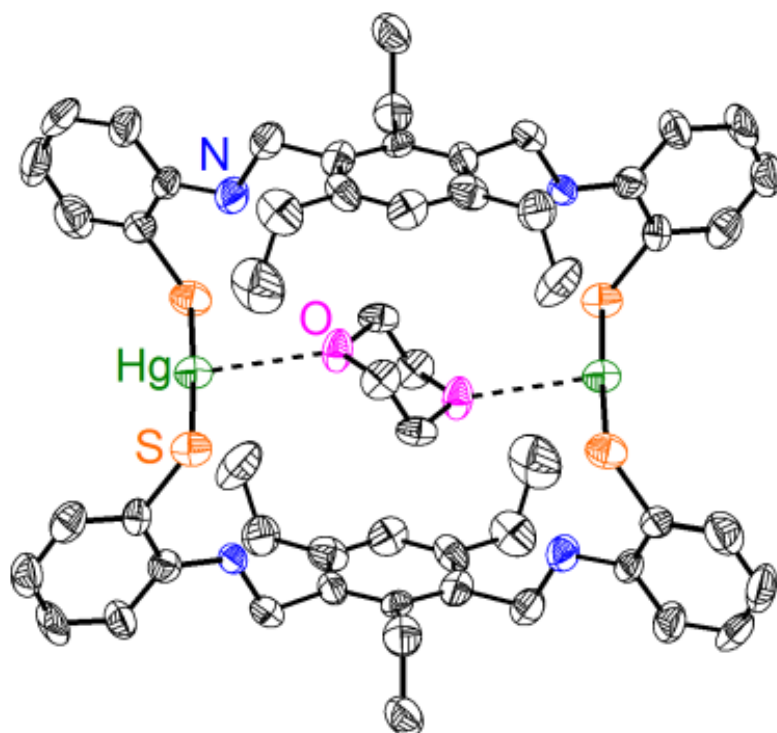


Fig. S3 ^1H NMR spectrum (CDCl_3 , 300K) of $(\text{ZnL})_{10}$

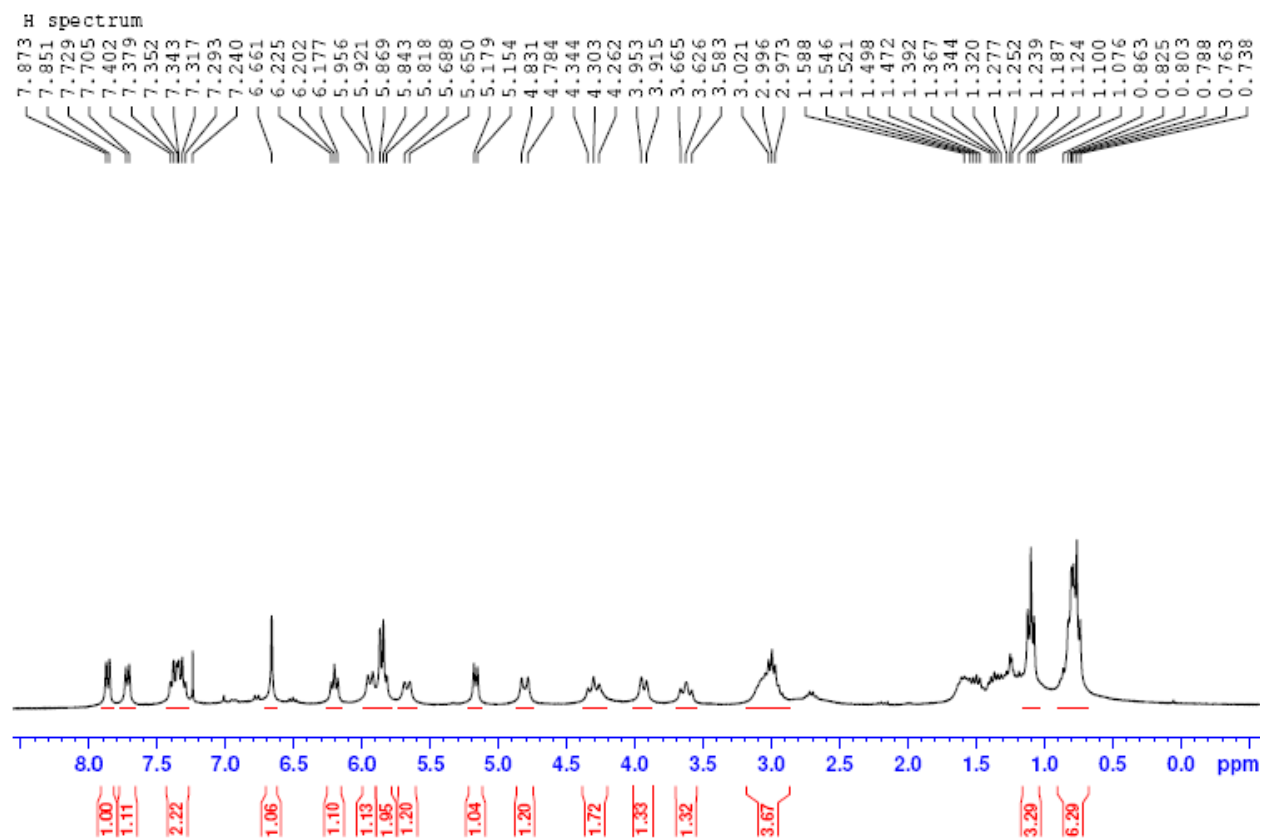


Figure S4. ^{13}C NMR spectrum (CDCl_3 , 300K) of $(\text{ZnL})_{10}$

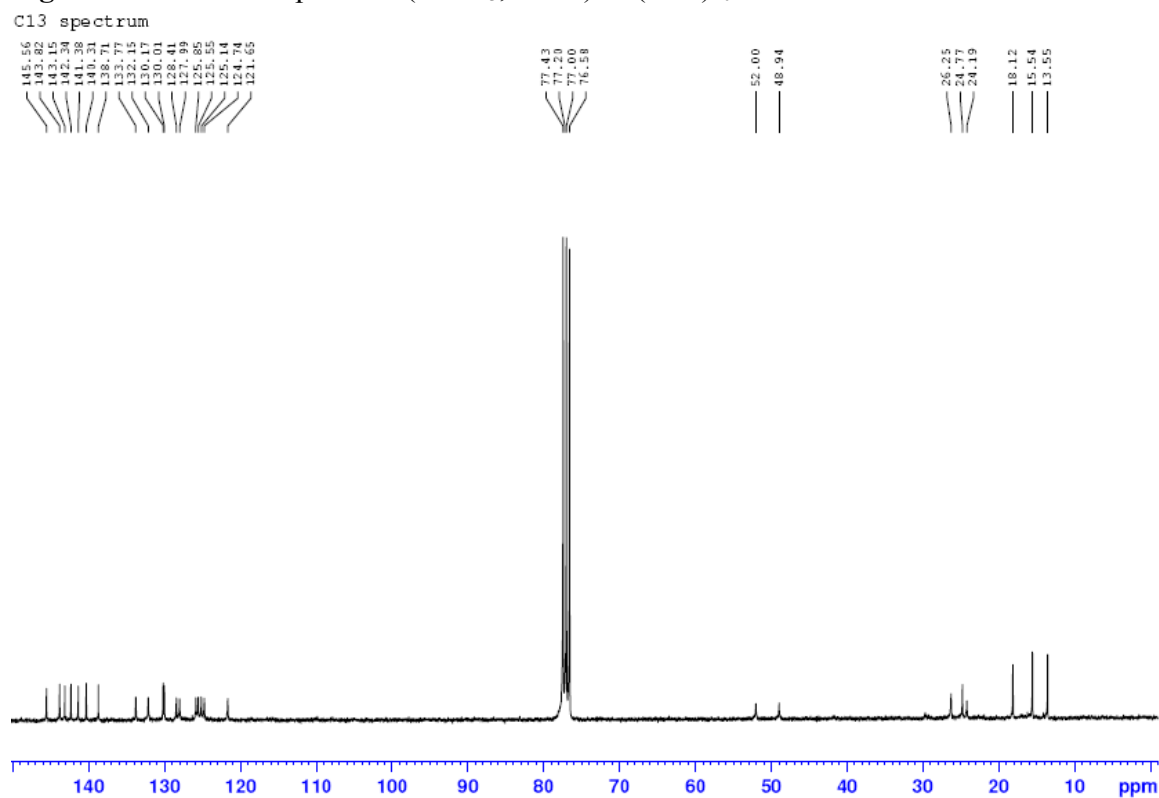
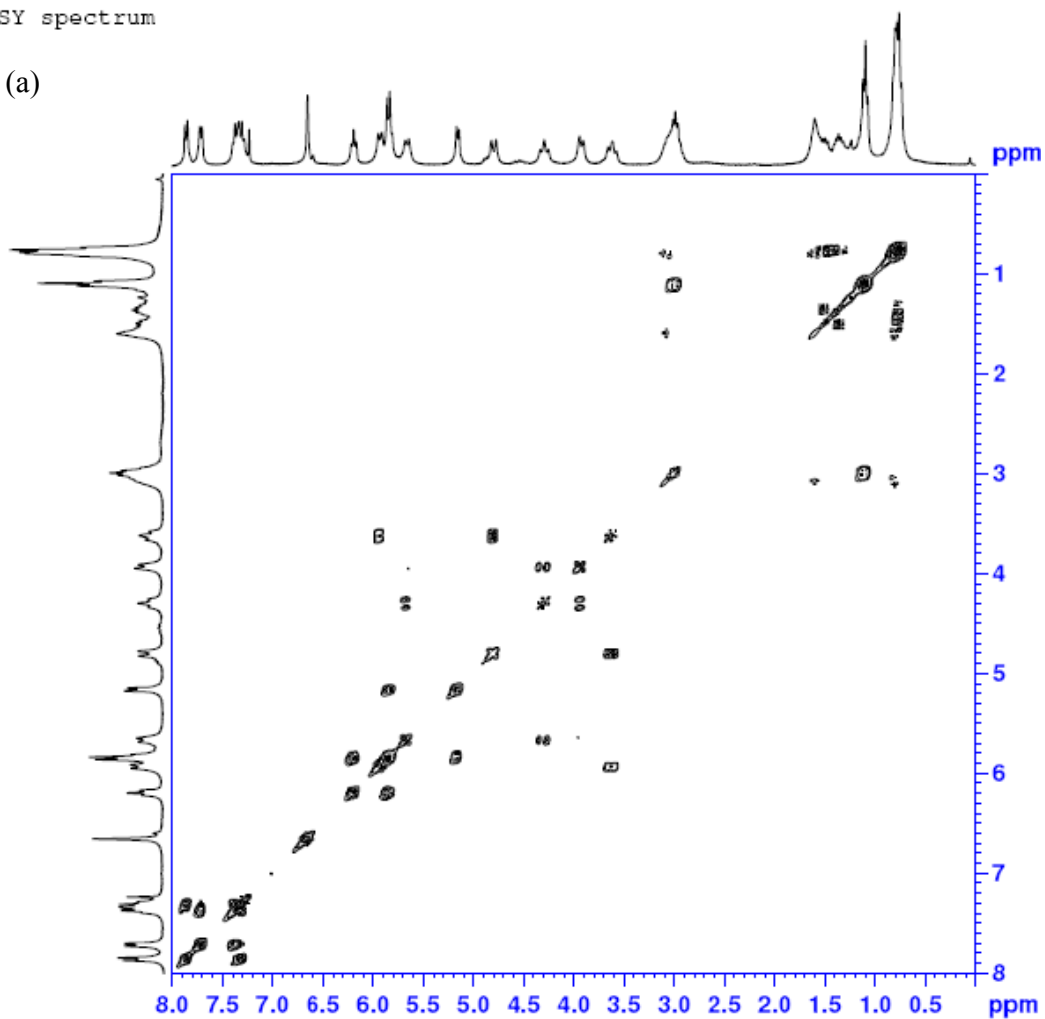


Fig. S5 $^1\text{H} - ^1\text{H}$ COSY NMR spectra (CDCl_3 , 300K) of $(\text{ZnL})_{10}$.

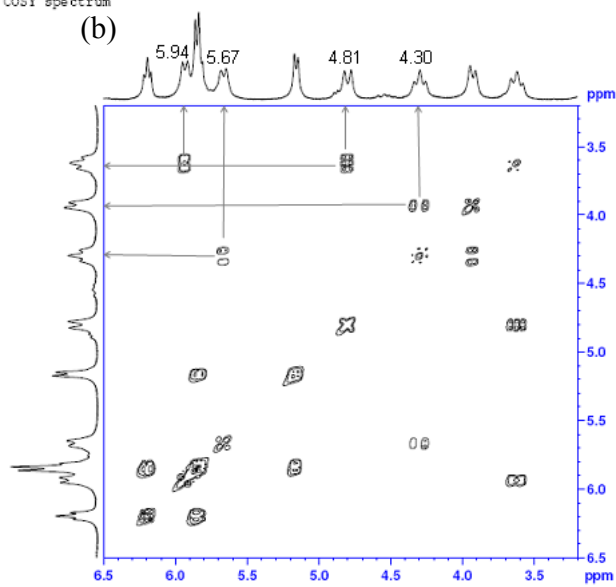
COSY spectrum

(a)



COSY spectrum

(b)



COSY spectrum

(c)

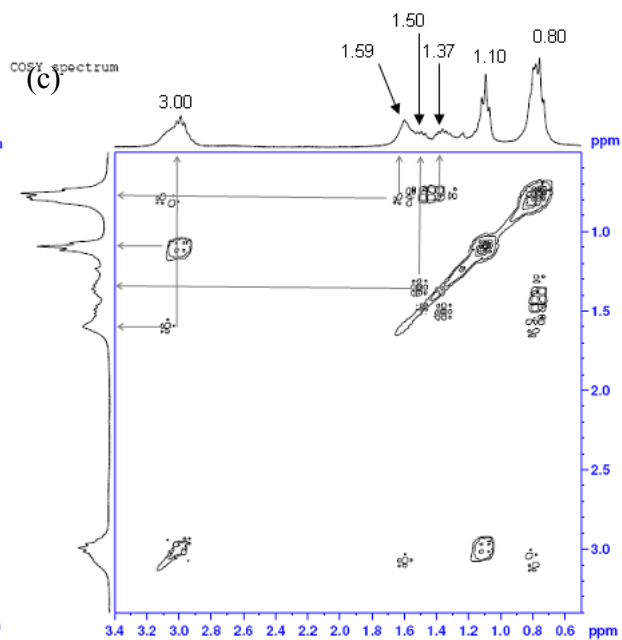


Fig. S6 $^1\text{H} - ^{13}\text{C}$ HSQC NMR spectra (CDCl_3 , 300K) of $(\text{ZnL})_{10}$.

HSQC spectrum

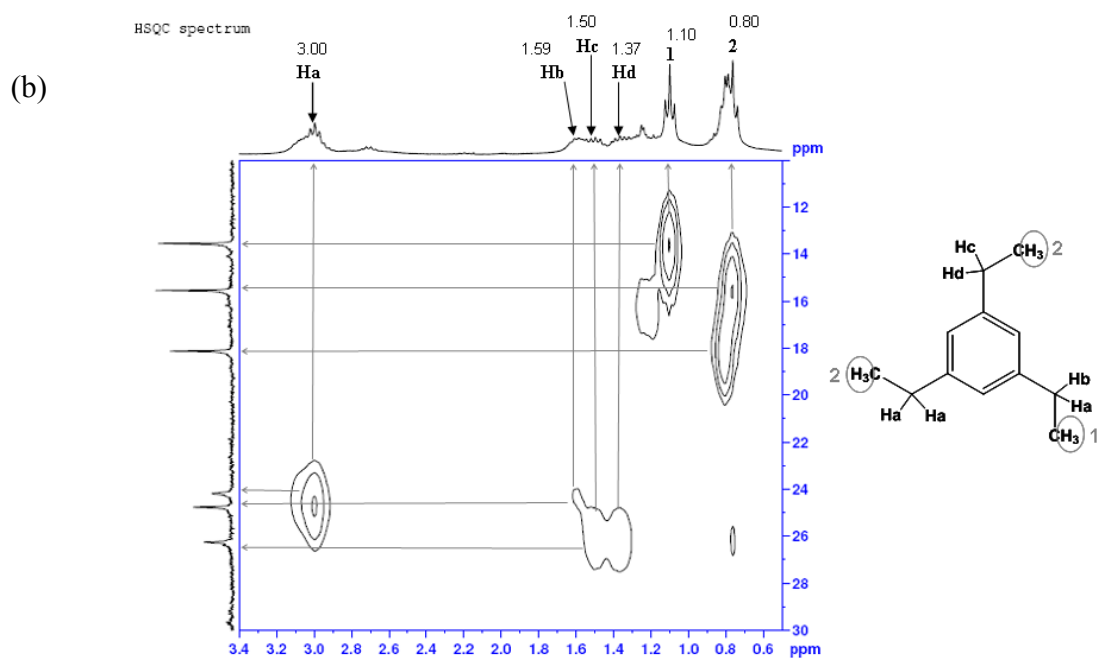
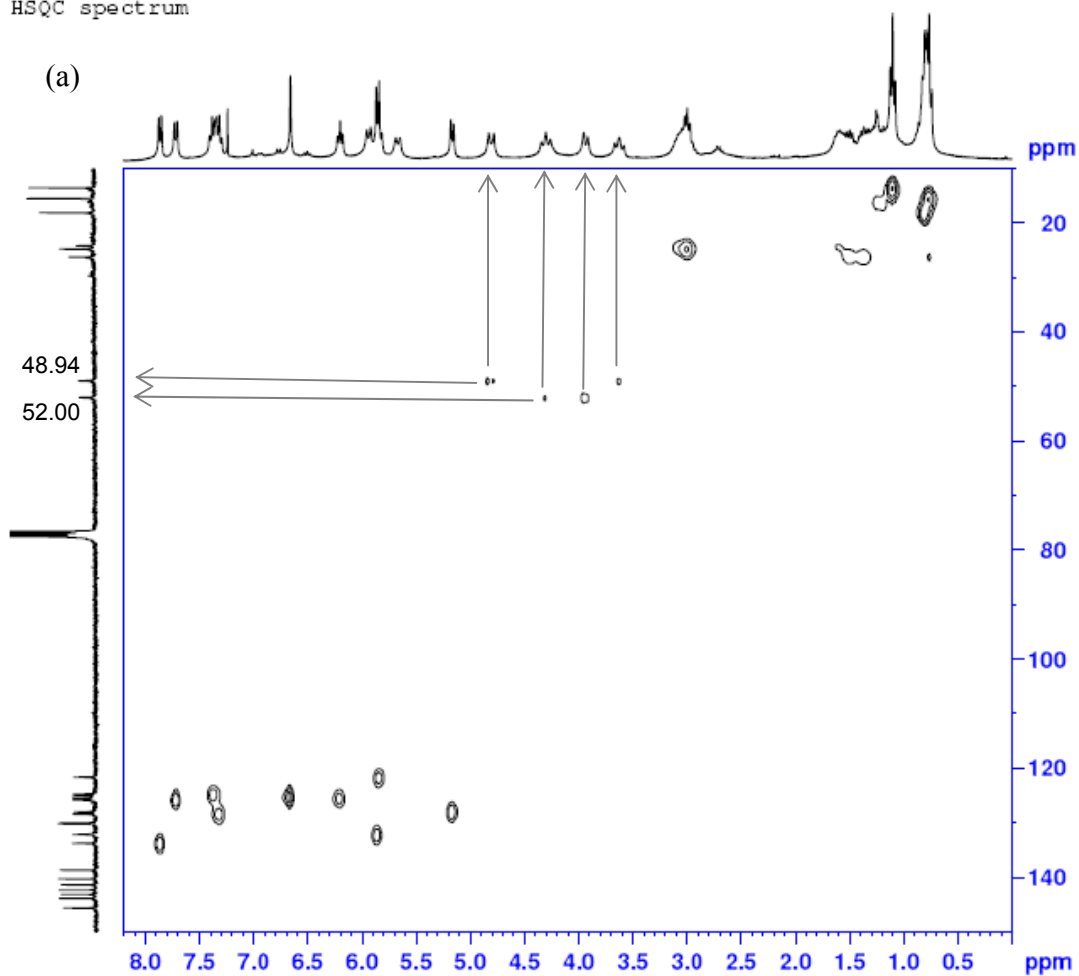


Fig. S7 The end-on view of the bond between the vicinal N(3) and C(31) atoms from the crystal structure of $(ZnL)_{10}$. The dihedral angles of 79.76° and 161.91° between vicinal protons are predicted to have coupling constants of 9 Hz and near zero Hz, respectively, from the vicinal Karplus correlation diagram.³ The calculated coupling constants match well with those from the experimental observation. This explains why H(31A) and H(31B) belonging to the same methylene carbon (C(31)) have triplet and doublet signals, respectively, from 1H NMR spectrum of $(ZnL)_{10}$.

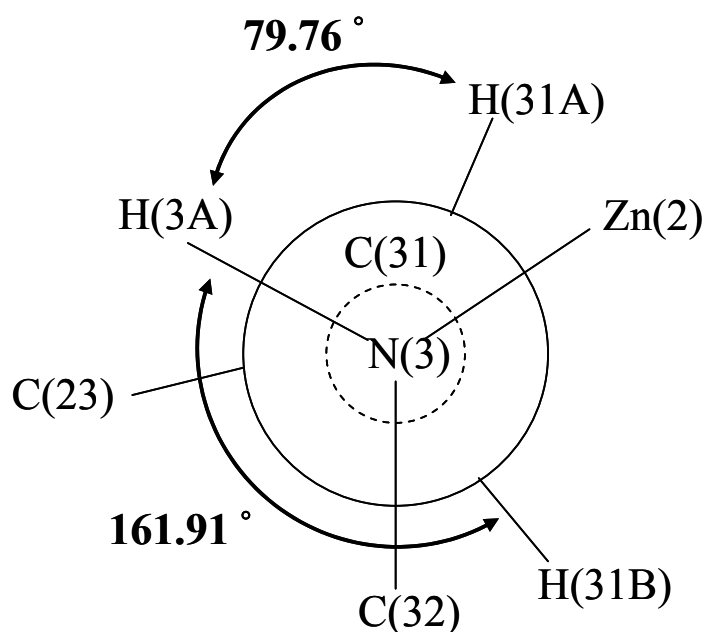


Fig. S8 Space-filling model of the molecular structure of $(ZnL)_{10}$: top view (left); side view (right). The same color representation of ligands as described in Fig. 2. Zn in violet, H in white.

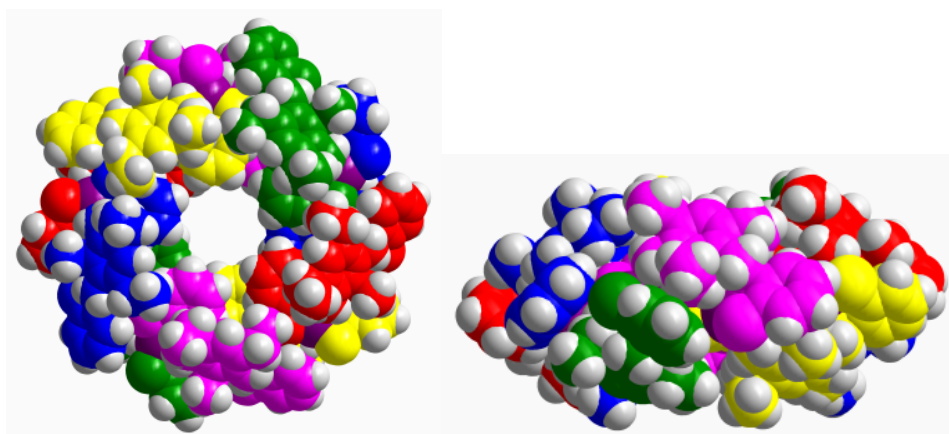
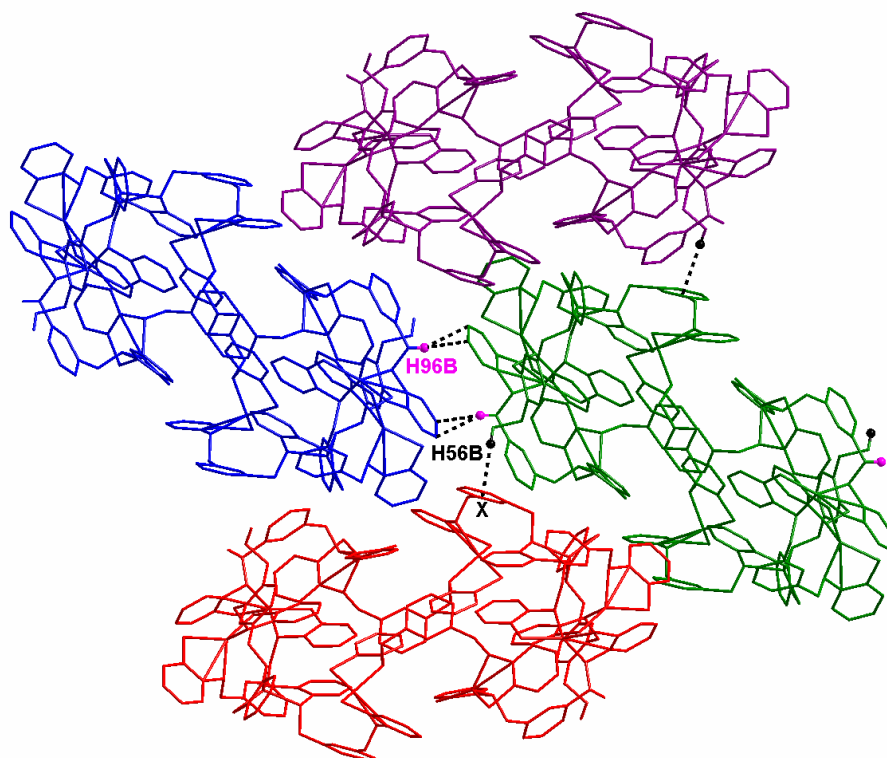


Fig. S9 (a) Packing diagram of the circular helicate showing the C-H \cdots π interactions. All ethyl groups and hydrogen atoms are omitted for clarity except C55, C56, H96B and H56B atoms. H56B \cdots X = 2.7205(1) Å (X = centroid of C19, C20, C21, C22, C23, C24); H96B \cdots C92 = 2.595(8) Å; H96B \cdots C93 = 2.72(1) Å. Each helicate is shown in a different color. (b) Space-filling picture of 3D packing of the circular helicate. Each helicate is shown in a different color.

(a)



(b)

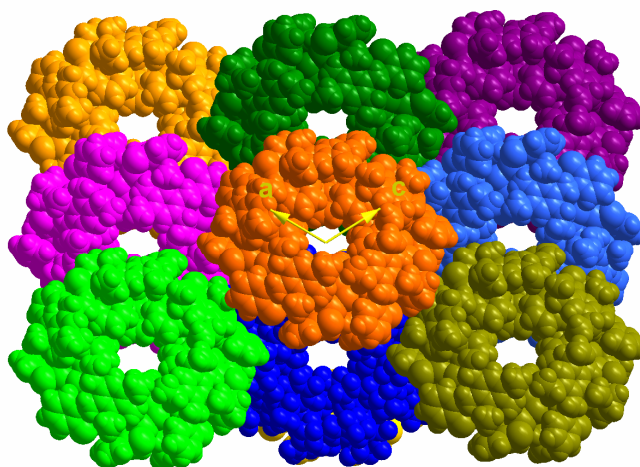
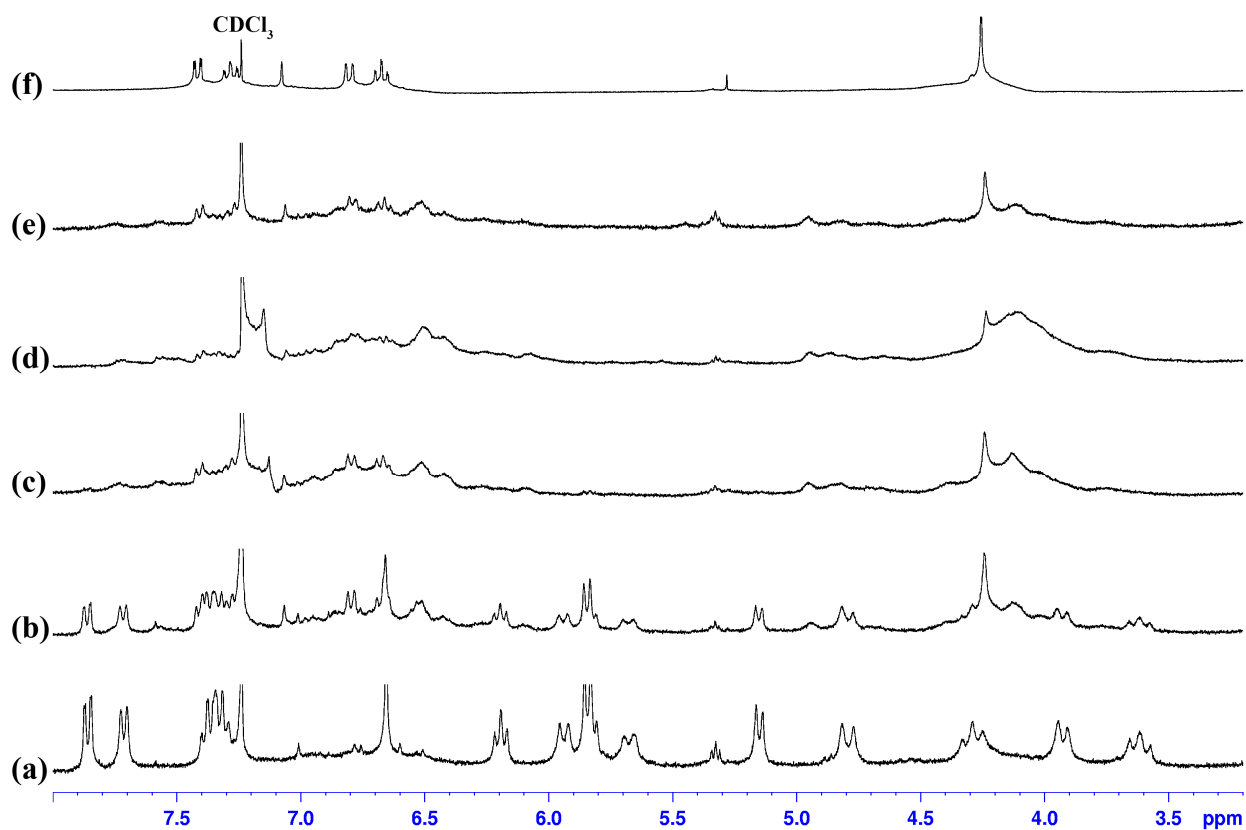


Fig. S10 ^1H NMR titration of $(\text{ZnL})_{10}$ with H_2PO_4^- anions. (a) $(\text{ZnL})_{10}$ + 2 equiv. H_2PO_4^- ; (b) $(\text{ZnL})_{10}$ + 4 equiv. H_2PO_4^- ; (c) $(\text{ZnL})_{10}$ + 7 equiv. H_2PO_4^- ; (d) $(\text{ZnL})_{10}$ + 10 equiv. H_2PO_4^- ; (e) $(\text{ZnL})_{10}$ + 13 equiv. H_2PO_4^- ; (f) purified H_2L .



Reference

1. G. M. Sheldrick, *SHELXTL, Version 5.1*. Bruker AXS Inc., Madison, WI, 1998.
2. L. E. Sutton, *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Chemical Society Publications, UK, 1965.
3. P. van der Sluis, A. L. Spek, *Acta Cryst.* 1990, **A46**, 194-201.
4. M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11-15.