

Self-Assembly of Concentric Hexagons and Hierarchical Self-Assembly of Supramolecular Metal-Organic Nanoribbons at Solid/Liquid Interface

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1. Experimental section

General Procedures. All reagents were purchased from Sigma-Aldrich, Matrix Scientific, Alfa Aesar and used without further purification. Column chromatography was conducted using basic Al_2O_3 (Brockman I, activity, 58 Å) or SiO_2 (VWR, 40-60 μm , 60 Å) and the separated products were visualized by UV light. NMR spectra data were recorded on a 400-MHz and 500 MHz Bruker Avance NMR spectrometer in CDCl_3 , CD_3CN or $\text{DMSO-}d_6$ with TMS as reference. ESI-MS and TWIM-MS were recorded with a Waters Synapt G2 tandem mass spectrometer, using solutions of 0.01 mg sample in 1 mL of $\text{CHCl}_3/\text{CH}_3\text{OH}$ (1:3, v/v) for ligands or 0.5 mg sample in 1 mL of MeCN/MeOH (3:1, v/v) for complexes. MALDI-TOF was carried out on Bruker AutoFlex TOF/TOF mass spectrometer.

TWIM-MS. The TWIM-MS experiments were performed under the following conditions: ESI capillary voltage, 3 kV; sample cone voltage, 30 V; extraction cone voltage, 3.5 V; source temperature 100 °C; desolvation temperature, 100 °C; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N_2); source gas control, 0 mL/min; trap gas control, 2 mL/min; helium cell gas control, 100 mL/min; ion mobility (IM) cell gas control, 30 mL/min; sample flow rate, 5 $\mu\text{L}/\text{min}$; IM traveling wave height, 25 V; and IM traveling wave velocity, 1000 m/s. Q was set in rf-only mode to transmit all ions produced by ESI into the triwave region for the acquisition of TWIM-MS data.

Collision cross-section calibration. The calibration procedure of Scrivens et al¹ was used to convert the drift time scale of the TWIM-MS experiments to a collision

cross-section (CCS) scale. The calibration curve was constructed by plotting the corrected CCSs of the molecular ions of myoglobin² against the corrected drift times of the corresponding molecular ions measured in TWIM-MS experiments at the same traveling wave velocity, traveling wave height and ion mobility gas flow settings *viz.*, 1000 m/s, 25 V, and 30 mL/min, respectively.

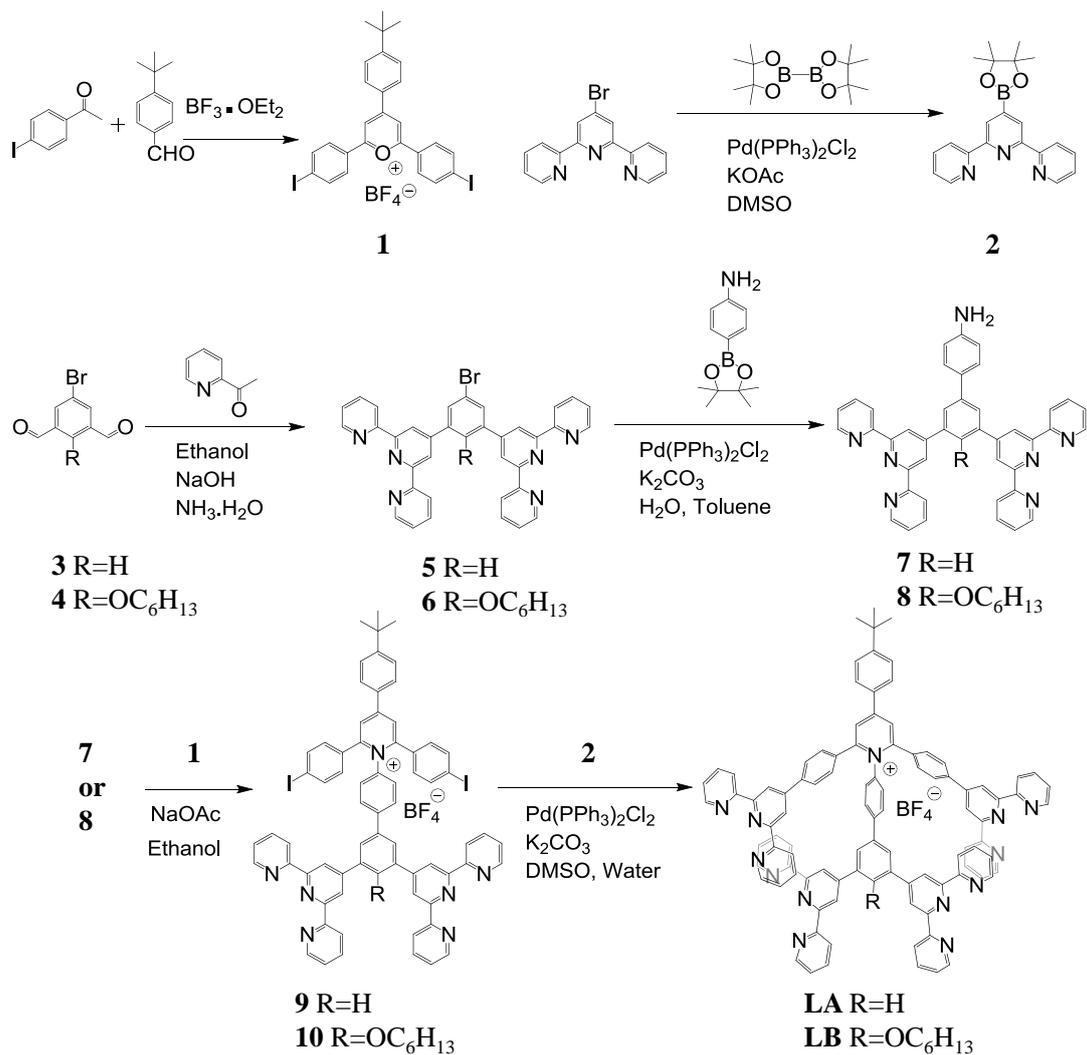
Molecular modeling. Energy minimization of the macrocycles was conducted with Materials Studio version 4.2, using the Anneal and Geometry Optimization tasks in the Forcite module (Accelrys Software, Inc.). All counterions are omitted. An initially energy-minimized structure was subjected to 70 - 100 annealing cycles with initial and mid-cycle temperatures of 300 and 1500 K, respectively, twenty heating ramps per cycle, one thousand dynamic steps per ramp, and one femtosecond per dynamic step. A constant volume/constant energy (NVE) ensemble was used and the geometry was optimized after each cycle. Geometry optimization used a universal force field with atom-based summation and cubic spline truncation for both the electrostatic and Van der Waals parameters. 70 - 100 energy-minimized structures were selected for the calculation of theoretical collision cross-sections using MOBCAL programs.

TEM: The sample was dissolved in CH₃CN at a concentration of 10⁻⁶ M. The solutions were drop cast on to a carbon-coated Cu grid and extra solution was absorbed by filter paper to avoid aggregation. The TEM images of the drop cast samples were taken with a JEOL 2010 transmission electron microscope.

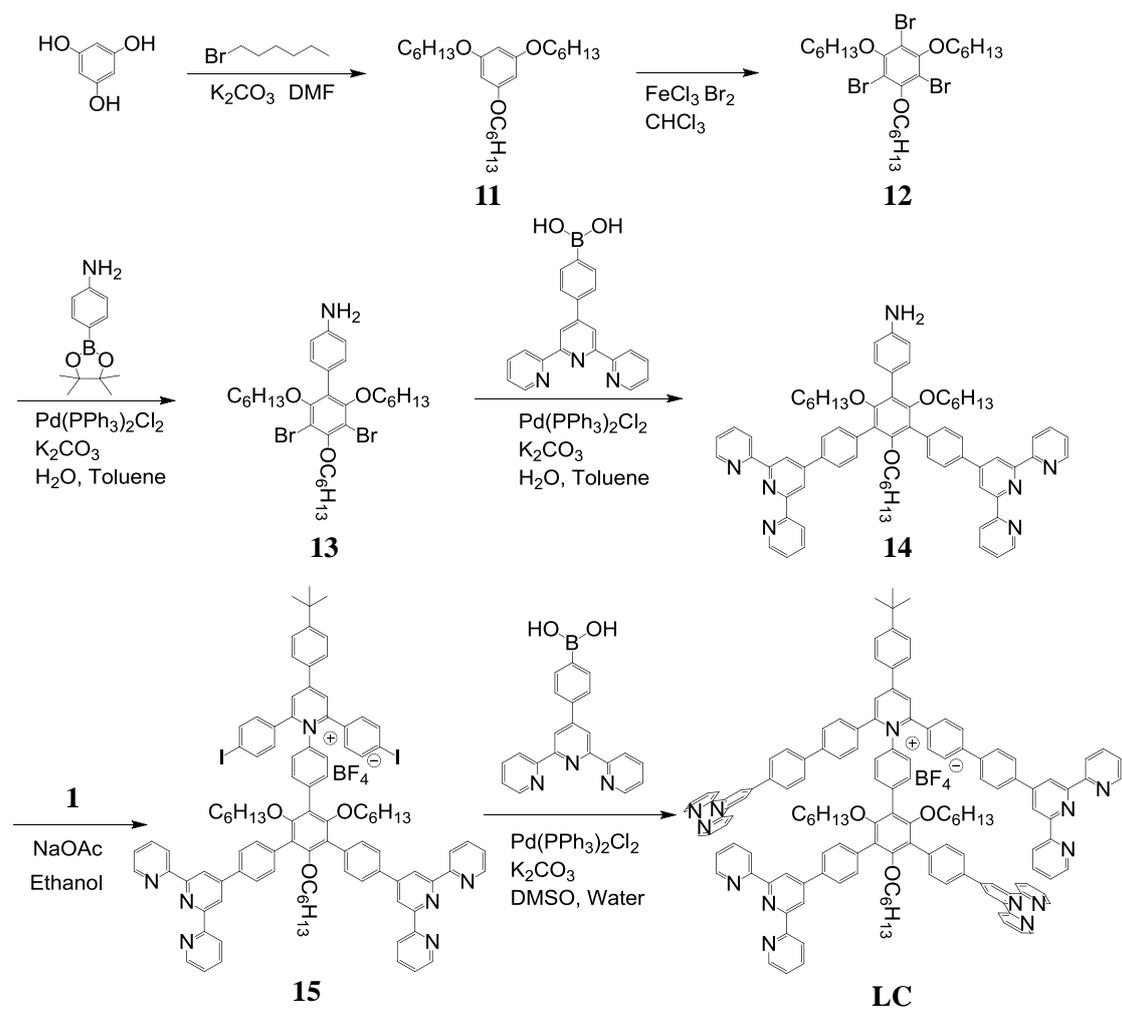
STM: The sample was dissolved in DMF at a concentration of 5.0 mg/ml.

Solution (5ul) was dropped on HOPG surface. After 30 seconds, surface was washed slightly with water for three times and totally dried in R.T. in air. The STM images were taken with a PicoPlus SPM system with a PicoScan 3000 Controller. The obtained STM images were processed by WSxM software.³

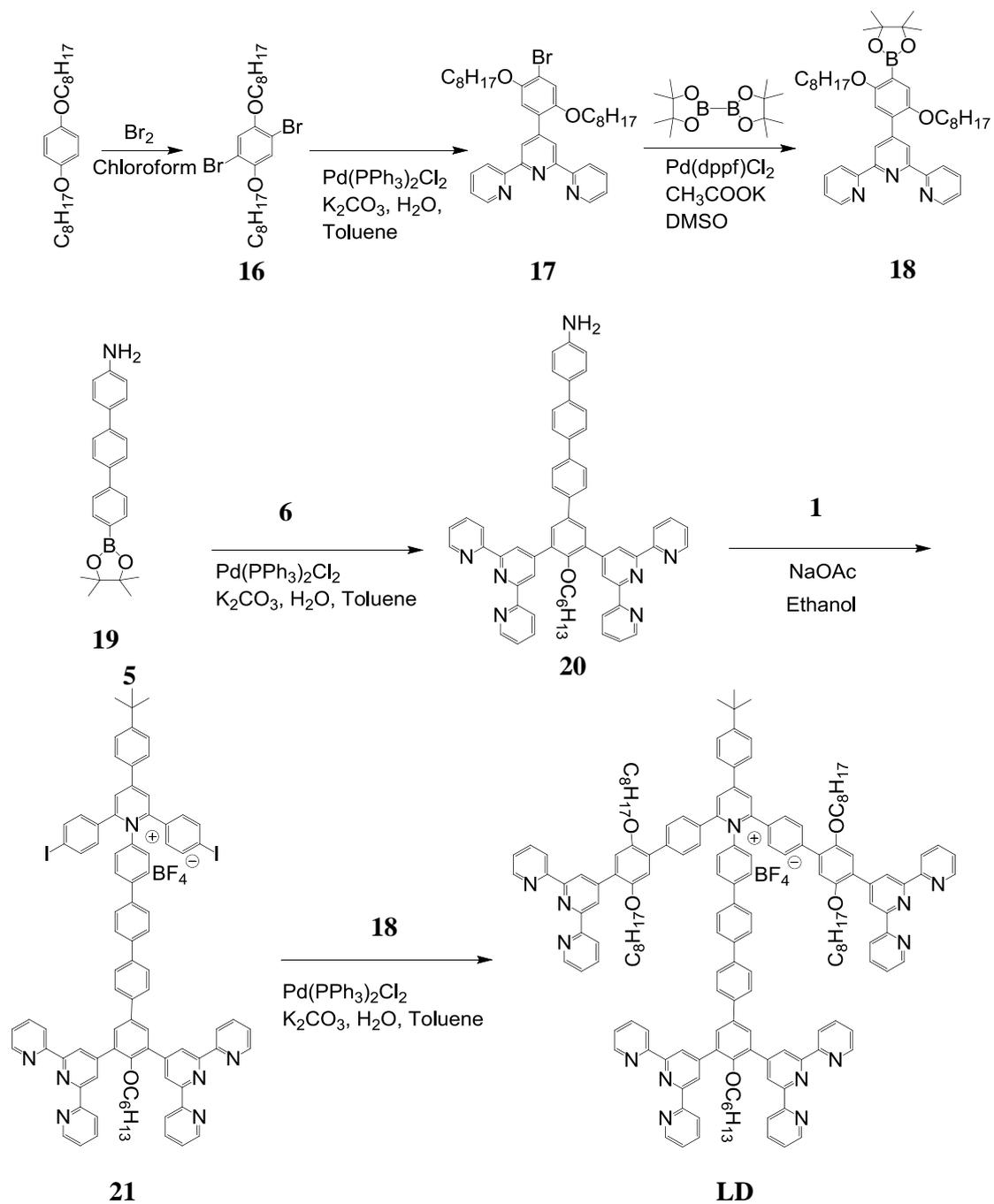
2. Synthesis of ligands LA, LB, LC and LD



Scheme 1. Synthesis of ligands LA and LB.

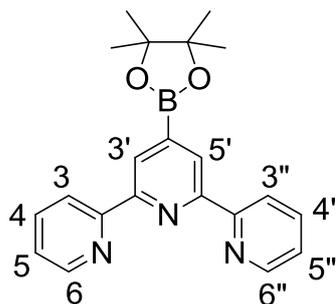


Scheme 2. Synthesis of ligand **LC**.

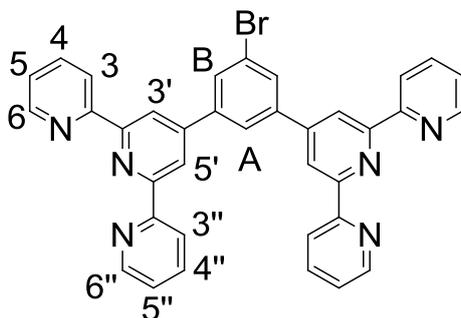


Scheme 3. Synthesis of ligand **LD**.

3. Synthesis of the ligands and complexes

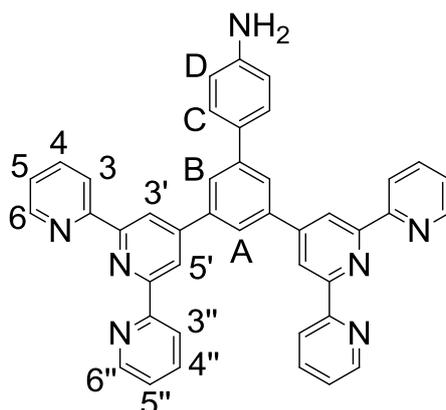


Compound **2**. The mixture of 4-Brom-terpyridine⁴ (3.12 g, 10 mmol), Bis-(pinacolato)diboron (2.54 g, 10 mmol), Pd(dppf)Cl₂ (326 mg, 0.4 mmol) and potassium acetate (2.9 g, 30 mmol) were added 35 mL anhydrous DMSO. The solution was heated at 85 °C for 8 h. The crude product was directly used in the following step. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (s, 2H, tpy-*H*^{3',5'}), 8.74 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 2H, tpy-*H*^{6,6''}), 8.62 (dt, *J* = 8.0, 1.1 Hz, 2H, tpy-*H*^{3,3''}), 7.86 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 2H, tpy-*H*^{4,4''}), 7.34 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2H, tpy-*H*^{5,5''}), 1.40 (s, 6H, *H*^A). ¹³C NMR (100 MHz, CDCl₃) δ 156.49, 154.76, 149.15, 136.76, 126.27, 123.60, 121.22, 84.48, 24.95. ESI-MS (*m/z*): Calcd. for [C₂₁H₂₂BN₃O₂+H]⁺: 360.2. Found: 360.2.



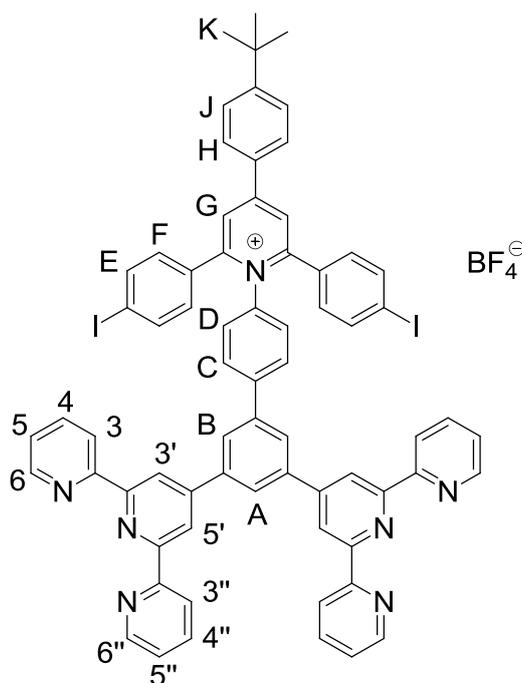
Compound **5**. To a solution of NaOH powder (4.8 g, 120 mmol) in EtOH (100 ml), 5-bromoisophthalaldehyde⁵ (2.1 g, 10 mmol) and 2-acetylpyridine (3.0 g, 25 mmol) was added. After stirring at room temperature for 24 h, aqueous NH₃•H₂O (35 mL)

was added and the mixture was refluxed for 40 h. After cooling to room temperature, the precipitate was filtered. The crude was purified by column chromatography on silica gel with chloroform: ethanol (100:2) as eluent to afford the product as a white solid (2.8 g, 45%). ^1H NMR (400 MHz, CDCl_3) δ 8.80 (s, 4H, tpy- $H^{3',5'}$), 8.77 (ddd, $J = 4.7, 1.7, 0.8$ Hz, 4H, tpy- $H^{6,6''}$), 8.73 (d, $J = 8.0$ Hz, 4H, tpy- $H^{3,3''}$), 8.27 (t, $J = 1.6$ Hz, 1H, Ph- H^A), 8.13 (d, $J = 1.6$ Hz, 2H, Ph- H^B), 7.93 (td, $J = 7.7, 1.8$ Hz, 4H, tpy- $H^{4,4''}$), 7.40 (ddd, $J = 7.4, 4.8, 1.2$ Hz, 4H, tpy- $H^{5,5''}$). ^{13}C NMR (100 MHz, CDCl_3) δ 156.17, 155.96, 149.15, 148.69, 141.45, 136.89, 130.75, 125.10, 123.98, 123.73, 121.44, 119.06. ESI-MS (m/z): Calcd. for $[\text{C}_{36}\text{H}_{23}\text{BrN}_6+\text{H}]^+$: 619.1. Found: 619.1.



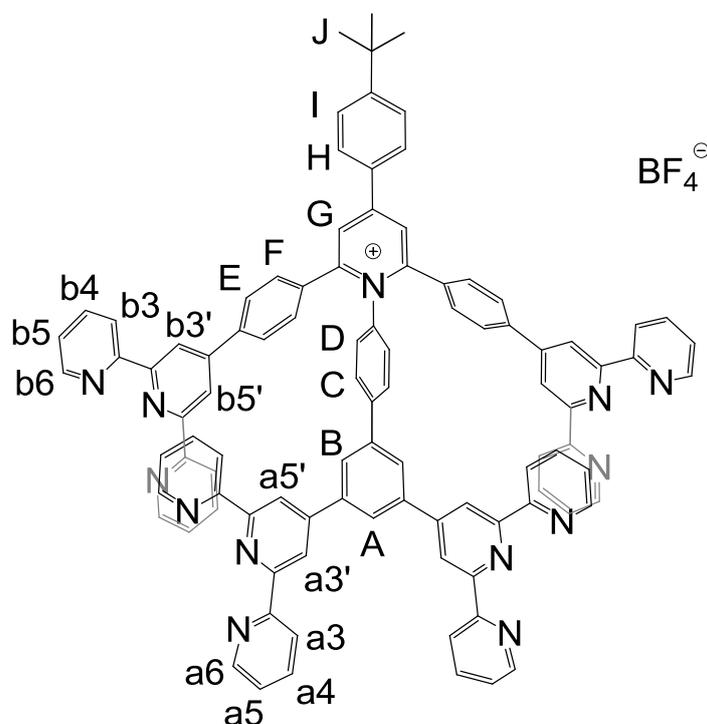
Compound 7. To a flask containing a degassed solution of compound **5** (620 mg, 1.0 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (330 mg, 1.5 mmol) in toluene (40 mL), an aqueous solution of 2 M K_2CO_3 (15 mL) was added. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (70 mg, 0.1 mmol) was then added under N_2 . The mixture was stirred at 90 $^\circ\text{C}$ for 24 h and then cooled to room temperature. The aqueous phase was extracted with CH_2Cl_2 . The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4 . After removal of volatile under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (100:1) as eluent to

afford the product as a white solid (505 mg, 80%). ^1H NMR (400 MHz, CDCl_3) δ 8.87 (s, 4H, tpy- $H^{3',5'}$), 8.76 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 4H, tpy- $H^{6,6''}$), 8.73 (dt, $J = 8.0, 1.1$ Hz, 4H, tpy- $H^{3,3''}$), 8.23 (t, $J = 1.7$ Hz, 1H, Ph- H^A), 8.11 (d, $J = 1.7$ Hz, 2H, Ph- H^B), 7.92 (ddd, $J = 7.9, 7.5, 1.8$ Hz, 4H, tpy- $H^{4,4''}$), 7.67 – 7.61 (m, 2H, Ph- H^C), 7.38 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 4H, tpy- $H^{5,5''}$), 6.88 – 6.82 (m, 2H, Ph- H^D), 3.78 (br, 2H, $-\text{NH}_2$). ^{13}C NMR (100 MHz, CDCl_3) δ 156.26, 156.02, 150.50, 149.14, 146.35, 142.84, 140.11, 136.85, 130.72, 128.42, 126.19, 124.31, 123.81, 121.42, 119.39, 115.43. ESI-MS (m/z): Calcd. for $[\text{C}_{42}\text{H}_{29}\text{N}_7+\text{H}]^+$: 632.3. Found: 632.3.



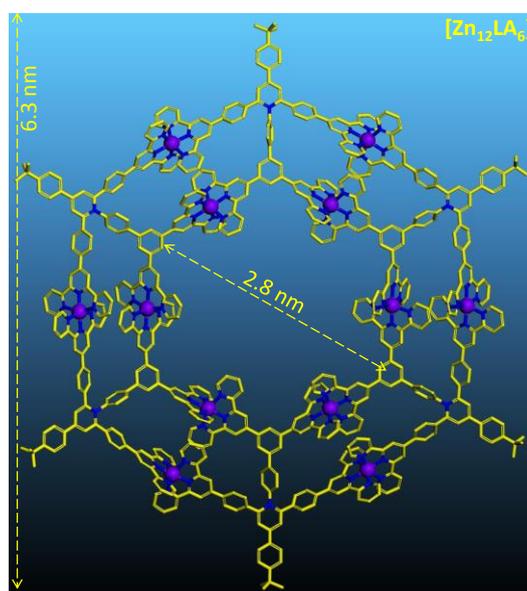
Compound **9**. Anhydrous sodium acetate (328 mg, 4.0 mmol) and the pyrylium salt **1⁶** (704 mg, 1.0 mmol) were added to a solution of **7** (631 mg, 1.0 mmol) in anhydrous ethanol (25 mL). The mixture was reflux for 8 h and then cooled to room temperature. The precipitate was filtered and washed with water and diethyl ether to give the product as a white solid (1.07 g, 81%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.72 (m, 8H, tpy- $H^{3',5'}$ and tpy- $H^{6,6''}$), 8.66 (s, 2H, Ph- H^G), 8.60 (d, $J = 7.8$ Hz, 4H, tpy- $H^{3,3''}$), 8.25

(m, 3H, Ph- H^A and Ph- H^H), 8.09 (s, 2H, Ph- H^B), 8.05 – 7.97 (m, 4H, tpy- $H^{4,4''}$), 7.84 (s, 2H, Ph- H^C), 7.79 (d, $J = 8.3$ Hz, 4H, Ph- H^E), 7.69 (d, $J = 8.5$ Hz, 2H, Ph- H^I), 7.62 (s, 2H, Ph- H^D), 7.51 (m, 4H, tpy- $H^{5,5''}$), 7.30 (d, $J = 8.6$ Hz, 4H, Ph- H^F), 1.36 (s, 9H, tert-butyl- H^K). ^{13}C NMR (100 MHz, DMSO- d_6) δ 156.09, 155.85, 155.37, 150.82, 149.72, 149.30, 140.53, 140.20, 139.90, 139.02, 138.07, 137.92, 137.60, 132.93, 132.10, 130.95, 129.84, 129.75, 129.13, 127.81, 127.15, 126.59, 125.41, 125.00, 121.51, 119.07, 99.98, 98.26, 35.4, 31.3. ESI-MS (m/z): Calcd. for $[\text{C}_{69}\text{H}_{50}\text{I}_2\text{N}_7]^+$: 1230.2. Found: 1230.2.

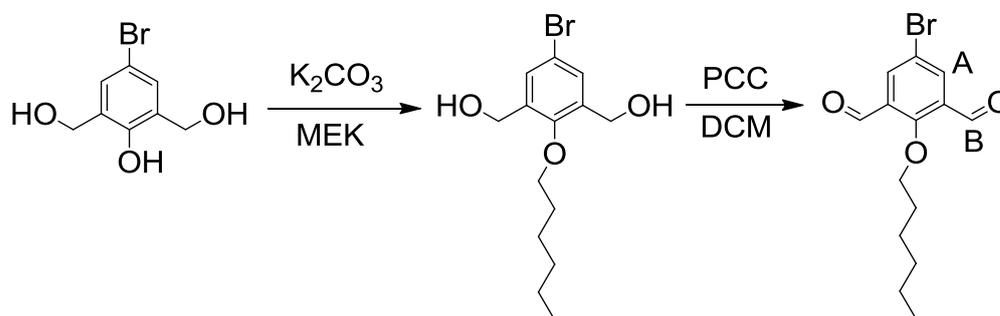


Ligand LA: To a solution of compound **9** (120.0 mg, 91.1 μmol), Pd(PPh₃)₂Cl₂ (14.0 mg, 20.0 μmol) and compound **2** (81.8 mg, 227.8 μmol) in DMSO (25 mL) under N₂, aqueous 2 M K₂CO₃ (8 mL) was added. The mixture was stirred at 80 °C for 30 h and then cooled to room temperature. The mixture was added into 200 ml water and was extracted with CHCl₃, and the combined organic phase was washed with brine and

dried over Na₂SO₄. After removal of solvent under vacuum, the residue was purified by column chromatography on Al₂O₃. The polarity of eluent was increased from chloroform/acetone 100/0 to 0/100, then a mixture of acetone/acetonitrile, 70/30 to 0/100 and finally a mixture of acetonitrile/water/NH₄BF₄ to afford **LA** as a white solid (61 % yield). ¹H NMR (400 MHz, CDCl₃) δ 8.55 – 8.51 (m, 4H, tpy-*H*^{a3,3''}), 8.45 – 8.40 (m, 4H, tpy-*H*^{b3,3''}), 8.40 – 8.32 (m, 8H, tpy-*H*^{a3',5'} and tpy-*H*^{b3',5'}), 8.28 (m, 8H, tpy-*H*^{a6,6''} and tpy-*H*^{b6,6''}), 7.98-7.95 (m, 4H, Ph-*H*^G and Ph-*H*^H), 7.94-7.90 (m, 4H, Ph-*H*^E), 7.84 – 7.75 (m, 8H, Ph-*H*^B, Ph-*H*^C and Ph-*H*^F), 7.72 – 7.67 (m, 4H, tpy-*H*^{b4,4''}), 7.60-7.54 (m, 9H, Ph-*H*^A, Ph-*H*^D, Ph-*H*^I and tpy-*H*^{a4,4''}), 7.23 – 7.15 (m, 4H, tpy-*H*^{b5,5''}), 7.14 – 7.04 (m, 4H, tpy-*H*^{a5,5''}), 1.36 (s, 9H, tert-butyl-*H*^J). ¹³C NMR (100 MHz, CDCl₃) δ 156.46, 156.45, 155.95, 155.91, 155.75, 155.71, 149.28, 149.08, 149.01, 148.95, 148.27, 141.62, 140.32, 140.00, 138.72, 136.77, 136.61, 133.65, 132.14, 131.92, 131.24, 130.80, 129.32, 128.43, 127.94, 127.47, 126.87, 126.36, 126.08, 123.82, 123.65, 121.35, 121.21, 121.11, 118.98, 118.74, 35.17, 31.10. MALDI-TOF MS (*m/z*): Calcd. for [C₁₀₅H₈₂N₁₃O]⁺ 1440.6. Found: 1440.6.

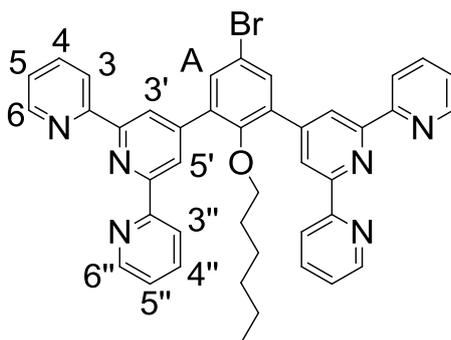


Complex [**Zn**₁₂**LA**₆]: To a solution of ligand **LA** (6.0 mg, 3.9 μmol) in CHCl₃ (3 mL), a solution of Zn(NO₃)₂•6H₂O (2.3 mg, 7.9 μmol) in MeOH (9 mL) was added. The mixture was stirred at 50 °C for 8 h and then cooled to room temperature. Upon addition of NH₄PF₆ (200 mg), a precipitate was formed and washed with water to give a white product (yield: 90%). ESI-MS (*m/z*): 1578.0 [M-8PF₆⁻]⁸⁺ (calcd *m/z*: 1578.0), 1386.6 [M-9PF₆⁻]⁹⁺ (calcd *m/z*: 1386.6), 1233.6 [M-10PF₆⁻]¹⁰⁺ (calcd *m/z*: 1233.6), 1108.1 [M-11PF₆⁻]¹¹⁺ (calcd *m/z*: 1108.1), 1003.6 [M-12PF₆⁻]¹²⁺ (calcd *m/z*: 1003.6), 915.2 [M-13PF₆⁻]¹³⁺ (calcd *m/z*: 915.2), 839.6 [M-14PF₆⁻]¹⁴⁺ (calcd *m/z*: 839.6), 773.8 [M-15PF₆⁻]¹⁵⁺ (calcd *m/z*: 773.8), 716.5 [M-16PF₆⁻]¹⁶⁺ (calcd *m/z*: 716.5), 665.9 [M-17PF₆⁻]¹⁷⁺ (calcd *m/z*: 665.9) and 620.8 [M-18PF₆⁻]¹⁸⁺ (calcd *m/z*: 620.8).

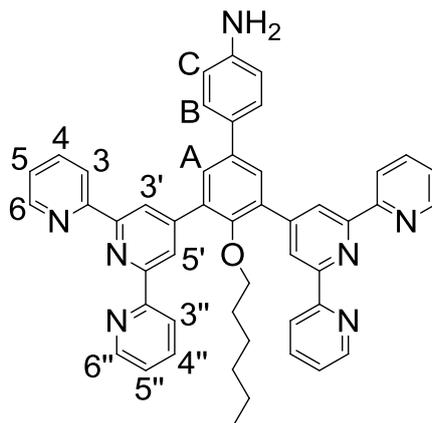


Compound **4**. A mixture of 4-bromo-2,6-bis(hydroxymethyl)phenol⁷ (6.0 g, 25.9 mmol), 1-bromohexane (5.1 g, 31.1 mmol), K₂CO₃ (7.2 g, 52.0 mmol) and methyl ethyl ketone (200 mL) was refluxed under N₂ for 24 h. The mixture was cooled to room temperature, filtrated and dried under vacuum. The white residue, PCC (11.8 g, 75 mmol) and celite (10 g) were dissolved in DCM (200 ml), and the mixture was stirred for 20 h at room temperature. The solution was filtered and poured onto silica gel column with DCM as eluent to afford

5-bromo-2-(hexyloxy)benzene-1,3-dialdehyde as a white solid (86% yield). ^1H NMR (400 MHz, CDCl_3) δ 10.36 (s, 2H, Ph- H^B), 8.20 (s, 2H, Ph- H^A), 4.14 (t, $J = 6.4$ Hz, 2H), 1.95-1.87 (m, 2H), 1.56 – 1.45 (m, 2H), 1.40 – 1.35 (m, 4H), 0.97 – 0.89 (t, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 187.13, 139.03, 137.24, 131.76, 118.29, 81.04, 31.48, 29.85, 25.45, 22.49, 13.94.

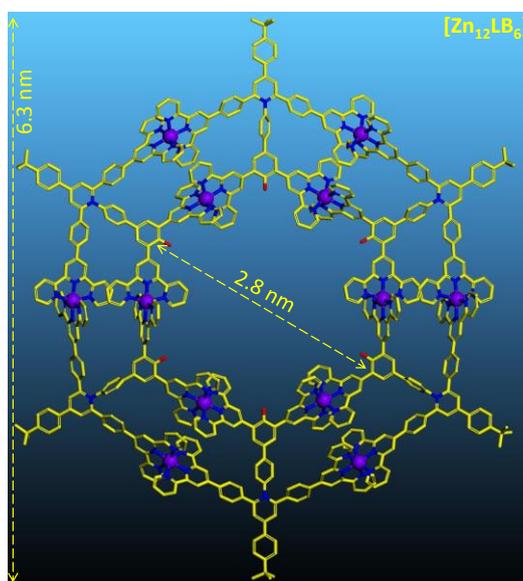


Compound **6**. To a solution of NaOH powder (6.24 g, 156.0 mmol) in EtOH (350 ml), 5-bromo-2-(hexyloxy)benzene-1,3-dialdehyde (4.0 g, 13.0 mmol) and 2-acetylpyridine (7.5 g, 62 mmol) were added. After stirring at room temperature for 20 h, aqueous $\text{NH}_3 \cdot \text{H}_2\text{O}$ (150 mL) was added and the mixture was refluxed for 40 h. Upon cooling to room temperature, the precipitate was filtered and washed with cold ethanol to give **6** as a white solid (4.8 g, 51%). ^1H NMR (400 MHz, CDCl_3) δ 8.80 (s, 4H, tpy- $H^{3',5'}$), 8.77 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 4H, tpy- $H^{6,6''}$), 8.70 (dt, $J = 8.0, 1.0$ Hz, 4H, tpy- $H^{3,3''}$), 7.91 (td, $J = 7.7, 1.8$ Hz, 4H, tpy- $H^{4,4''}$), 7.80 (s, 2H, Ph- H^A), 7.38 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 4H, tpy- $H^{5,5''}$), 3.37 (t, $J = 6.4$ Hz, 2H), 1.24 – 1.17 (dd, $J = 9.1, 6.2$ Hz, 2H), 0.92 (s, 2H), 0.83 – 0.66 (m, 4H), 0.55 – 0.41 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.10, 155.58, 153.98, 149.20, 147.08, 136.80, 135.89, 133.66, 123.82, 121.45, 121.25, 117.05, 74.33, 31.29, 29.70, 25.39, 22.11, 13.77. ESI-MS (m/z): Calcd. for $[\text{C}_{42}\text{H}_{35}\text{BrN}_6\text{O}+\text{H}]^+$: 719.2. Found: 719.2.



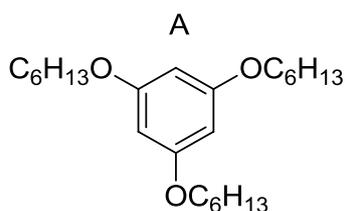
Compound **8**. To a flask containing a degassed solution of compound **6** (720 mg, 1 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (330 mg, 1.5 mmol) in toluene (30 mL), an aqueous solution of 2 M K_2CO_3 (15 mL) was added. The $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (70 mg, 0.1 mmol) was added into the mixture under N_2 . The mixture was stirred at 90 °C for 20 h and then cooled to room temperature. The aqueous phase was extracted with CH_2Cl_2 , and the combined organic phase was washed with brine and dried with anhydrous Na_2SO_4 . After removal of solvent under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (100:1) as eluent to afford the product as a white solid (636 mg, 87%). ^1H NMR (400 MHz, CDCl_3) δ 8.85 (s, 4H, tpy- $H^{3',5'}$), 8.76 (ddd, $J = 4.8, 1.6, 0.8$ Hz, 4H, tpy- $H^{6,6''}$), 8.70 (d, $J = 8.0$ Hz, 4H, tpy- $H^{3,3''}$), 7.89 (td, $J = 7.7, 1.8$ Hz, 4H, tpy- $H^{4,4''}$), 7.78 (s, 2H, Ph- H^A), 7.52 (d, $J = 8.5$ Hz, 2H, Ph- H^B), 7.35 (ddd, $J = 7.5, 4.8, 1.1$ Hz, 4H, tpy- $H^{5,5''}$), 6.78 (d, $J = 8.5$ Hz, 2H, Ph- H^C), 3.76 (br, 2H, $-\text{NH}_2$), 3.40 (t, $J = 6.1$ Hz, 2H), 1.28 – 1.10 (m, 2H), 0.97 – 0.89 (m, 2H), 0.82 – 0.68 (m, 4H), 0.58 – 0.43 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.42, 155.41, 153.38, 149.19, 148.77, 145.95, 137.51, 136.73, 134.10, 130.41, 129.08, 128.12, 123.65, 121.82, 121.26, 115.41, 74.22, 31.36, 29.78, 25.47, 22.15, 13.79. ESI-MS (m/z): Calcd. for $[\text{C}_{48}\text{H}_{41}\text{N}_7\text{O}+\text{H}]^+$: 732.3. Found:

Hz, 12H, tpy- $H^{a6,6''}$, tpy- $H^{a3,3''}$ and tpy- $H^{b6,6''}$), 8.59 (d, $J = 8.0$ Hz, 4H, tpy- $H^{b3,3''}$), 8.26 (s, 2H, Ph- H^F), 7.98 (d, $J = 8.5$ Hz, 2H, Ph- H^G), 7.92 (d, $J = 8.4$ Hz, 4H, Ph- H^D), 7.88 – 7.78 (m, 14H, Ph- H^E , Ph- H^B , tpy- $H^{a4,4''}$ and tpy- $H^{b4,4''}$), 7.71 (s, 2H, Ph- H^A), 7.64 (d, $J = 8.6$ Hz, 2H, Ph- H^H), 7.60 (d, $J = 8.1$ Hz, 2H, Ph- H^C), 7.35 – 7.23 (m, 8H, tpy- $H^{a5,5''}$ and tpy- $H^{b5,5''}$), 3.27 (t, $J = 6.0$ Hz, 2H), 1.40 (s, 9H, tert-butyl- H^I), 1.19 – 1.05 (m, 2H), 0.90 – 0.80 (m, 2H), 0.79 – 0.62 (m, 4H), 0.45 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.94, 156.48, 156.46, 156.17, 156.02, 155.89, 155.36, 155.07, 149.12, 149.10, 148.50, 147.94, 141.27, 140.37, 138.16, 136.70, 136.61, 134.37, 134.33, 133.57, 131.24, 130.66, 129.68, 129.20, 128.39, 127.54, 126.88, 126.12, 123.78, 123.68, 123.58, 121.56, 121.38, 121.21, 121.15, 118.90, 74.23, 67.09, 35.16, 31.27, 31.09, 29.63, 25.32, 22.07, 13.72. MALDI-TOF MS (m/z): Calcd. for $[\text{C}_{105}\text{H}_{82}\text{N}_{13}\text{O}]^+$ 1540.7. Found: 1540.8.

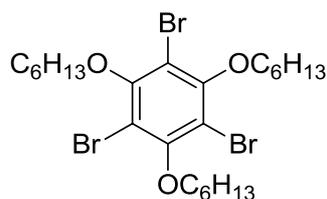


Complex $[\text{Zn}_{12}\text{LB}_6]$: To a solution of ligand **LB** (6.8 mg, 4.2 μmol) in CHCl_3 (1 mL), a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.5 mg, 8.4 μmol) in MeOH (3 mL) was added. The mixture was stirred at 55 $^\circ\text{C}$ for 8 h and then cooled to room temperature. Upon

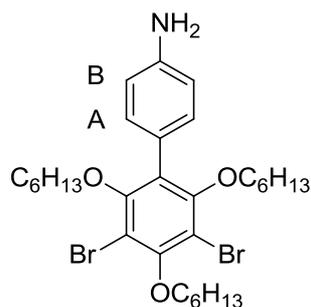
addition of NH_4PF_6 (200 mg), a precipitate was formed and washed with water to give a white product (yield: 92%). ^1H NMR (400 MHz, CD_3CN) δ 9.18 (s, 4H, tpy- $H^{a3',5'}$), 9.07 (s, 4H, tpy- $H^{b3',5'}$), 8.68 (m, tpy- $H^{a3,3''}$ and Ph- H^F), 8.60 (m, 4H, tpy- $H^{b3,3''}$), 8.42 (m, 4H, Ph- H^D), 8.27 (m, 2H, Ph- H^G), 8.22 (s, 2H, Ph- H^A), 8.02 (m, 4H, Ph- H^E), 7.94 (br, 4H, Ph- H^B and Ph- H^C), 7.87 (m, 2H, Ph- H^H), 7.79 (m, 8H, tpy- $H^{a4,4''}$ and tpy- $H^{a6,6''}$), 7.73 – 7.65 (m, 4H, tpy- $H^{b4,4''}$), 7.63 (m, 4H, tpy- $H^{b6,6''}$), 7.18 – 7.10 (m, 4H, tpy- $H^{a5,5''}$), 6.90 (s, 4H, tpy- $H^{b5,5''}$), 3.55 (br, 2H), 1.50 (s, 9H, tert-butyl- H^I), 1.28 – 1.20 (m, 2H), 1.13 – 1.05 (m, 2H), 0.75 – 0.66 (m, 2H), 0.57 – 0.42 (m, 2H), 0.16 – 0.06 (m, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 156.08, 154.69, 152.98, 149.81, 149.14, 148.07, 147.89, 147.72, 141.08, 138.00, 137.89, 135.62, 132.67, 132.25, 131.22, 131.09, 130.69, 129.32, 128.71, 128.39, 127.60, 127.18, 124.69, 123.50, 123.44, 123.09, 121.92, 35.01, 31.10, 30.31, 30.21, 25.91, 21.80, 12.75. ESI-MS (m/z): 1653.0 $[\text{M}-8\text{PF}_6]^{-8+}$ (calcd m/z : 1653.0), 1452.2 $[\text{M}-9\text{PF}_6]^{-9+}$ (calcd m/z : 1452.2), 1293.5 $[\text{M}-10\text{PF}_6]^{-10+}$ (calcd m/z : 1293.5), 1162.7 $[\text{M}-11\text{PF}_6]^{-11+}$ (calcd m/z : 1162.7), 1053.8 $[\text{M}-12\text{PF}_6]^{-12+}$ (calcd m/z : 1053.8), 961.5 $[\text{M}-13\text{PF}_6]^{-13+}$ (calcd m/z : 961.5), 882.5 $[\text{M}-14\text{PF}_6]^{-14+}$ (calcd m/z : 882.5), 814.0 $[\text{M}-15\text{PF}_6]^{-15+}$ (calcd m/z : 814.0), 754.1 $[\text{M}-16\text{PF}_6]^{-16+}$ (calcd m/z : 754.1), 701.2 $[\text{M}-17\text{PF}_6]^{-17+}$ (calcd m/z : 701.2), 654.2 $[\text{M}-18\text{PF}_6]^{-18+}$ (calcd m/z : 654.2), 612.2 $[\text{M}-19\text{PF}_6]^{-19+}$ (calcd m/z : 612.2), 574.3 $[\text{M}-20\text{PF}_6]^{-20+}$ (calcd m/z : 574.3) and 540.1 $[\text{M}-21\text{PF}_6]^{-21+}$ (calcd m/z : 540.1).



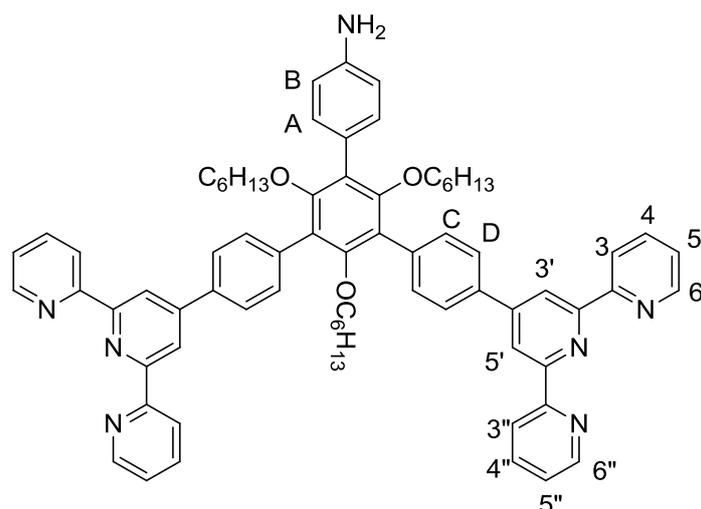
Compound **11**. Benzene-1,3,5-triol (3.78 g, 30 mmol) and K_2CO_3 (24.8 g 180 mmol) were degassed solution three times. 1-bromohexane (20 g, 120 mmol) and DMF 150 ml were added. The solution was stirred at 85 °C for 3d under N_2 . After that, it was cooled to room temperature. Solution was added 500 ml water and extracted with CH_2Cl_2 , and the combined organic phase was washed with brine and dried with anhydrous Na_2SO_4 . The crude was purified by column chromatography on silica gel with DCM: hexane (1:4) as eluent to afford the product as a liquid (7.5 g, 66 %). 1H NMR (400 MHz, $CDCl_3$) δ 6.09 (s, 1H, Ph- H^A), 3.93 (t, J = 6.6 Hz, 2H), 1.89 – 1.69 (m, 2H), 1.52 – 1.41 (m, 2H), 1.36 (m, 4H), 0.94 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.98, 93.79, 68.01, 31.60, 29.24, 25.75, 22.62, 14.04.



Compound **12**. Compound **11** (4.0 g, 10.5 mmol) was dissolved in 70 ml $CHCl_3$. $FeCl_3$ (170 mg, 1.05 mmol) was added and solution was stirred at room temperature 10 min. A solution of Br_2 (6.7 g, 42 mmol) in 15 ml $CHCl_3$ was slowly added. Solution was stirred at room temperature 1 h and refluxed overnight. It was cooled down and added water 40 ml with $Na_2S_2O_3$ 4.0 g. Solvent was removed and purified with column chromatography on silica gel with hexane as eluent to afford a white solid (5.5 g, 85 %). 1H NMR (400 MHz, $CDCl_3$) δ 4.00 (t, J = 6.4 Hz, 2H), 1.96 – 1.85 (m, 2H), 1.64 – 1.49 (m, 2H), 1.47 – 1.34 (m, 4H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.27, 110.23, 73.66, 31.65, 29.94, 25.52, 22.62, 14.06.



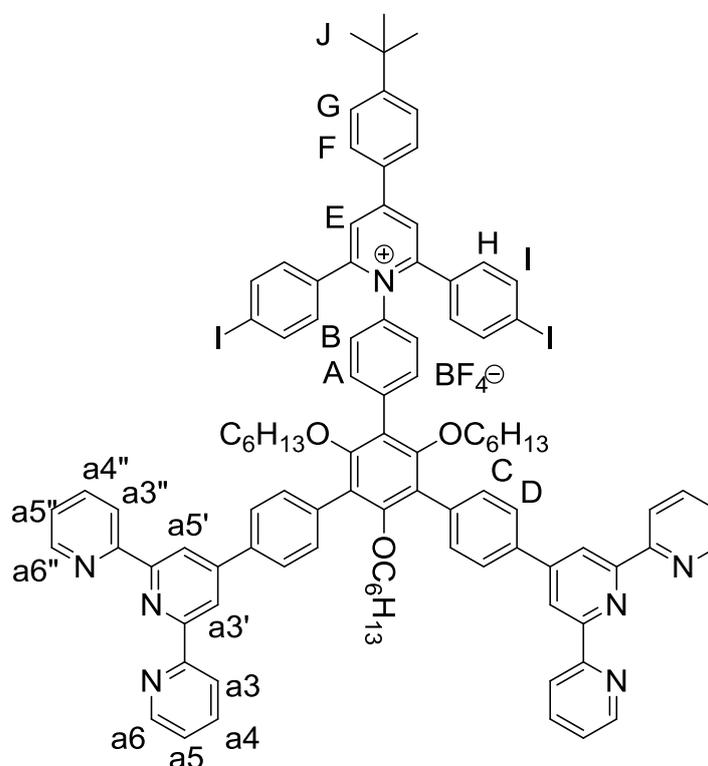
Compound **13**. To a flask containing a degassed solution of compound **12** (6.0 g, 9.8 mmol), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (700 mg, 3.2 mmol) in toluene (60 mL), an aqueous solution of 2 M K_2CO_3 (25 mL) was added. $Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol) was then added under N_2 . The mixture was stirred at 75 °C overnight and then cooled to room temperature. The aqueous phase was extracted with CH_2Cl_2 . The combined organic phase was washed with brine and dried with anhydrous Na_2SO_4 . The crude was purified by column chromatography on silica gel with DCM: hexane (1:2) as eluent to afford the product as a white solid (1.1 g, 55 %). 1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, $J = 8.5$ Hz, 2H, Ph- H^A), 6.75 (d, $J = 8.4$ Hz, 2H, Ph- H^B), 4.05 (t, $J = 6.6$ Hz, 2H), 3.48 (t, $J = 6.5$ Hz, 4H), 1.97 – 1.86 (m, 2H), 1.62 – 1.52 (m, 2H), 1.50 – 1.38 (m, 8H), 1.32 – 1.10 (m, 12H), 0.97 – 0.82 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.82, 153.37, 145.43, 131.63, 128.08, 123.23, 114.63, 109.90, 73.48, 73.15, 31.70, 31.45, 30.02, 29.77, 25.59, 25.42, 22.64, 22.55, 14.09, 14.02. ESI-MS (m/z): Calcd. for $[C_{30}H_{45}Br_2NO_3+H]^+$: 626.2. Found: 626.2.



Compound **14**. To a solution of compound **13** (700 mg, 1.1 mmol), Pd(PPh₃)₂Cl₂ (80 mg, 114 μmol) and 4'-(4-Boronatophenyl)[2,2':6',2'']terpyridine (1.58 g, 4.5 mmol) in toluene (50 mL) and tert-butyl alcohol (8 ml) under N₂, aqueous 1 M K₂CO₃ (20 mL) was added. After refluxing for 48 h, the mixture was cooled to room temperature. The aqueous layer was extracted with CHCl₃ and the combined organic phase was washed with brine and dried over Na₂SO₄. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel with chloroform: ethanol (100:2) as eluent to afford a white solid in 82 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (s, 4H, tpy-*H*^{3',5'}), 8.76 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 4H, tpy-*H*^{6,6''}), 8.71 (dt, *J* = 8.0, 1.1 Hz, 4H, tpy-*H*^{3,3''}), 8.02 – 7.95 (d, *J* = 4.4 Hz, 4H, Ph-*H*^D), 7.90 (ddd, *J* = 7.9, 7.5, 1.8 Hz, 4H, tpy-*H*^{4,4''}), 7.74 – 7.69 (d, *J* = 4.4 Hz, 4H, Ph-*H*^C), 7.40 – 7.34 (m, 6H, tpy-*H*^{5,5''} and Ph-*H*^A), 6.80 – 6.74 (d, *J* = 4.4 Hz, 2H, Ph-*H*^B), 3.28 (q, *J* = 6.6 Hz, 6H), 1.16 – 1.00 (m, 12H), 1.00 – 0.83 (m, 12H), 0.75 (t, *J* = 7.2 Hz, 6H), 0.66 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.35, 155.87, 155.66, 154.71, 150.41, 149.10, 145.07, 136.90, 136.65, 136.12, 132.15, 132.05, 131.62, 128.55, 128.43, 126.50, 123.78, 121.39, 118.89, 114.59, 73.57, 73.26, 31.42, 31.38, 30.90, 29.68, 25.35, 25.34,

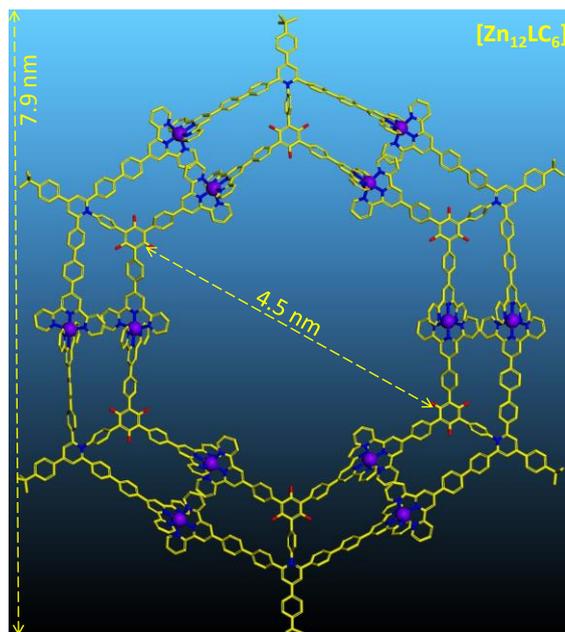
22.53, 22.50, 13.97,13.91. ESI-MS (m/z): Calcd. for $[C_{72}H_{73}N_7O_3+H]^+$: 1084.6.

Found: 1084.6.



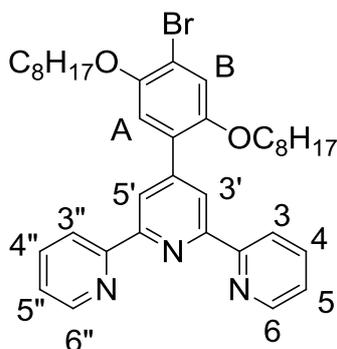
Compound **15**. Anhydrous sodium acetate (164 mg, 2.0 mmol) and the pyrylium salt **1** (352 mg, 0.5 mmol) were added to a solution of **14** (541 mg, 0.5 mmol) in dry ethanol (15 mL). The mixture was reflux for 8 h and then cooled to room temperature. The precipitate was filtered and washed with water and diethyl ether to give the product as a white solid (708 mg, 80%). 1H NMR (400 MHz, DMSO- d_6) δ 8.79 (s, 4H, tpy- $H^{3',5'}$), 8.78 – 8.75 (m, 4H, tpy- $H^{6,6''}$), 8.70 (d, $J = 8.0$ Hz, 4H, tpy- $H^{3,3''}$), 8.61 (s, 2H, Ph- H^E), 8.28 (d, $J = 8.7$ Hz, 2H, Ph- H^F), 8.10 – 8.01 (m, 4H, tpy- $H^{4,4''}$), 7.97 (d, $J = 8.4$ Hz, 4H, Ph- H^D), 7.75 (d, $J = 8.4$ Hz, 4H, Ph- H^I), 7.70 – 7.64 (m, 4H, Ph- H^G and Ph- H^A), 7.62 (d, $J = 8.3$ Hz, 4H, Ph- H^C), 7.57 – 7.50 (m, 4H, tpy- $H^{5,5''}$), 7.44 (d, $J = 8.6$ Hz, 2H, Ph- H^B), 7.30 (d, $J = 8.4$ Hz, 4H, Ph- H^H), 3.33 (m, 2H), 2.90 (m, 4H), 1.36 (s, 9H, tert-butyl- H^J), 1.04 – 0.94 (m, 8H), 0.94 – 0.80 (m, 8H), 0.80 – 0.70 (m, 8H), 0.60 (t,

of eluent was increased from chloroform/acetone 100/0 to 0/100, then a mixture of acetone/acetonitrile, 70/30 to 0/100 and finally a mixture of acetonitrile/water/ NH_4BF_4 to afford ligand **LC** as a white solid (66 % yield). ^1H NMR (400 MHz, CDCl_3) δ 8.76 (s, 4H, tpy- $H^{a3',5'}$), 8.75 (s, 4H, tpy- $H^{b3',5'}$), 8.69 – 8.63 (m, 16H, tpy- $H^{a3,3''}$, tpy- $H^{a6,6''}$, tpy- $H^{b3,3''}$ and tpy- $H^{b6,6''}$), 8.23 (s, 2H, Ph- H^E), 8.00 – 7.95 (m, 6H, Ph- H^D and Ph- H^F), 7.93 (d, $J = 8.4$ Hz, 4H, Ph- H^K), 7.90 – 7.83 (m, 8H, tpy- $H^{a4,4''}$ and tpy- $H^{b4,4''}$), 7.79 (d, $J = 8.4$ Hz, 4H, Ph- H^I), 7.74 (d, $J = 8.6$ Hz, 2H, Ph- H^A), 7.69 – 7.63 (m, 8H, Ph- H^C and Ph- H^H), 7.62 (d, $J = 5.5$ Hz, 2H, Ph- H^G), 7.60 – 7.54 (m, 6H, Ph- H^B and Ph- H^J), 7.35 – 7.29 (m, 8H, tpy- $H^{a5,5''}$ and tpy- $H^{b5,5''}$), 3.23 (t, $J = 6.5$ Hz, 2H), 2.95 (t, $J = 6.0$ Hz, 4H), 1.41 (s, 9H, tert-butyl- H^L), 1.03 (m, 6H), 0.94 – 0.78 (m, 10H), 0.78 – 0.70 (m, 4H), 0.68 – 0.59 (m, 7H), 0.55 (t, $J = 7.6$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.87, 156.65, 156.36, 156.24, 156.08, 156.05, 155.93, 155.81, 155.18, 150.11, 149.34, 149.07, 149.06, 141.84, 139.73, 138.28, 137.76, 137.09, 137.02, 136.84, 136.80, 135.46, 132.52, 131.84, 131.49, 131.40, 130.69, 128.40, 128.16, 127.97, 127.95, 127.42, 126.86, 126.63, 126.19, 126.16, 123.80, 123.71, 123.69, 121.30, 121.26, 118.86, 118.71, 73.68, 73.32, 35.15, 31.40, 31.32, 31.11, 29.74, 29.53, 25.40, 25.23, 22.59, 22.44, 13.95, 13.86. MALDI-TOF MS (m/z): Calcd. for $[\text{C}_{105}\text{H}_{82}\text{N}_{13}\text{O}]^+$ 2045.0. Found: 2045.1.



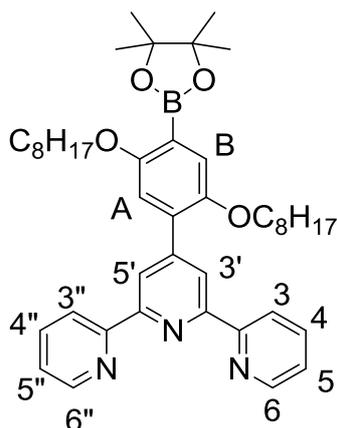
Complex [**Zn₁₂LC₆**]: To a solution of ligand **LC** (6.2 mg, 2.9 μmol) in CHCl_3 (1 mL), a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.7 mg, 5.8 μmol) in MeOH (3 mL) was added. The mixture was stirred at 50 $^\circ\text{C}$ for 8 h and then cooled to room temperature. Upon addition of NH_4PF_6 (150 mg), a precipitate was formed and washed with water to give a white product (yield: 91%). ^1H NMR (400 MHz, CD_3CN) δ 8.98 (m, 8H, tpy- $H^{\text{a}3,5'}$ and tpy- $H^{\text{b}3,5'}$), 8.73 – 8.49 (m, 10H, tpy- $H^{\text{a}3,3''}$, tpy- $H^{\text{b}3,3''}$ and Ph- H^{E}), 8.33 (m, 4H, Ph- H^{D}), 8.27 (d, $J = 7.0$ Hz, 4H, Ph- H^{K}), 8.21 (d, $J = 7.6$ Hz, 2H, Ph- H^{F}), 8.15 (d, $J = 7.1$ Hz, 4H, Ph- H^{C}), 8.02 (d, $J = 7.5$ Hz, 4H, Ph- H^{I}), 7.76 (m, 28H, tpy- $H^{\text{a}4,4''}$, tpy- $H^{\text{b}4,4''}$, tpy- $H^{\text{a}6,6''}$, tpy- $H^{\text{b}6,6''}$, Ph- H^{H} , Ph- H^{G} , Ph- H^{A} and Ph- H^{J}), 7.59 (m, 2H, Ph- H^{B}), 7.12 – 6.92 (m, 8H, tpy- $H^{\text{a}5,5''}$ and tpy- $H^{\text{b}5,5''}$), 3.35 (s, 2H), 3.12 (s, 4H), 1.47 (s, 9H, tert-butyl- H^{L}), 1.10 (m, 6H), 0.95 (m, 10H), 0.71– 0.50 (m, 17H). ^{13}C NMR (100 MHz, CD_3CN) δ 157.06, 156.58, 155.72, 149.62, 147.84, 147.70, 141.23, 140.99, 140.67, 136.13, 134.80, 133.20, 132.30, 130.83, 128.99, 128.57, 127.94, 127.47, 127.29, 127.05, 126.88, 123.29, 123.10, 121.58, 121.33, 73.71, 73.62, 34.94, 31.23,

31.08, 30.29, 29.68, 29.30, 25.43, 25.10, 22.79, 22.35, 13.82, 13.40. ESI-MS (m/z): 1438.1 [M-11PF₆⁻]¹¹⁺ (calcd m/z : 1438.1), 1306.2 [M-12PF₆⁻]¹²⁺ (calcd m/z : 1306.2), 1194.5 [M-13PF₆⁻]¹³⁺ (calcd m/z : 1194.5), 1098.8 [M-14PF₆⁻]¹⁴⁺ (calcd m/z : 1098.8), 1015.9 [M-15PF₆⁻]¹⁵⁺ (calcd m/z : 1015.9), 943.4 [M-16PF₆⁻]¹⁶⁺ (calcd m/z : 943.4), 879.3 [M-17PF₆⁻]¹⁷⁺ (calcd m/z : 879.3), 822.5 [M-18PF₆⁻]¹⁸⁺ (calcd m/z : 822.5), 771.5 [M-19PF₆⁻]¹⁹⁺ (calcd m/z : 771.5), 725.7 [M-20PF₆⁻]²⁰⁺ (calcd m/z : 725.7), 684.3 [M-21PF₆⁻]²¹⁺ (calcd m/z : 684.3), 646.6 [M-22PF₆⁻]²²⁺ (calcd m/z : 646.6), 612.1[M-23PF₆⁻]²³⁺ (calcd m/z : 612.1) and 580.6 [M-24PF₆⁻]²⁴⁺ (calcd m/z : 580.6)

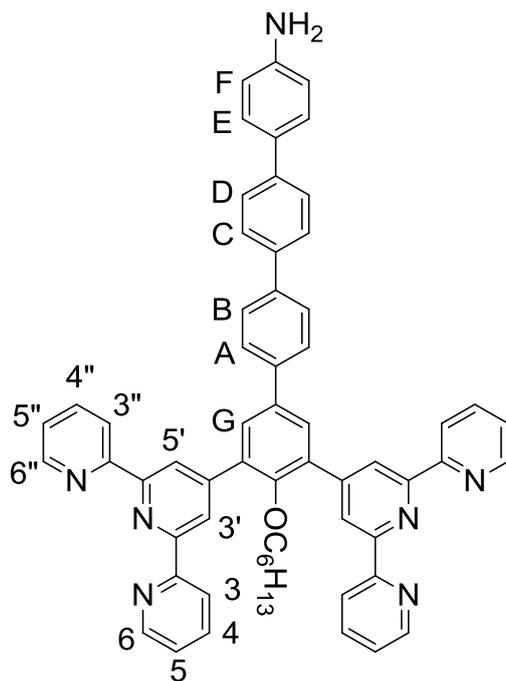


Compound **17**. To a flask containing a degassed solution of 1,4-dibromo-2,5-bis(octyloxy)benzene⁸ (4.4 g, 9.0 mmol), 4'-(4-Boronatophenyl)[2,2':6',2'']terpyridine (1.08 g, 3.0 mmol) in toluene (60 mL), an aqueous solution of 2 M K₂CO₃ (25 mL) was added. Pd(PPh₃)₂Cl₂ (105 mg, 0.15 mmol) was then added under N₂. The mixture was stirred at 80 °C for 20 h and then cooled to room temperature. The aqueous phase was extracted with CHCl₃. The combined organic phase was washed with brine and dried with anhydrous Na₂SO₄. After removal of volatile under vacuum, the crude was purified by column chromatography on silica gel with chloroform: ethanol (200:1) as eluent to afford the product as a white solid (1.08 g, 56%). ¹H NMR (400 MHz, CDCl₃) δ 8.72 (ddd, J =

4.8, 1.8, 0.9 Hz, 2H, tpy- $H^{6,6''}$), 8.71 – 8.67 (m, 4H, tpy- $H^{3,3''}$ and tpy- $H^{3',5'}$), 7.92 – 7.86 (m, 2H, tpy- $H^{4,4''}$), 7.35 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 2H, tpy- $H^{5,5''}$), 7.23 (s, 1H, Ph- H^A), 7.13 (d, $J = 4.7$ Hz, 1H, Ph- H^B), 4.07 (t, $J = 6.5$ Hz, 2H), 3.95 (t, $J = 6.3$ Hz, 2H), 1.91 – 1.80 (m, 2H), 1.74 – 1.65 (m, 2H), 1.57 – 1.48 (m, 2H), 1.43 – 1.27 (m, 10H), 1.25 – 1.05 (m, 8H), 0.91 (t, $J = 7.2$ Hz, 3H), 0.82 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.37, 155.21, 150.75, 150.00, 149.07, 147.73, 136.82, 128.49, 123.66, 121.66, 121.28, 118.23, 116.03, 113.08, 70.55, 69.70, 31.82, 31.76, 29.34, 29.33, 29.24, 29.21, 29.05, 26.10, 26.02, 22.67, 22.58, 14.11, 14.06. ESI-MS (m/z): Calcd. for $[\text{C}_{37}\text{H}_{46}\text{BrN}_3\text{O}_2+\text{H}]^+$: 644.3. Found: 644.3.

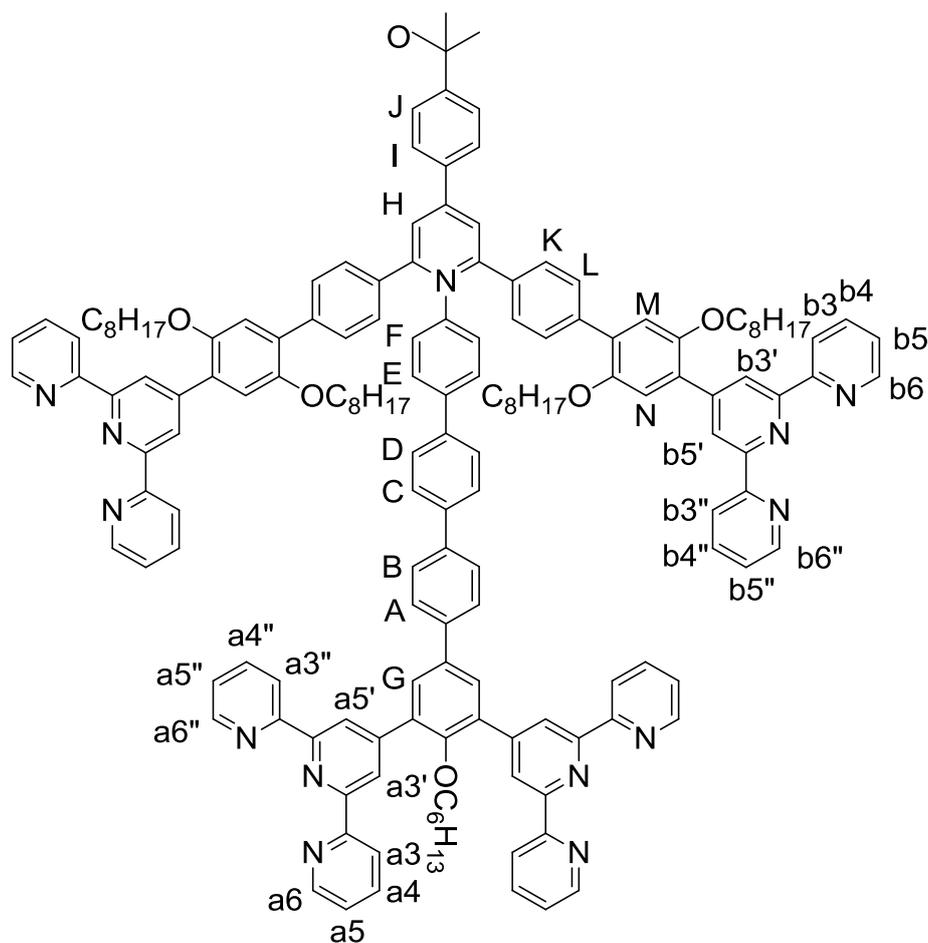


Compound **18**. A mixture of compound **17** (1.28 g, 2.0 mmol), Bis-(pinacolato)diboron (508 mg, 2.0 mmol), $\text{Pd}(\text{dppf})\text{Cl}_2$ (65 mg, 0.08 mmol) and potassium acetate (980 mg, 10 mmol) was degassed three times. After that, 30 ml anhydrous DMSO was added and then the mixture was stirred at 80 $^{\circ}\text{C}$ for 16 h and then cooled to room temperature. The aqueous phase was extracted with CHCl_3 . The combined organic phase was washed with water. After removal of volatile under vacuum, the crude was directly used for next step.



Compound **20**. To a solution of compound **19**⁹ (668 mg, 1.8 mmol), Pd(PPh₃)₂Cl₂ (100 mg, 143 μmol) and compound **6** (1.08 g, 1.5 mmol) in toluene (40 mL) under N₂, aqueous 1.5 M K₂CO₃ (20 mL) was added. It was heated at 75 °C overnight. The mixture was cooled to room temperature. The aqueous layer was extracted with CHCl₃, and the combined organic phase was washed with brine and dried over Na₂SO₄. After removal of solvent under vacuum, the residue was purified by column chromatography on silica gel with chloroform: ethanol (100:3) as eluent to afford a white solid in 75 % yield. ¹H NMR (400 MHz, CDCl₃) δ 8.90 (s, 4H, tpy-*H*^{3',5'}), 8.79 (d, *J* = 4.0 Hz, 4H, tpy-*H*^{6,6''}), 8.74 (d, *J* = 8.0 Hz, 4H, tpy-*H*^{3,3''}), 7.97 – 7.88 (m, 6H, tpy-*H*^{4,4''} and Ph-*H*^G), 7.83 (d, *J* = 8.4 Hz, 2H, Ph-*H*^A), 7.76 (d, *J* = 8.5 Hz, 2H, Ph-*H*^B), 7.72 (d, *J* = 8.5 Hz, 2H, Ph-*H*^C), 7.66 (d, *J* = 8.5 Hz, 2H, Ph-*H*^D), 7.50 (d, *J* = 8.5 Hz, 2H, Ph-*H*^E), 7.42 – 7.37 (m, 4H, tpy-*H*^{5,5''}), 6.81 (d, *J* = 8.4 Hz, 2H, Ph-*H*^F), 3.45 (t, *J* = 6.1 Hz, 2H), 1.25 (m, 2H), 0.96 (m, 2H), 0.78 (m, 4H), 0.53 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.28, 155.43, 154.28, 149.16, 148.59, 145.92, 140.20,

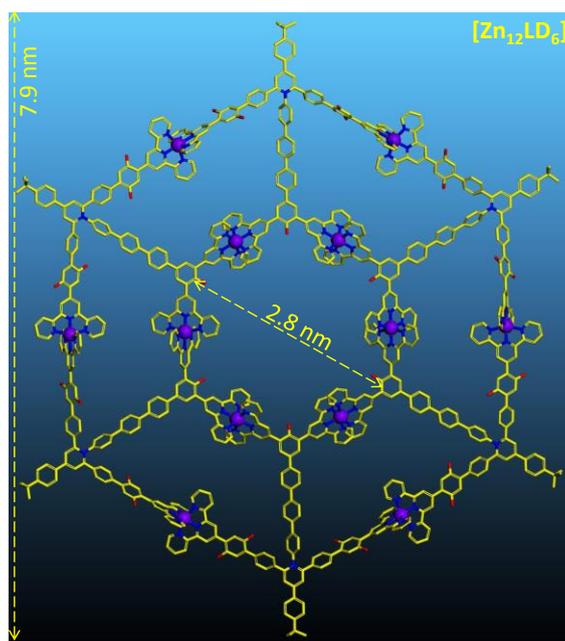
Ph- H^I), 7.83 (d, $J = 8.6$ Hz, 2H, Ph- H^A), 7.71 – 7.77 (m, 4H, Ph- H^B and Ph- H^C), 7.70 – 7.66 (m, 4H, tpy- H^L), 7.64 – 7.60 (m, 4H, Ph- H^J and Ph- H^D), 7.52 (d, $J = 8.8$ Hz, 2H, Ph- H^F), 7.43 – 7.36 (m, 6H, tpy- $H^{5,5''}$ and tpy- H^E), 7.28 – 7.23 (m, 4H, tpy- H^K), 3.45 (t, $J = 6.0$ Hz, 2H), 1.49 (s, 9H, tert-butyl- H^M), 1.28 – 1.18 (m, 2H), 0.95 (s, 2H), 0.78 (m, 4H), 0.53 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, DMSO- d_6) δ 157.87, 156.57, 156.34, 155.83, 155.52, 154.42, 149.22, 148.48, 142.36, 140.98, 139.44, 139.19, 139.07, 137.82, 136.80, 134.44, 132.36, 131.29, 131.23, 129.80, 129.75, 128.87, 128.31, 127.74, 127.67, 127.47, 127.44, 126.92, 126.46, 126.34, 126.08, 123.75, 121.76, 121.30, 99.99, 97.38, 74.35, 35.17, 31.36, 31.08, 29.79, 25.47, 22.16, 13.79. ESI-MS (m/z): Calcd. for $[\text{C}_{87}\text{H}_{70}\text{I}_2\text{N}_7\text{O}]^+$: 1482.4. Found: 1482.2.



Ligand **LD**: To a solution of compound **21** (340 mg, 216 μmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (15 mg,

21.6 μmol) and compound **18** (599 mg, 867 μmol) in DMSO (40 mL) under N_2 , aqueous 2 M K_2CO_3 (10 mL) was added. The mixture was stirred at 80 $^\circ\text{C}$ for 2 d and then cooled to room temperature. The mixture was extracted with CHCl_3 , and the combined organic phase was washed with brine and dried over Na_2SO_4 . After removal of solvent under vacuum, the residue was purified by column chromatography on Al_2O_3 . The polarity of eluent was increased from chloroform/acetone 100/0 to 0/100, then a mixture of acetone/acetonitrile, 70/30 to 0/100 and finally a mixture of acetonitrile/water/ NH_4BF_4 to afford LD as a white solid (61 % yield). ^1H NMR (400 MHz, CDCl_3) δ 8.89 – 8.86 (s, 4H, tpy- $H^{\text{a}3',5'}$), 8.76 (ddd, $J = 4.8, 1.8, 0.9$ Hz, 4H, tpy- $H^{\text{a}6,6''}$), 8.72 (dd, $J = 5.5, 2.3$ Hz, 12H, tpy- $H^{\text{a}3,3''}$, tpy- $H^{\text{b}3',5'}$ and tpy- $H^{\text{b}6,6''}$), 8.68 (d, $J = 8.0$ Hz, 4H, tpy- $H^{\text{b}3,3''}$), 8.29 (s, 2H, Ph- H^{H}), 8.01 (d, $J = 8.8$ Hz, 2H, Ph- H^{I}), 7.94 – 7.85 (m, 14H, tpy- $H^{\text{a}4,4''}$, tpy- $H^{\text{b}4,4''}$ Ph- H^{F} and Ph- H^{G}), 7.79 (d, $J = 8.4$ Hz, 2H, Ph- H^{A}), 7.76 (d, $J = 8.6$ Hz, 4H, Ph- H^{L}), 7.71 (d, $J = 8.1$ Hz, 4H, Ph- H^{B} and Ph- H^{C}), 7.68 – 7.63 (m, 6H, Ph- H^{K} and Ph- H^{J}), 7.59 (d, $J = 8.6$ Hz, 2H, Ph- H^{D}), 7.56 – 7.52 (m, 2H, Ph- H^{E}), 7.39 – 7.31 (m, 8H, tpy- $H^{\text{a}5,5''}$ and tpy- $H^{\text{b}5,5''}$), 7.17 (s, 2H, Ph- H^{N}), 6.97 (s, 2H, Ph- H^{M}), 3.98 (t, $J = 6.2$ Hz, 4H), 3.90 (t, $J = 6.7$ Hz, 4H), 3.43 (t, $J = 6.0$ Hz, 2H), 1.69 (m, 4H), 1.59 (m, 4H), 1.42 (s, 9H, tert-butyl- H^{O}), 1.35 (m, 4H), 1.31 – 1.20 (m, 22H), 1.20 – 1.12 (m, 8H), 1.07 (m, 8H), 0.97 (m, 2H), 0.86 (t, $J = 6.9$ Hz, 6H), 0.82 – 0.75 (m, 10H), 0.52 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.98, 156.45, 156.41, 156.30, 155.46, 155.15, 154.36, 150.79, 150.26, 149.17, 149.06, 148.51, 148.02, 141.94, 140.59, 140.32, 139.30, 139.20, 138.50, 137.71, 136.88, 136.84, 134.38, 131.70, 131.37, 130.44, 129.75, 129.74, 129.60, 129.53,

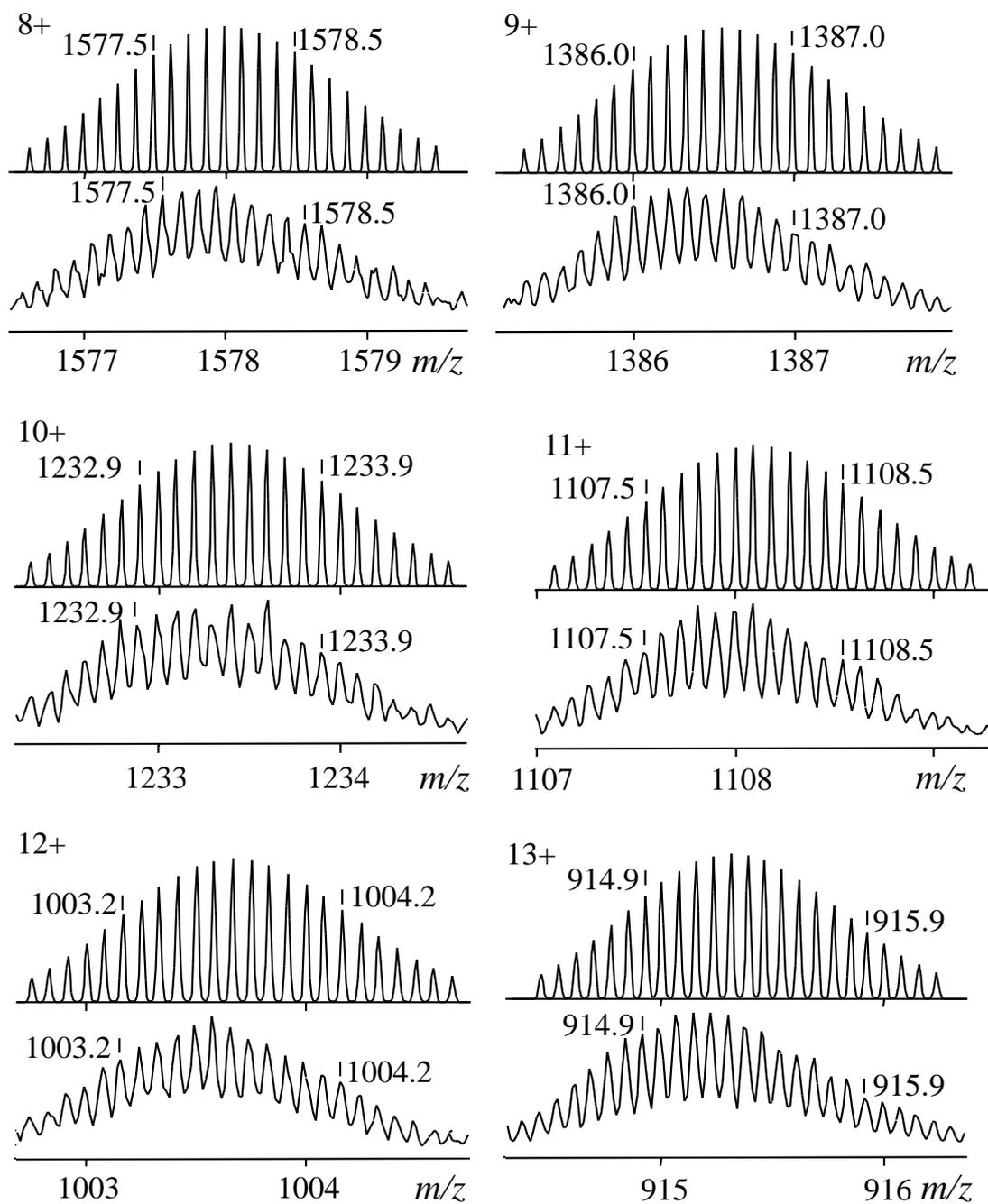
129.10, 128.31, 127.68, 127.51, 127.42, 127.35, 127.08, 126.85, 125.81, 123.74, 123.60, 121.84, 121.79, 121.30, 115.98, 115.70, 100.00, 74.35, 69.79, 69.71, 35.18, 31.83, 31.76, 31.35, 31.12, 29.79, 29.38, 29.36, 29.28, 29.20, 29.18, 29.05, 26.17, 25.90, 25.46, 22.66, 22.58, 22.15, 14.13, 14.06, 13.79. MALDI-TOF MS (m/z): Calcd. for $[C_{105}H_{82}N_{13}O]^+$ 2357.3. Found: 2357.4.



Complex $[Zn_{12}LD_6]$: To a solution of ligand **LD** (6.1 mg, 2.5 μ mol) in $CHCl_3$ (1 mL), a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (1.5 mg, 5.0 μ mol) in MeOH (3 mL) was added. The mixture was stirred at 50 $^{\circ}C$ for 10 h and then cooled to room temperature. Upon addition of NH_4PF_6 (130 mg), a precipitate was formed and washed with water to give a white product (yield: 88%). 1H NMR (400 MHz, CD_3CN) δ 9.35 (s, 4H, tpy- $H^{a3',5'}$), 9.05 (s, 4H, tpy- $H^{b3',5'}$), 8.84 (d, $J = 8.2$ Hz, 4H, tpy- $H^{a3,3''}$), 8.67 (d, $J = 7.8$ Hz, 4H, tpy- $H^{b3,3''}$), 8.61 (s, 2H, Ph- H^H), 8.52 (s, 2H, Ph- H^G), 8.21 (m, 12H, tpy- $H^{a4,4''}$, tpy- $H^{b4,4''}$, Ph- H^I and Ph- H^F), 8.02 (d, $J = 7.8$ Hz, 2H, Ph- H^J), 7.96 (m, 6H, tpy- $H^{a6,6''}$ and Ph- H^A), 7.90 (d, $J = 5.1$ Hz, 4H, tpy- $H^{b6,6''}$), 7.82 (d, $J = 6.7$ Hz, 8H, Ph- H^L , Ph- H^E

and Ph- H^B), 7.73 (d, $J = 8.3$ Hz, 2H, Ph- H^C), 7.65 (d, $J = 7.5$ Hz, 4H, Ph- H^K), 7.55 (m, 4H, Ph- H^D and Ph- H^N), 7.51 – 7.41 (m, 8H, tpy- $H^{a5,5''}$ and tpy- $H^{b5,5''}$), 7.30 (s, 2H, Ph- H^M), 4.26 (t, $J = 6.0$ Hz, 4H), 4.12 (t, $J = 6.3$ Hz, 4H), 3.74 (s, 2H), 1.89 (m, 4H), 1.65 (m, 4H), 1.49 (s, 15H), 1.30 (m, 30H), 1.08 – 0.95 (m, 20H), 0.90 (t, $J = 6.5$ Hz, 6H), 0.62 (t, $J = 6.8$ Hz, 6H), 0.28 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR (100 MHz, CD_3CN) δ 157.00, 156.60, 154.76, 154.05, 153.52, 150.84, 150.59, 149.45, 149.00, 147.98, 141.47, 141.32, 140.08, 139.79, 139.65, 138.42, 138.26, 137.65, 132.88, 132.76, 132.55, 132.22, 130.98, 129.68, 129.62, 129.36, 129.29, 128.56, 127.89, 127.59, 127.52, 127.05, 125.90, 124.52, 124.17, 123.26, 123.07, 116.06, 115.69, 69.60, 69.57, 34.95, 31.67, 31.46, 31.26, 30.31, 29.32, 29.15, 29.13, 28.96, 28.92, 26.40, 26.11, 25.79, 22.47, 22.20, 21.97, 13.51, 13.24, 12.88. ESI-MS (m/z): 1608.5 $[\text{M}-11\text{PF}_6]^{11+}$ (calcd m/z : 1608.5), 1462.4 $[\text{M}-12\text{PF}_6]^{12+}$ (calcd m/z : 1462.4), 1338.8 $[\text{M}-13\text{PF}_6]^{13+}$ (calcd m/z : 1338.8), 1232.8 $[\text{M}-14\text{PF}_6]^{14+}$ (calcd m/z : 1232.8), 1140.9 $[\text{M}-15\text{PF}_6]^{15+}$ (calcd m/z : 1140.9), 1060.5 $[\text{M}-16\text{PF}_6]^{16+}$ (calcd m/z : 1060.5), 989.7 $[\text{M}-17\text{PF}_6]^{17+}$ (calcd m/z : 989.7), 926.6 $[\text{M}-18\text{PF}_6]^{18+}$ (calcd m/z : 926.6), 870.2 $[\text{M}-19\text{PF}_6]^{19+}$ (calcd m/z : 870.2), 819.5 $[\text{M}-20\text{PF}_6]^{20+}$ (calcd m/z : 819.5) and 773.5 $[\text{M}-21\text{PF}_6]^{21+}$ (calcd m/z : 773.5)

4. ESI mass spectra data of complex $[\text{Zn}_{12}\text{LA}_6]$, $[\text{Zn}_{12}\text{LB}_6]$, $[\text{Zn}_{12}\text{LC}_6]$ and $[\text{Zn}_{12}\text{LD}_6]$ (PF_6^- as counterion).



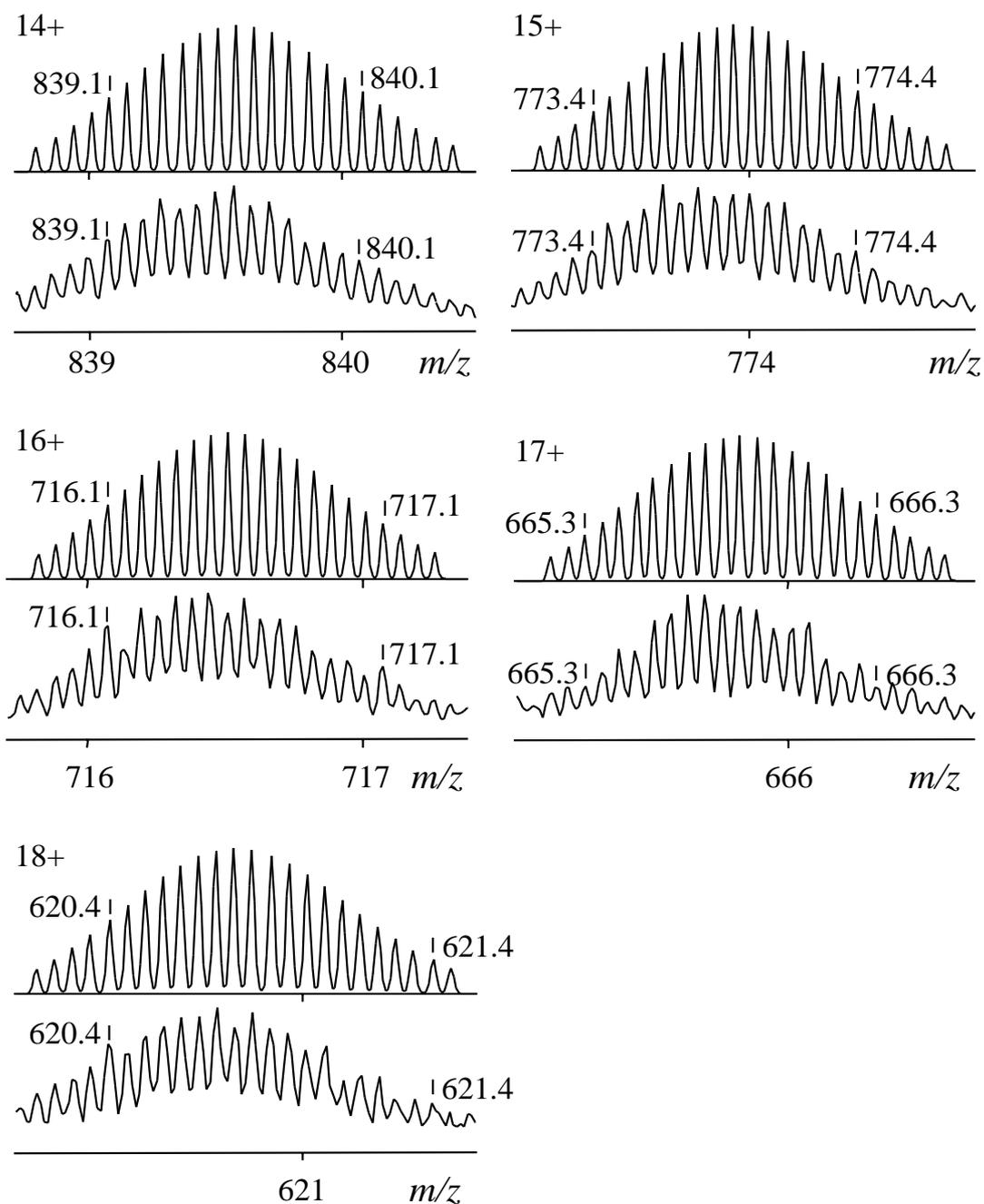
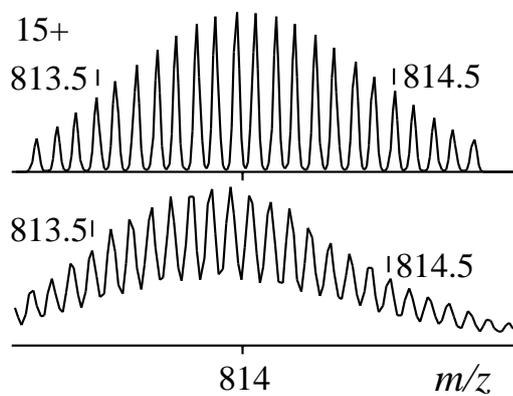
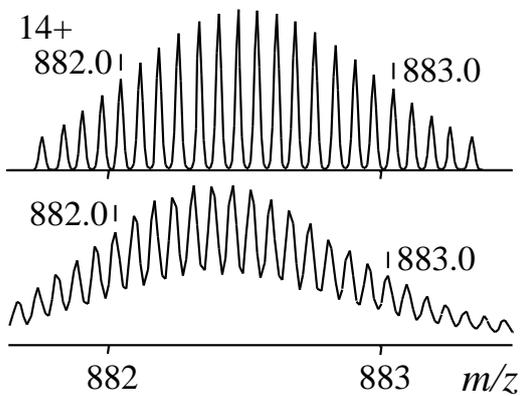
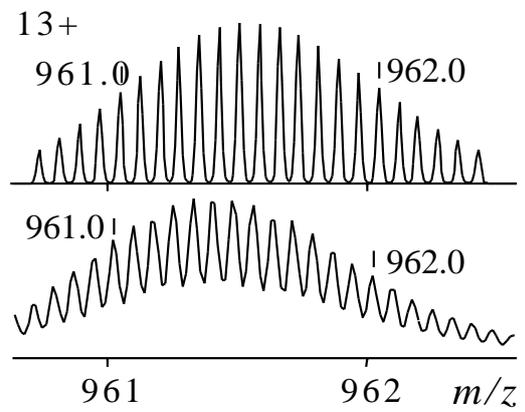
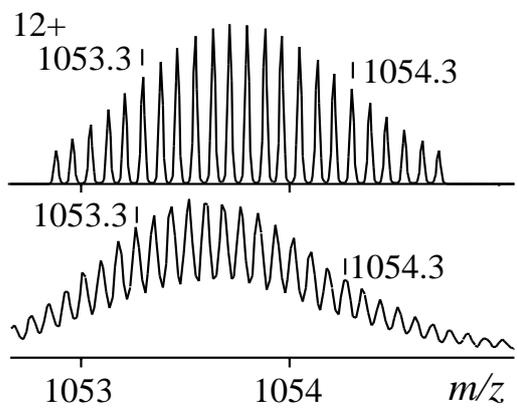
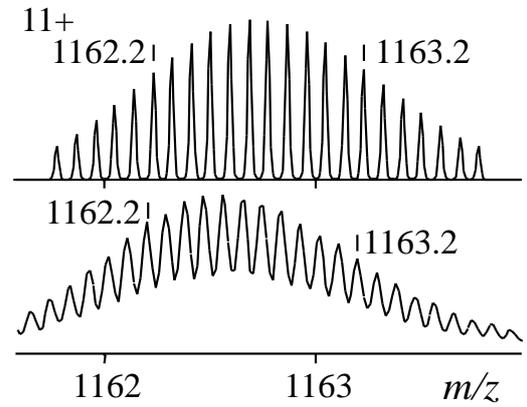
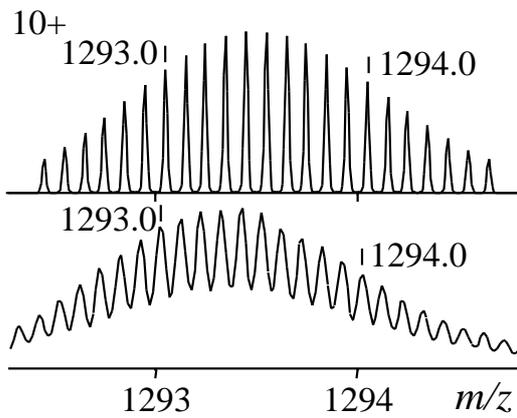
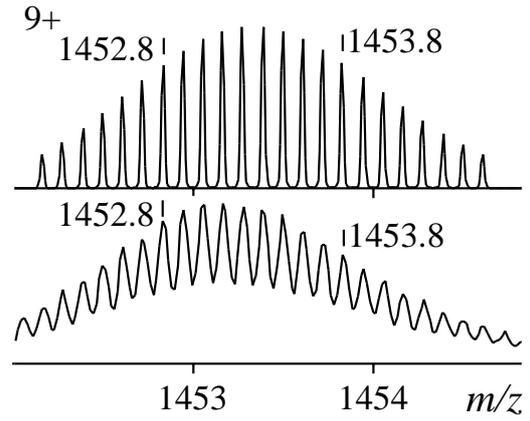
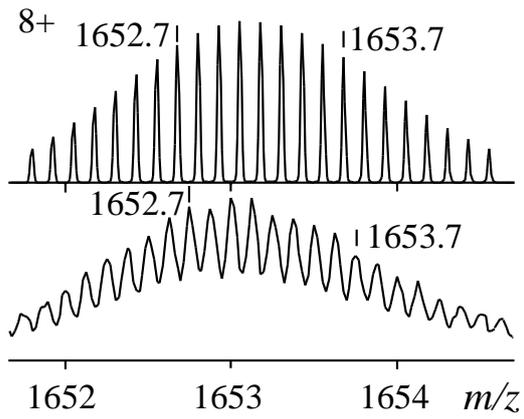


Figure S1. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from $[\text{Zn}_{12}\text{LA}_6]$ (PF_6^- as counterion).



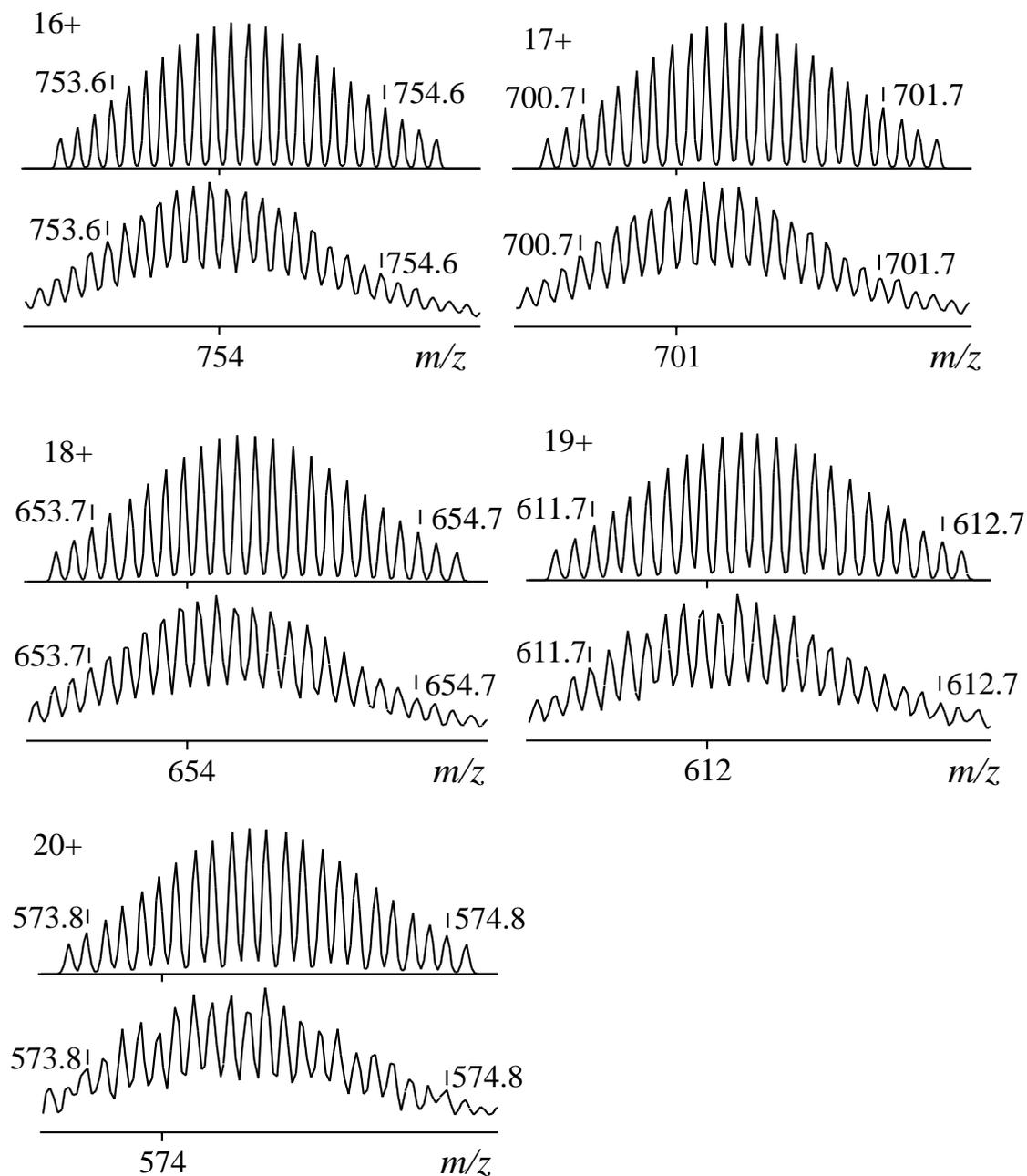
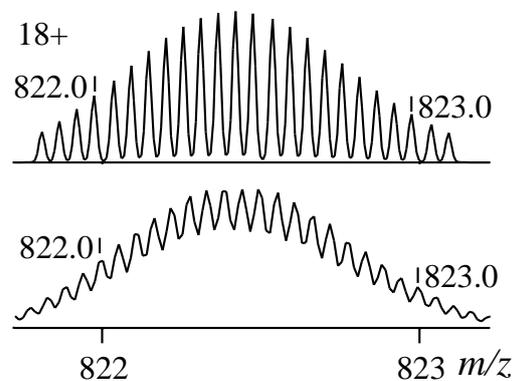
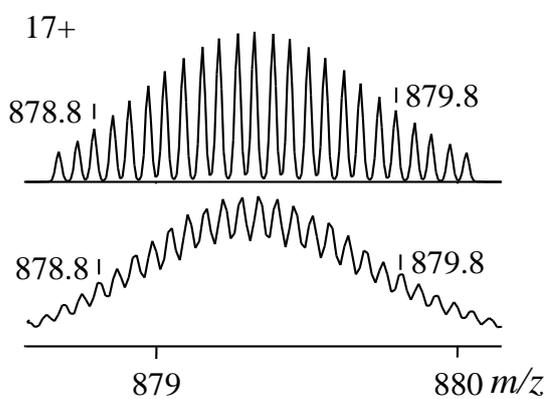
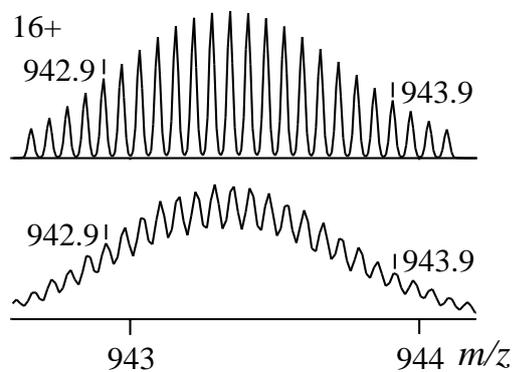
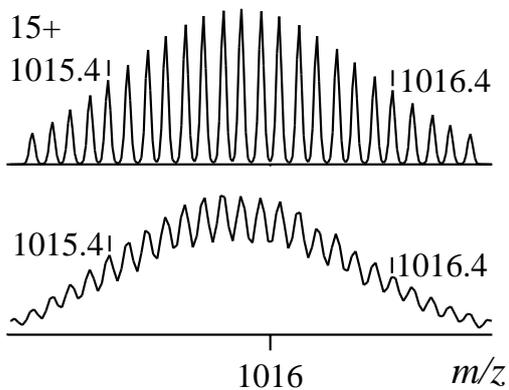
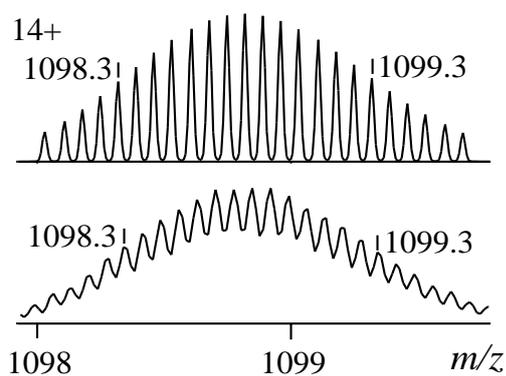
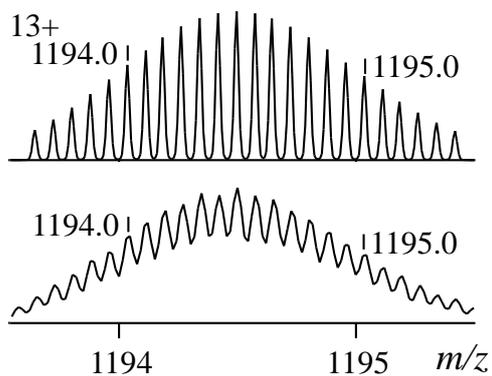
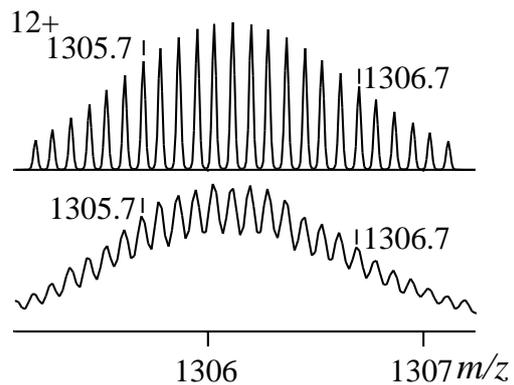
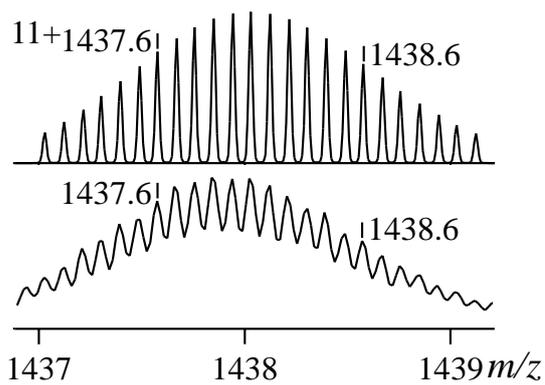


Figure S2. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from $[\text{Zn}_{12}\text{LB}_6]$ (PF_6^- as counterion).



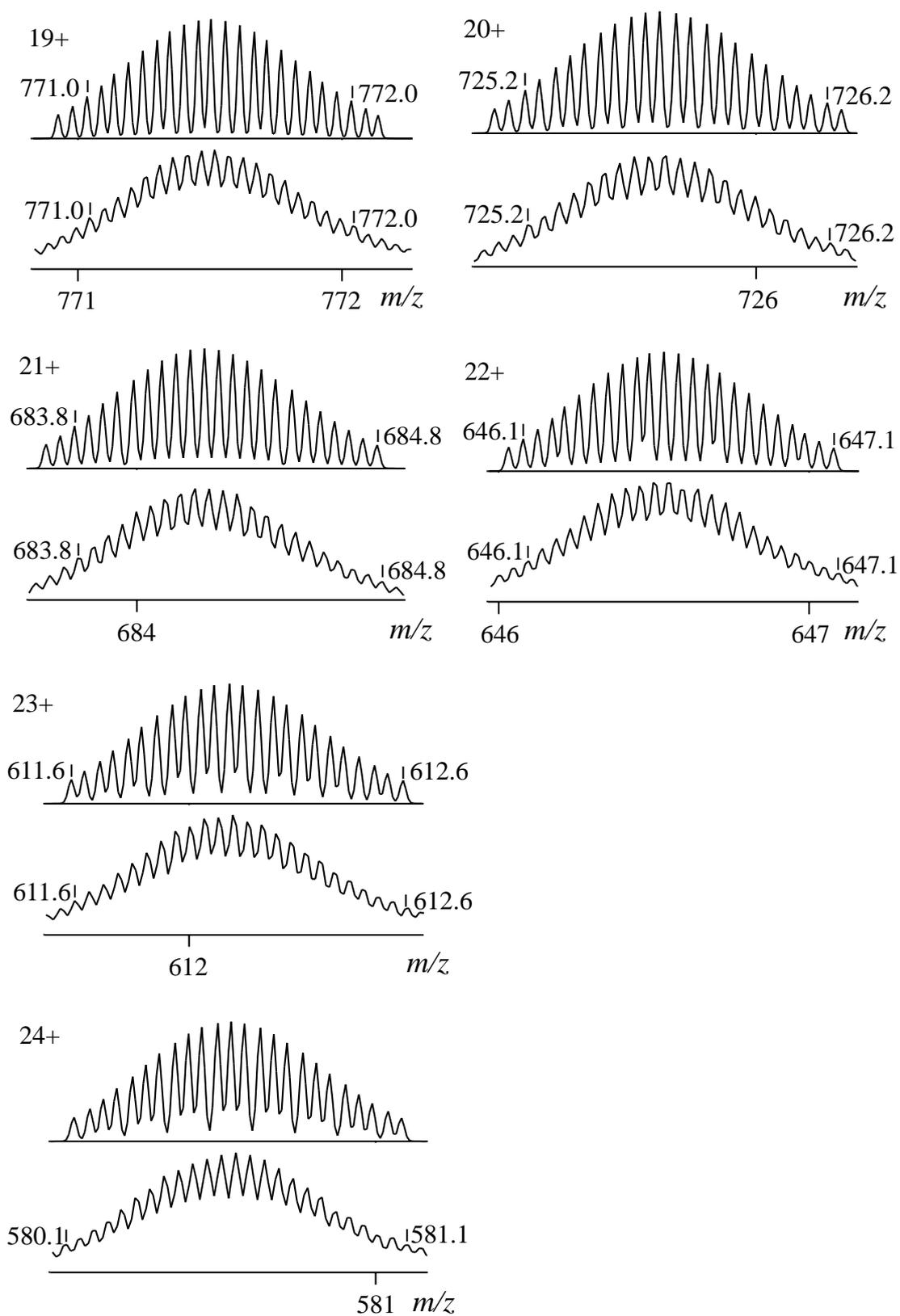
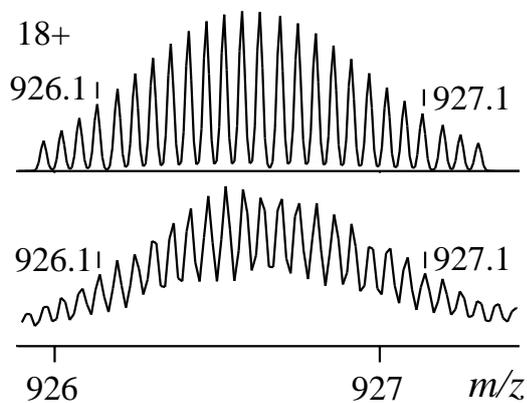
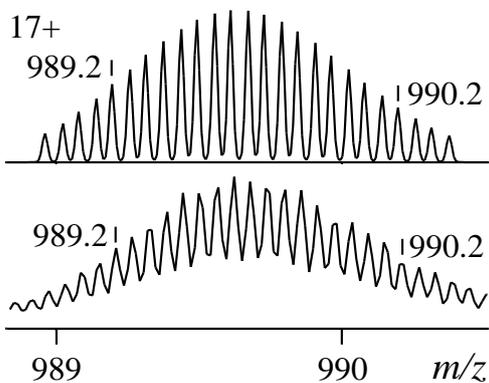
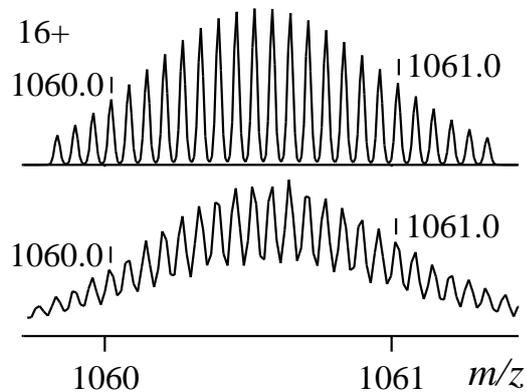
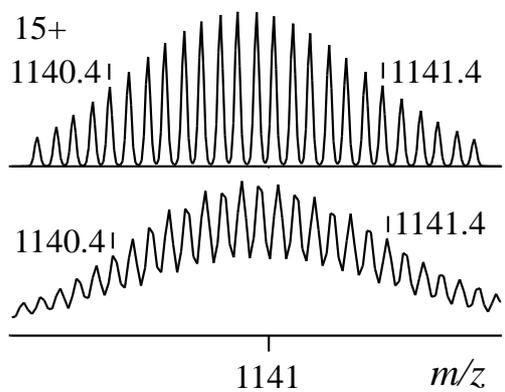
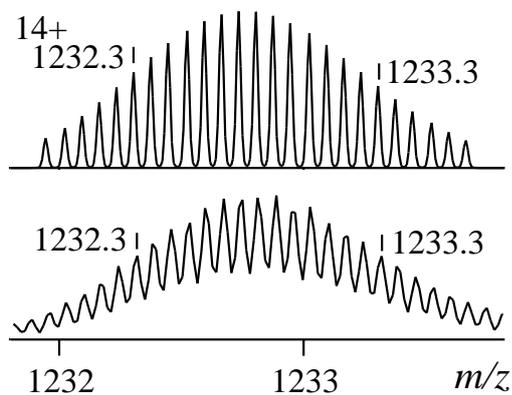
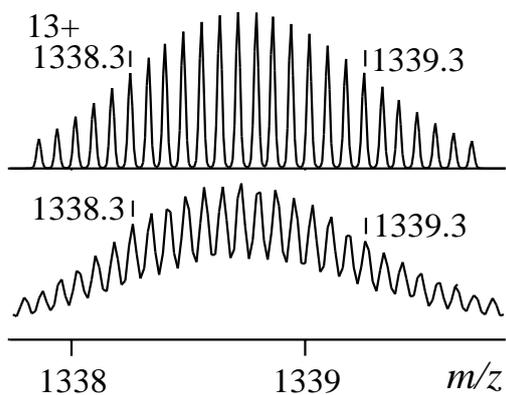
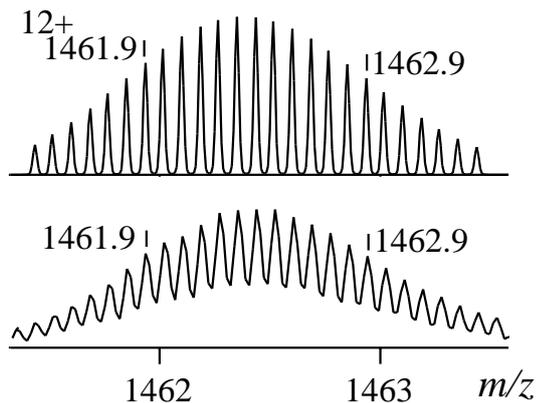
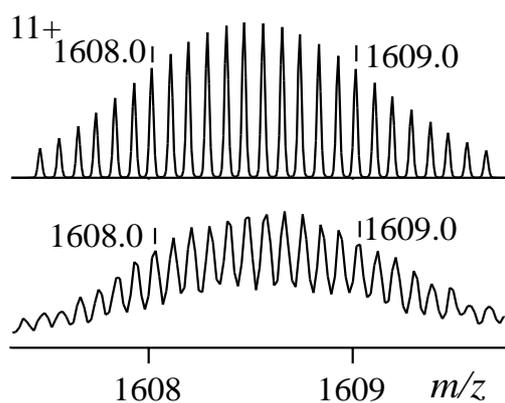


Figure S3. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from $[\text{Zn}_{12}\text{LC}_6]$ (PF_6^- as counterion).



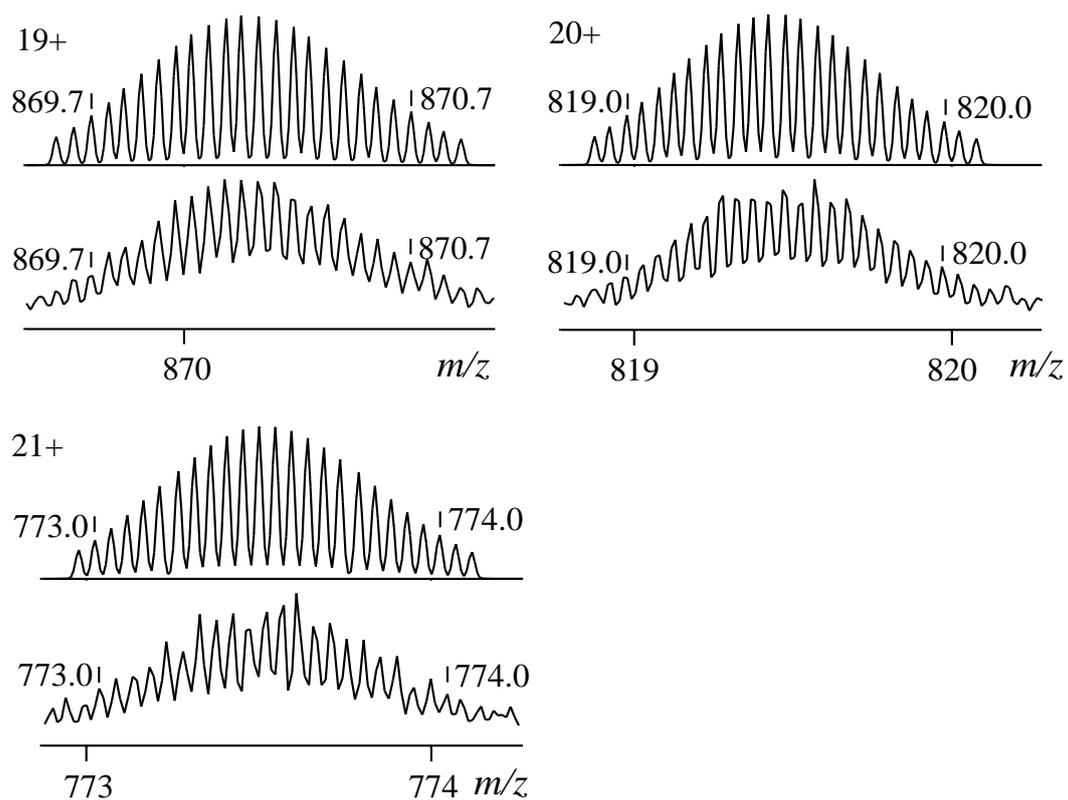


Figure S4. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from $[\text{Zn}_{12}\text{LD}_6]$ (PF_6^- as counterion).

5. Energy-minimized structure from molecular modeling, ESI-MS and TWIM-MS plots of complex $[\text{Zn}_{12}\text{LA}_6]$.

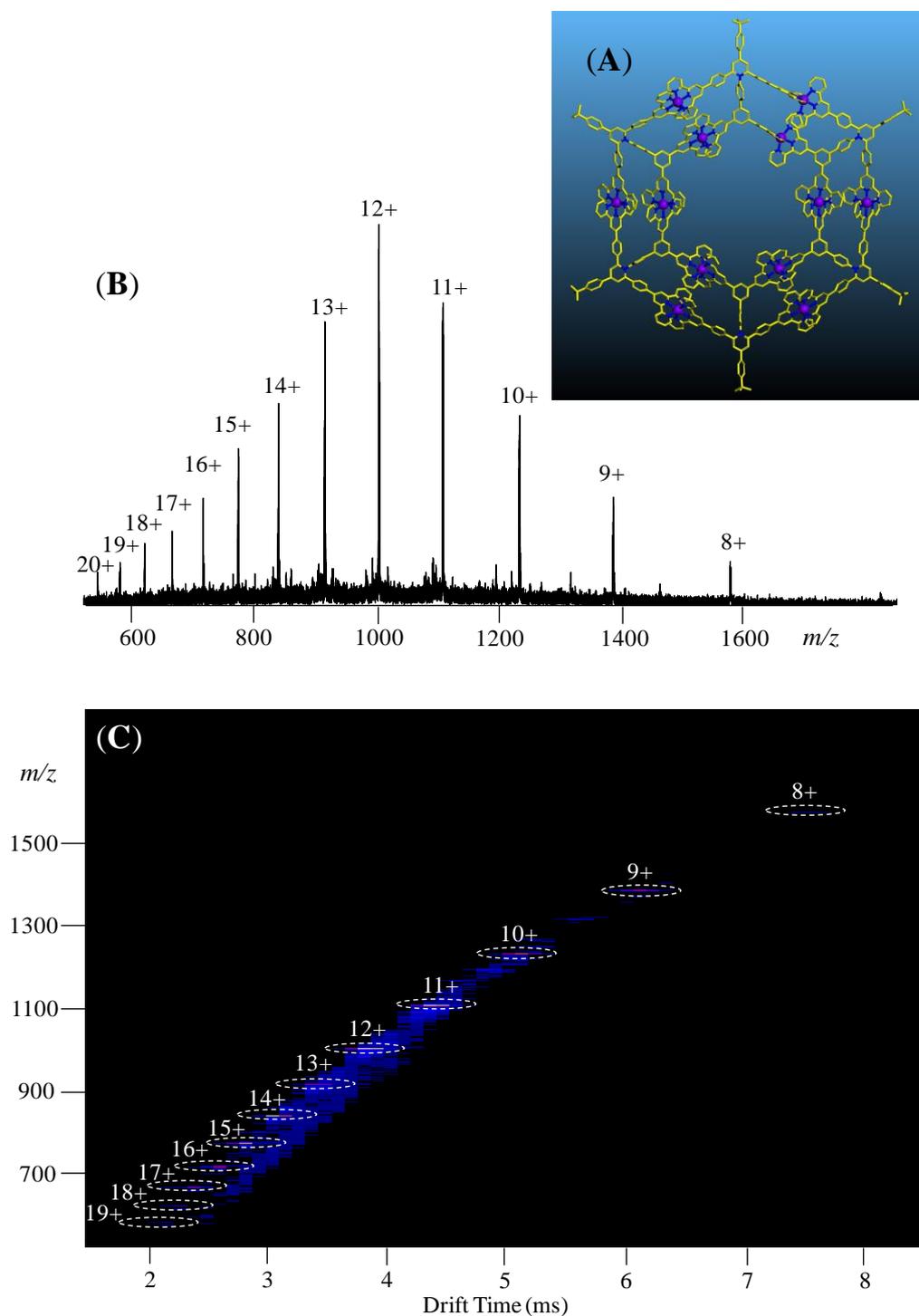


Figure S5. Energy-minimized structure from molecular modeling of complex $[\text{Zn}_{12}\text{LA}_6]$. (B) ESI-MS and (C) 2D TWIM-MS plot (m/z vs drift time). The charge states of intact assemblies are marked.

6. Calibration of drift time scale

Corrected drift times (arrival times) were plotted against corrected published cross sections for the multiply charged ions arising from myoglobin. Drift times were measured at a traveling wave velocity of 1000 m/s and a traveling wave height of 25 V. This calibration plot was utilized to obtain the experimental collision cross sections (CCSs) listed in Table 1.

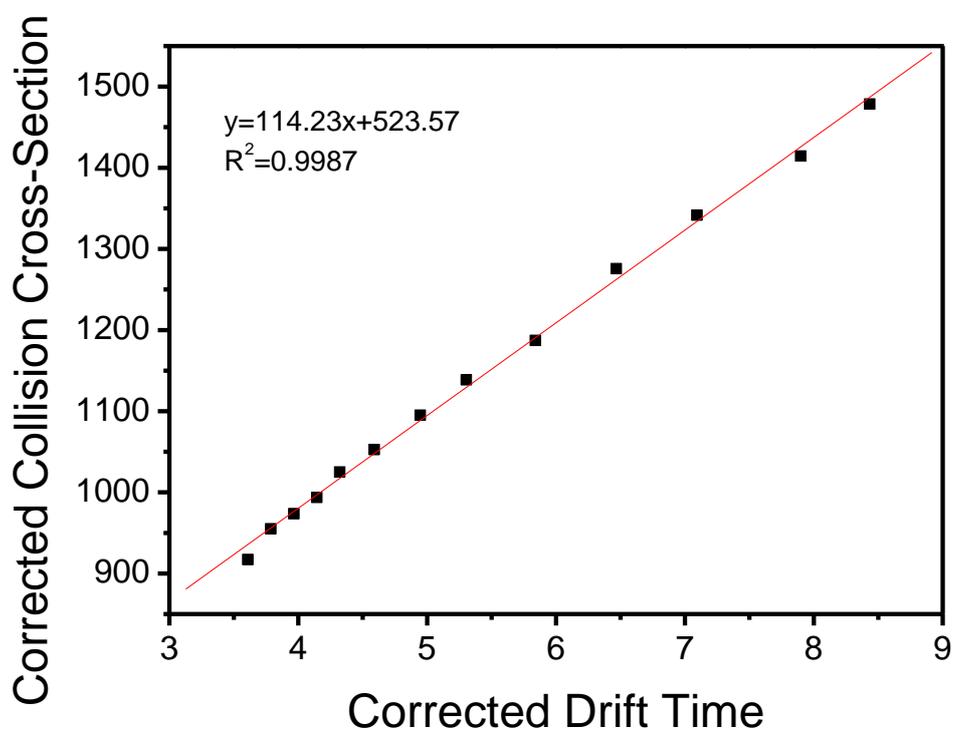


Figure S6. The calibration curve was constructed by plotting the corrected CCSs of the molecular ions of myoglobin at different corrected drift times.

7. Molecular modeling

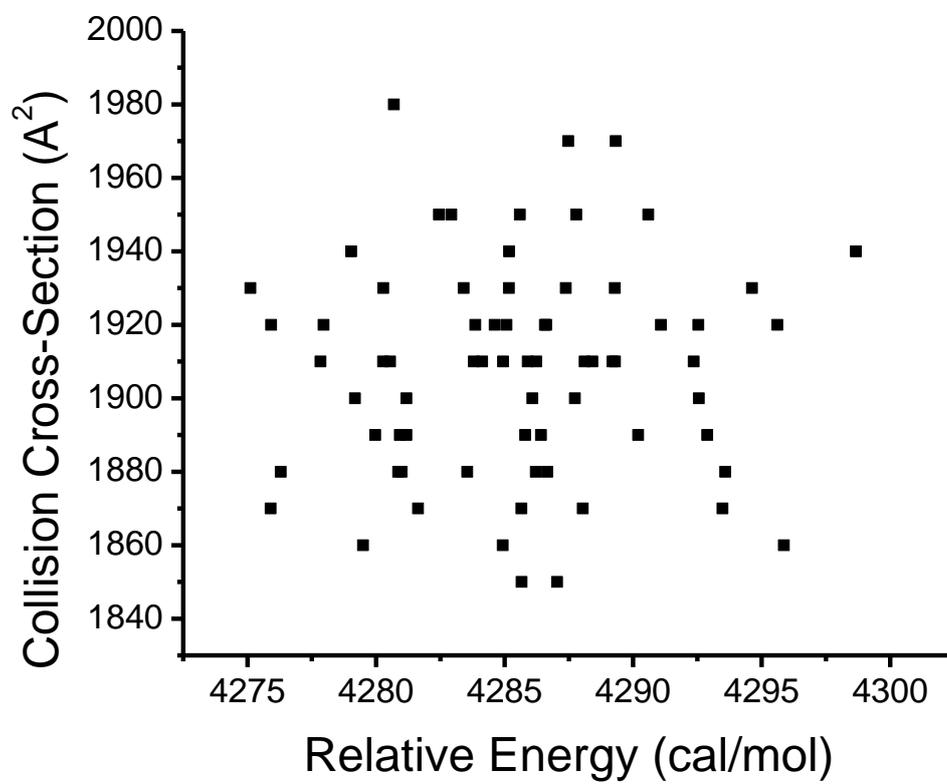


Figure S7. Plot of collision cross-section (CCS) vs. relative energy for 70 candidate structures of $[\text{Zn}_{12}\text{LB}_6]$ generated by annealing simulations. CCSs were calculated by the TM method using the MOBCAL program. The average TM cross section area is $1907.7 \pm 29.8 \text{ \AA}^2$.

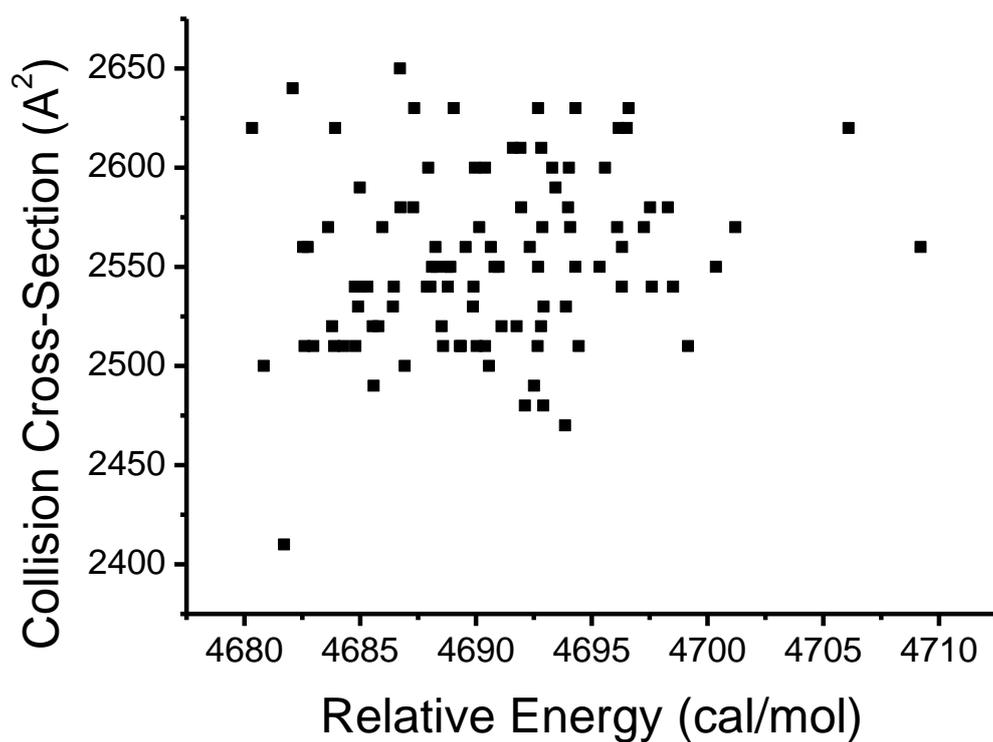


Figure S8. Plot of collision cross-section (CCS) vs. relative energy for 100 candidate structures of [Zn₁₂LC₆] generated by annealing simulations. CCSs were calculated by the TM method using the MOBCAL program. The average TM cross section area is $2554.2 \pm 44.1 \text{ \AA}^2$.

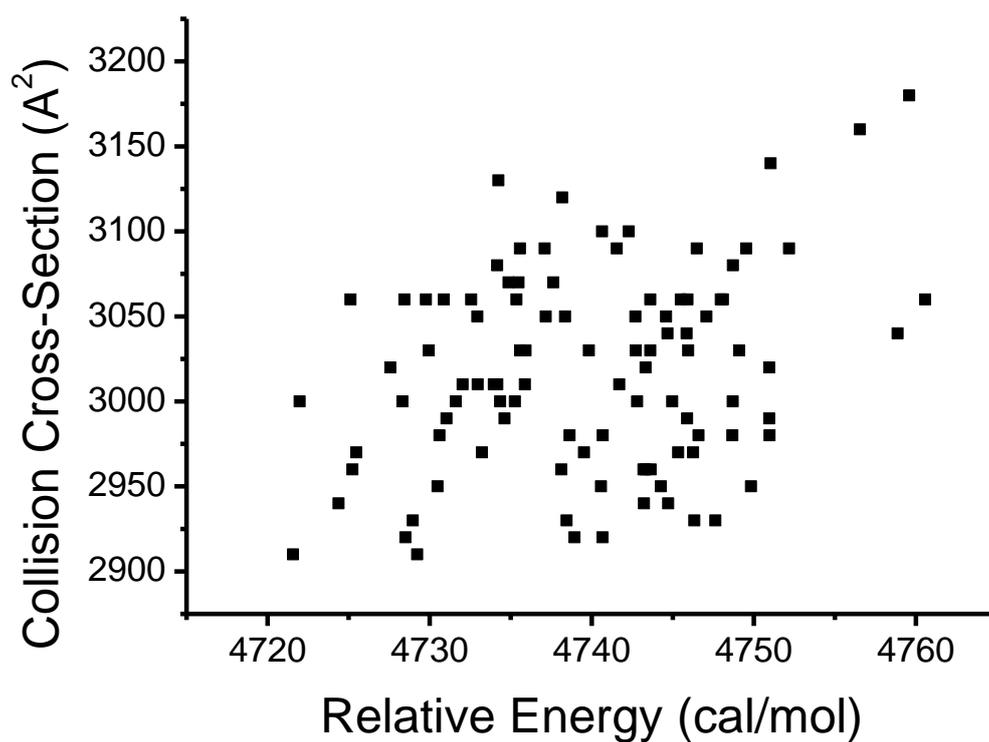


Figure S9. Plot of collision cross-section (CCS) vs. relative energy for 100 candidate structures of $[\text{Zn}_{12}\text{LD}_6]$ generated by annealing simulations. CCSs were calculated by the TM method using the MOBCAL program. The average TM cross section area is $3018.9 \pm 58.3 \text{ \AA}^2$.

8. ^1H NMR, ^{13}C NMR, 2D COSY NMR, 2D NOESY NMR and MALDI-TOF.

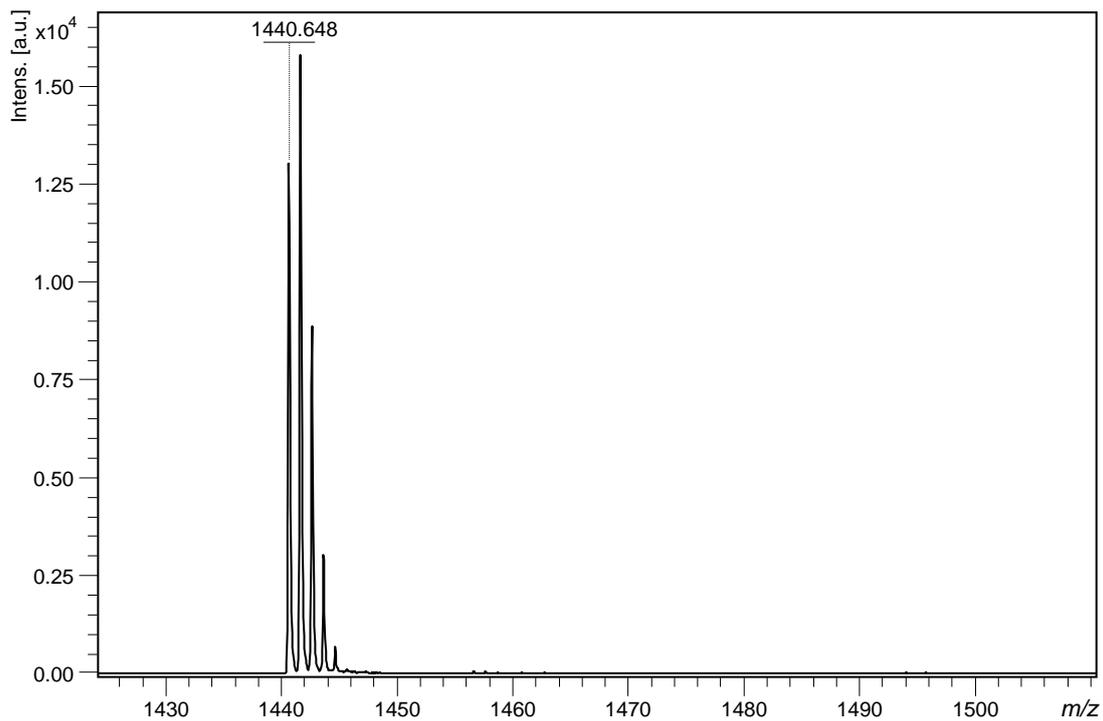
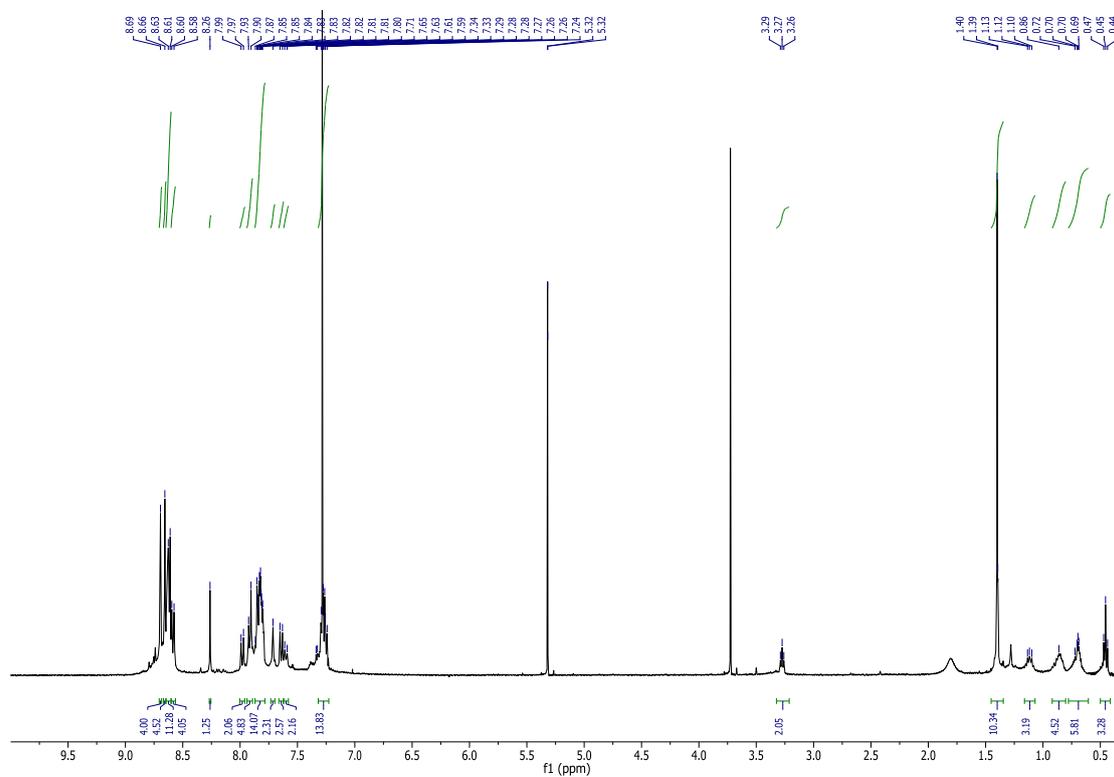


Figure S10. MALDI-TOF mass spectrum of ligand LA.



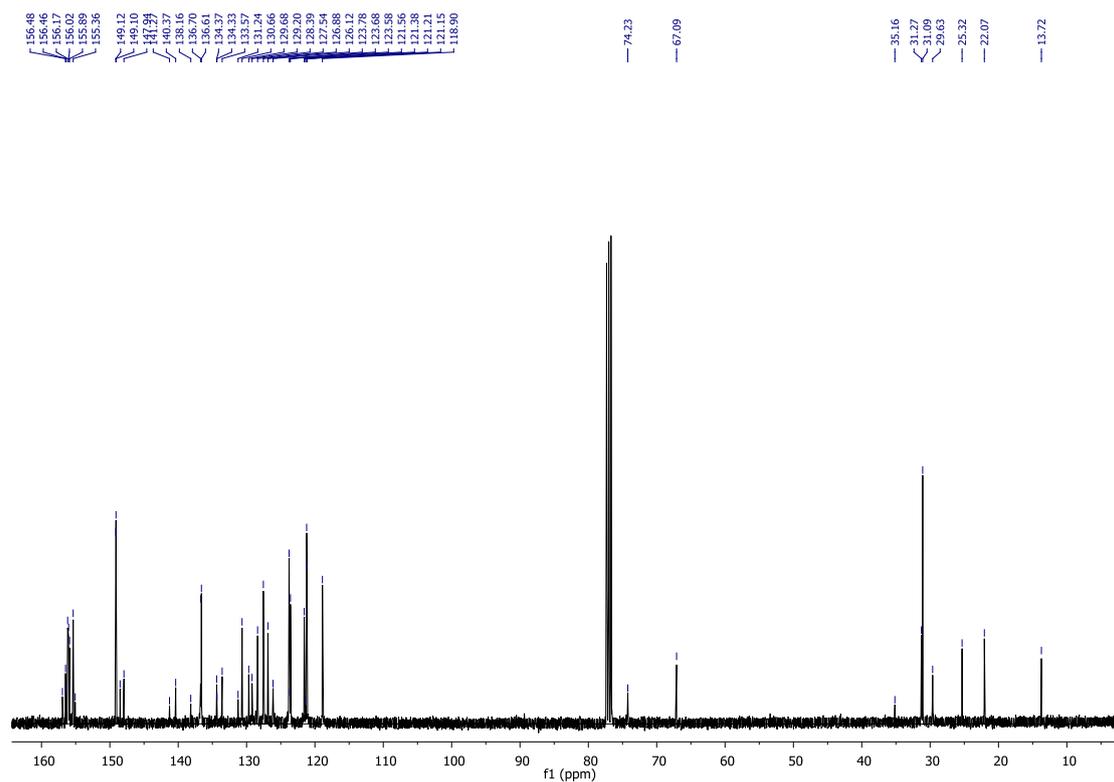


Figure S12. ^{13}C NMR (400 MHz) spectrum of ligand **LB**.

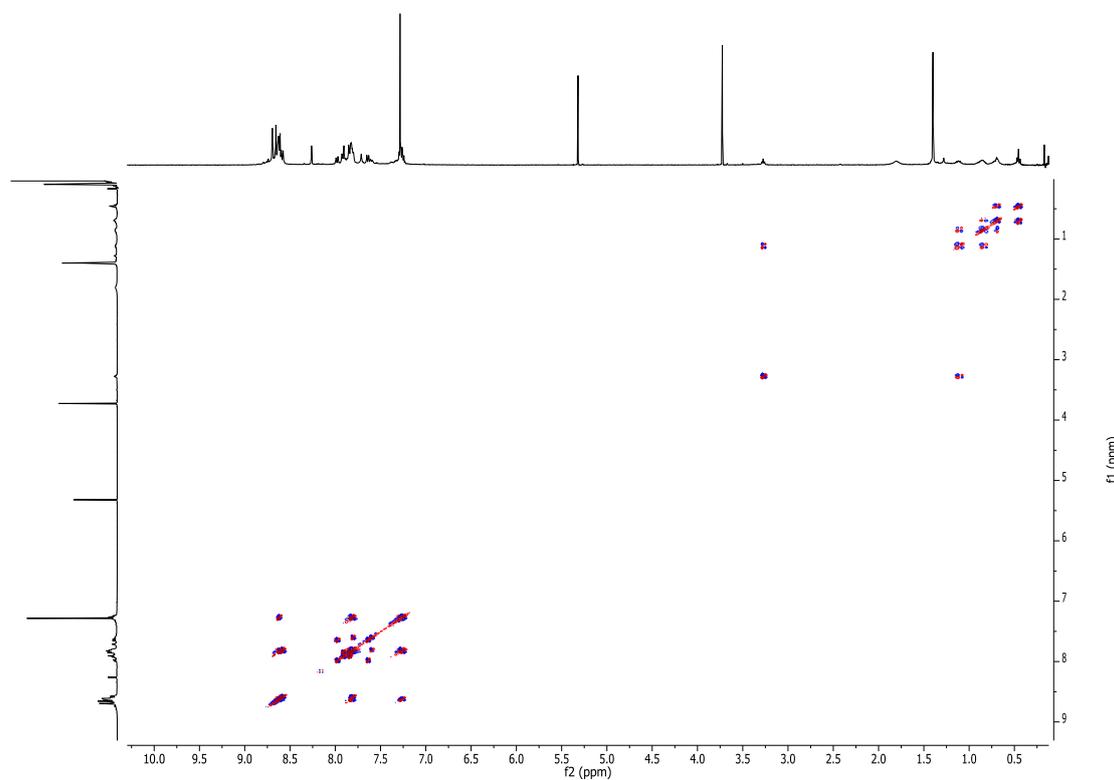


Figure S13. 2D COSY NMR (400 MHz) spectrum of ligand **LB**.

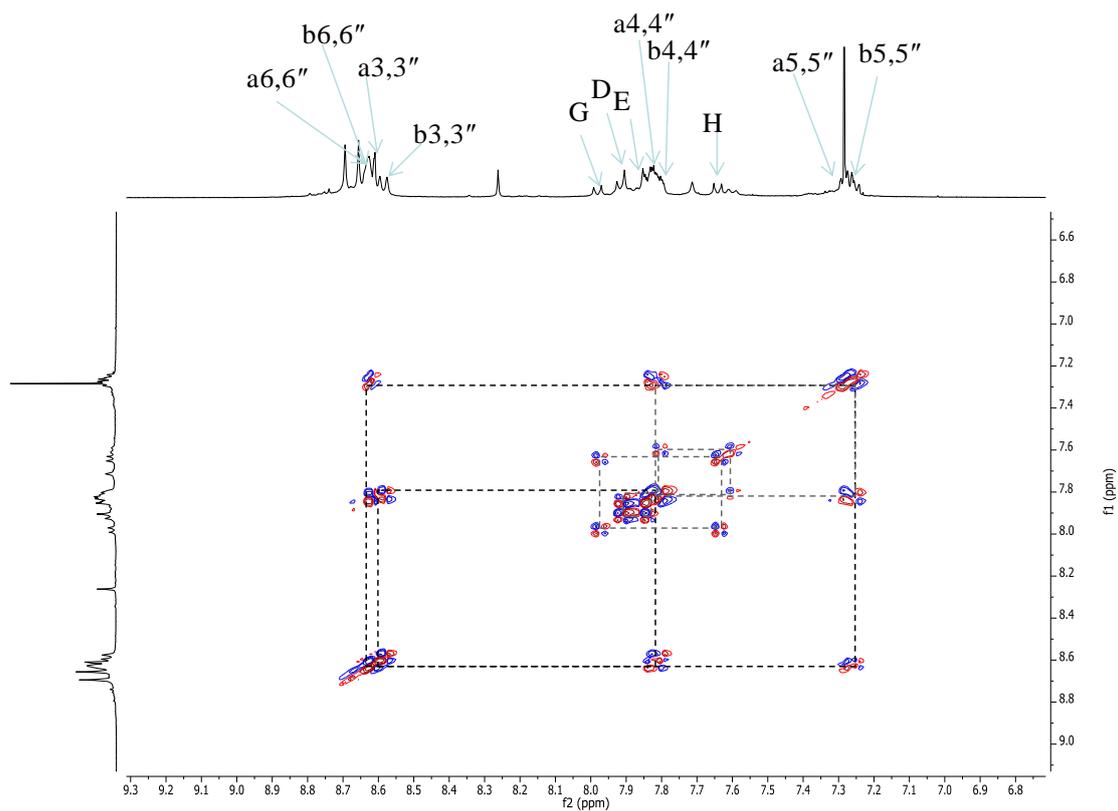


Figure S14. 2D COSY NMR (400 MHz) spectrum of ligand **LB** (aromatic region).

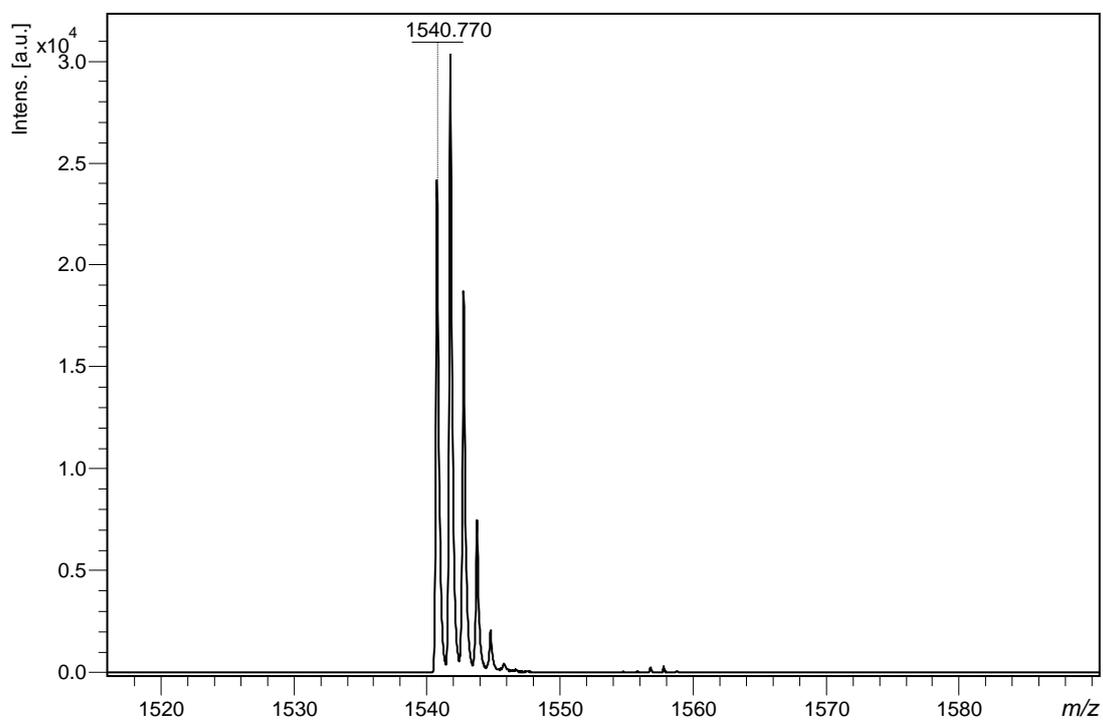


Figure S15. MALDI-TOF mass spectrum of ligand **LB**.

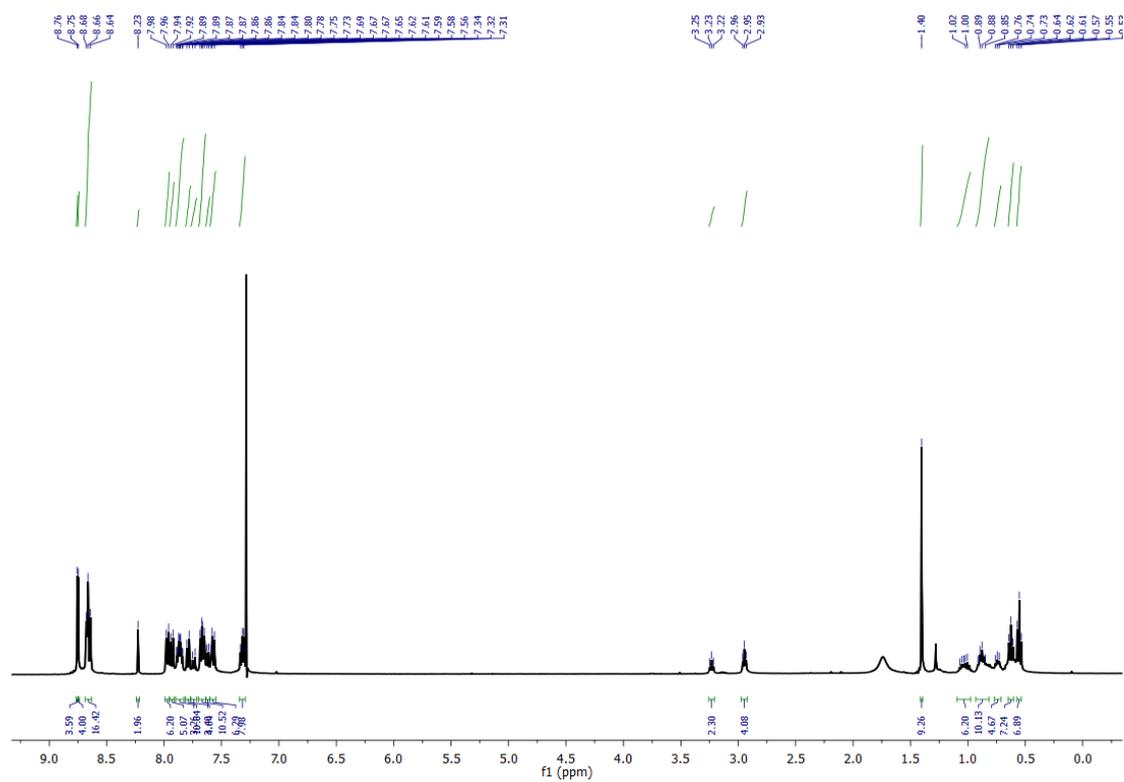


Figure S16. ^1H NMR (400 MHz) spectrum of ligand LC.

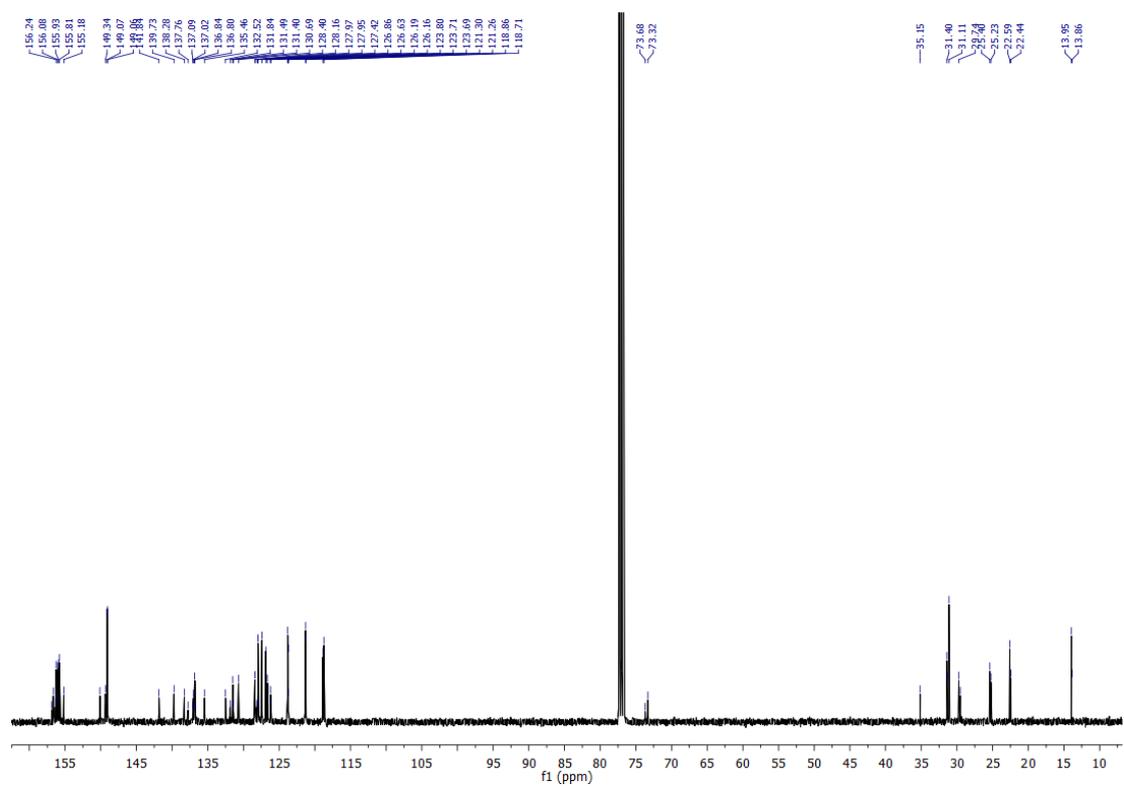


Figure S17. ^{13}C NMR (400 MHz) spectrum of ligand LC.

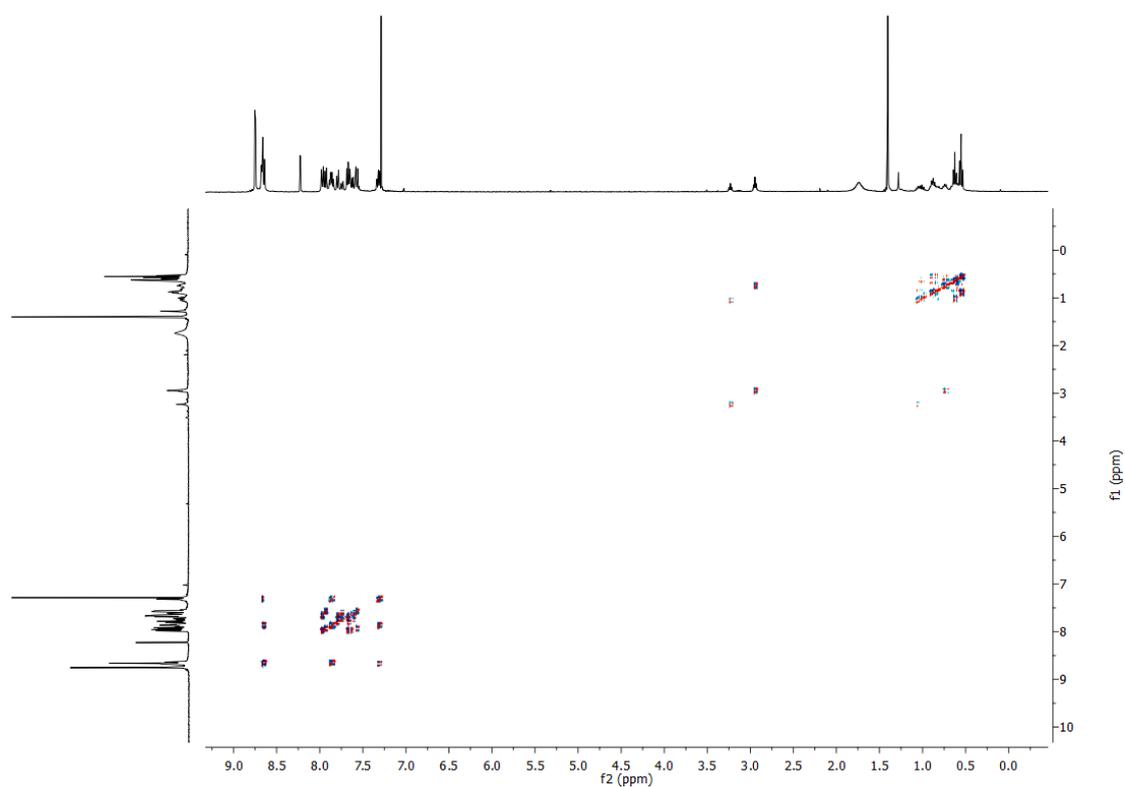


Figure S18.2D COSY NMR (400 MHz) spectrum of ligand **LC**.

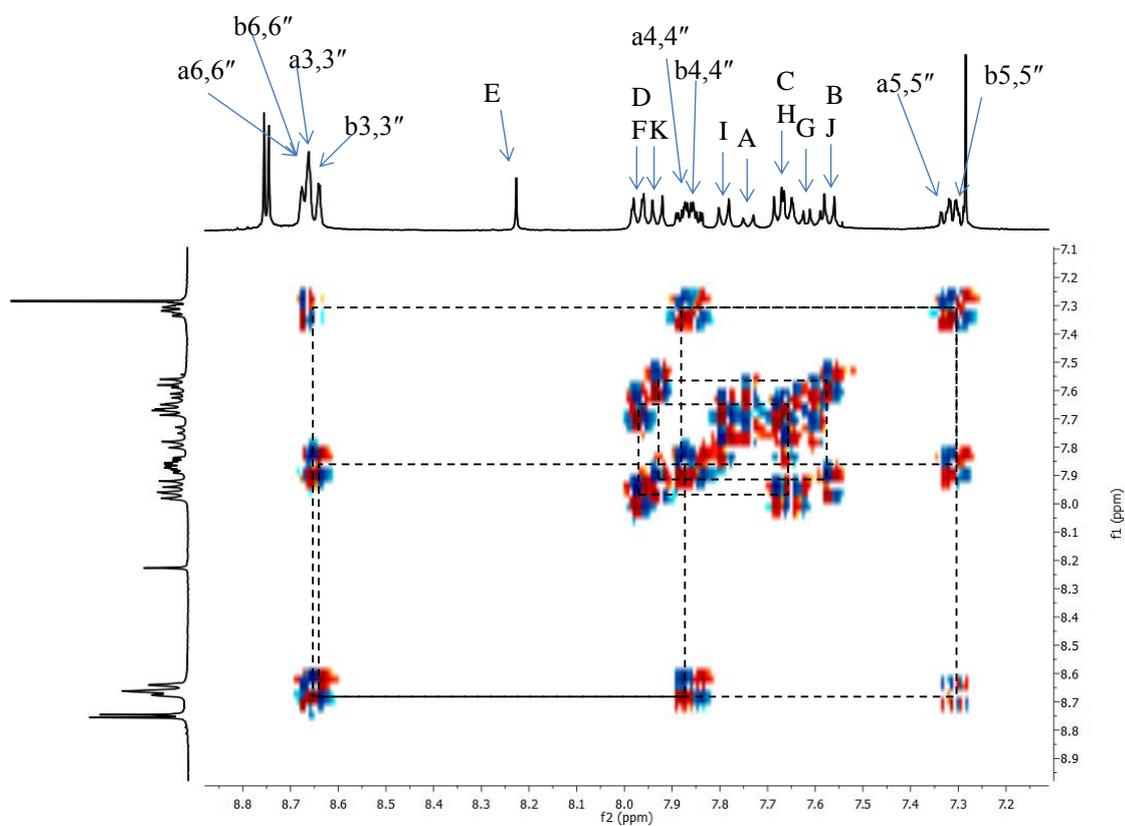


Figure S19. 2D COSY NMR (400 MHz) spectrum of ligand **LC** (aromatic region).

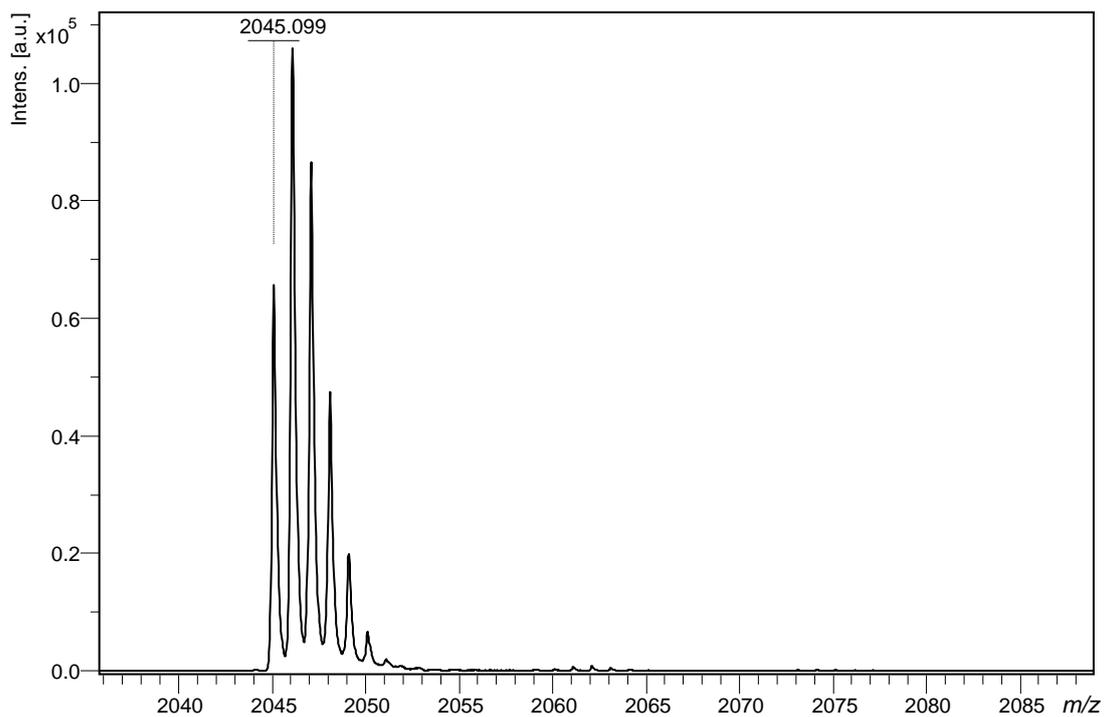


Figure S20. MALDI-TOF mass spectrum of ligand LC.

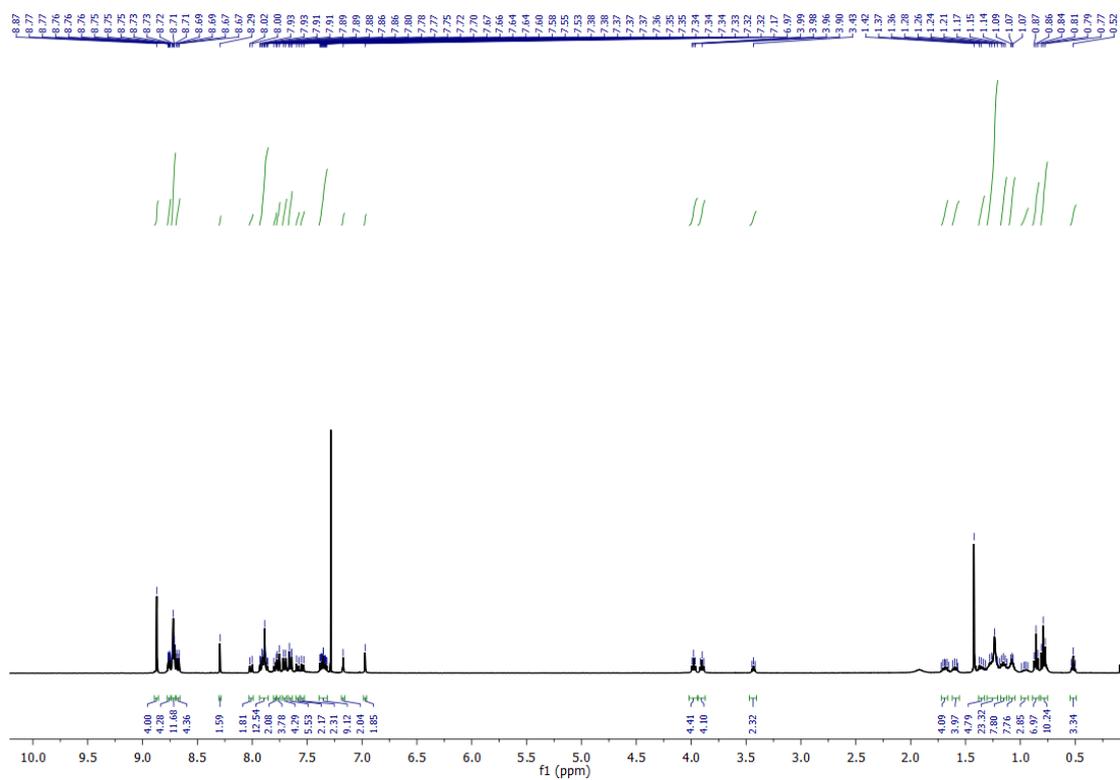


Figure S21. ^1H NMR (400 MHz) spectrum of ligand LD.

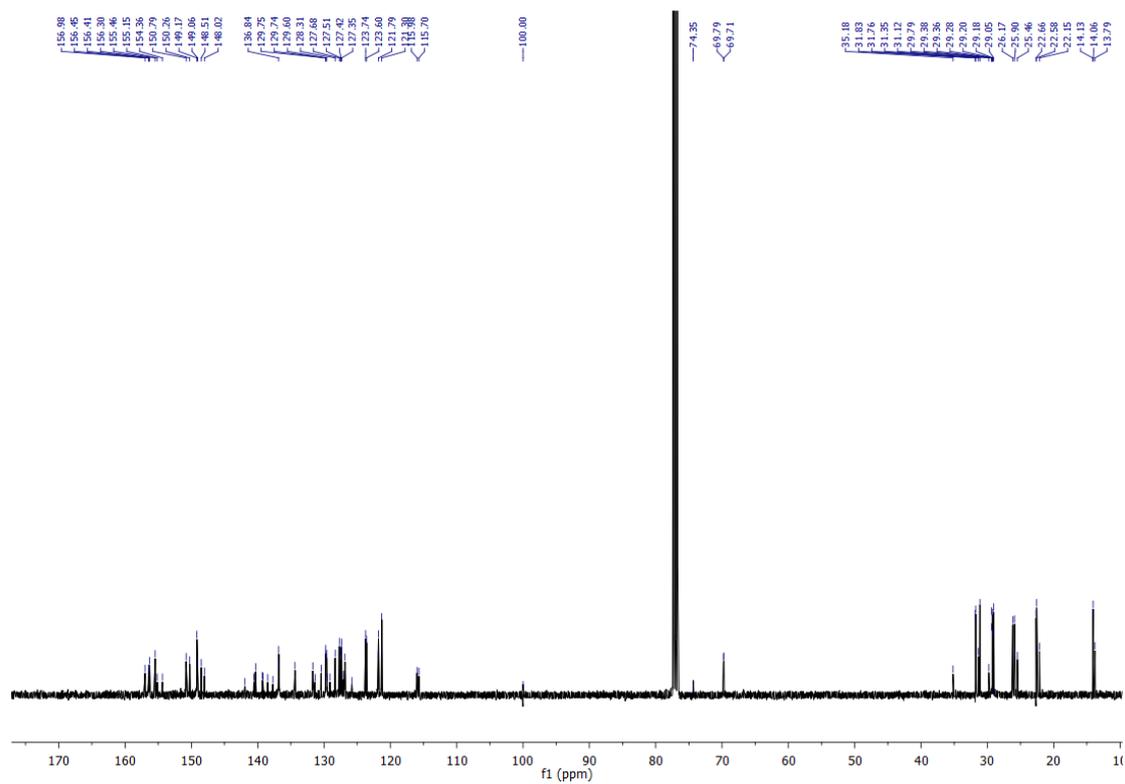


Figure S22. ^{13}C NMR (400 MHz) spectrum of ligand **LD**.

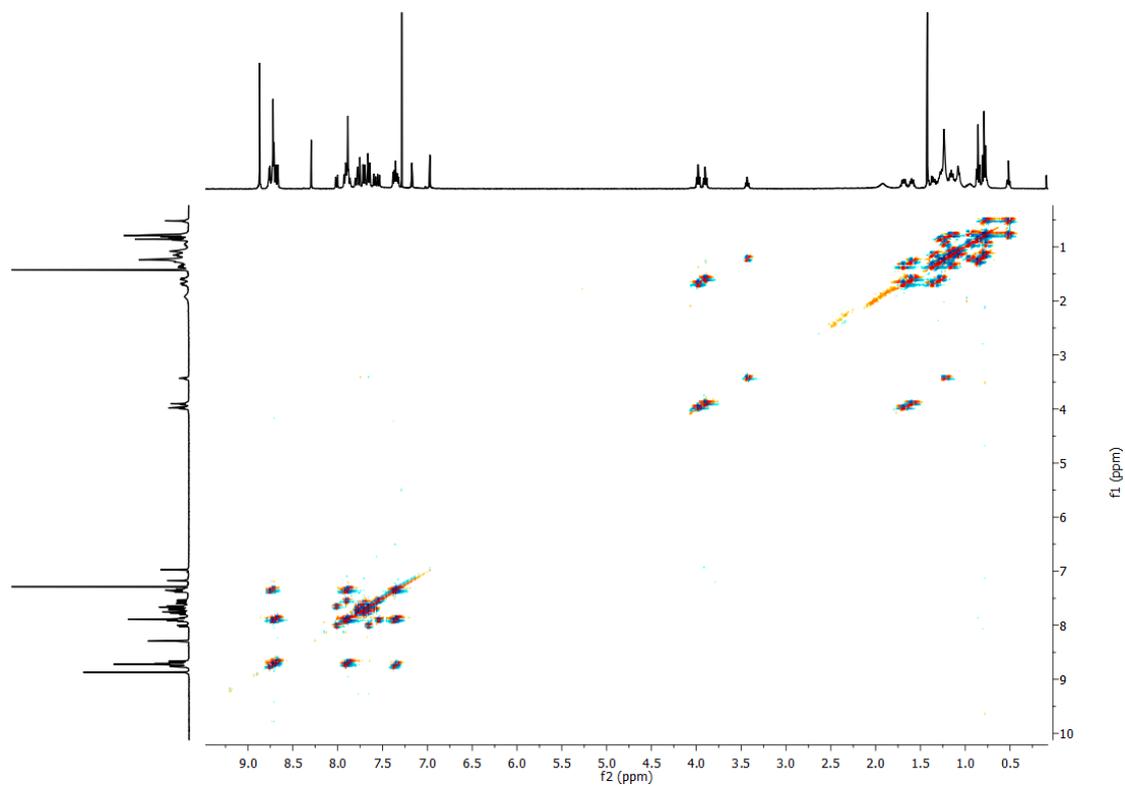


Figure S23. 2D COSY NMR (400 MHz) spectrum of ligand **LD**.

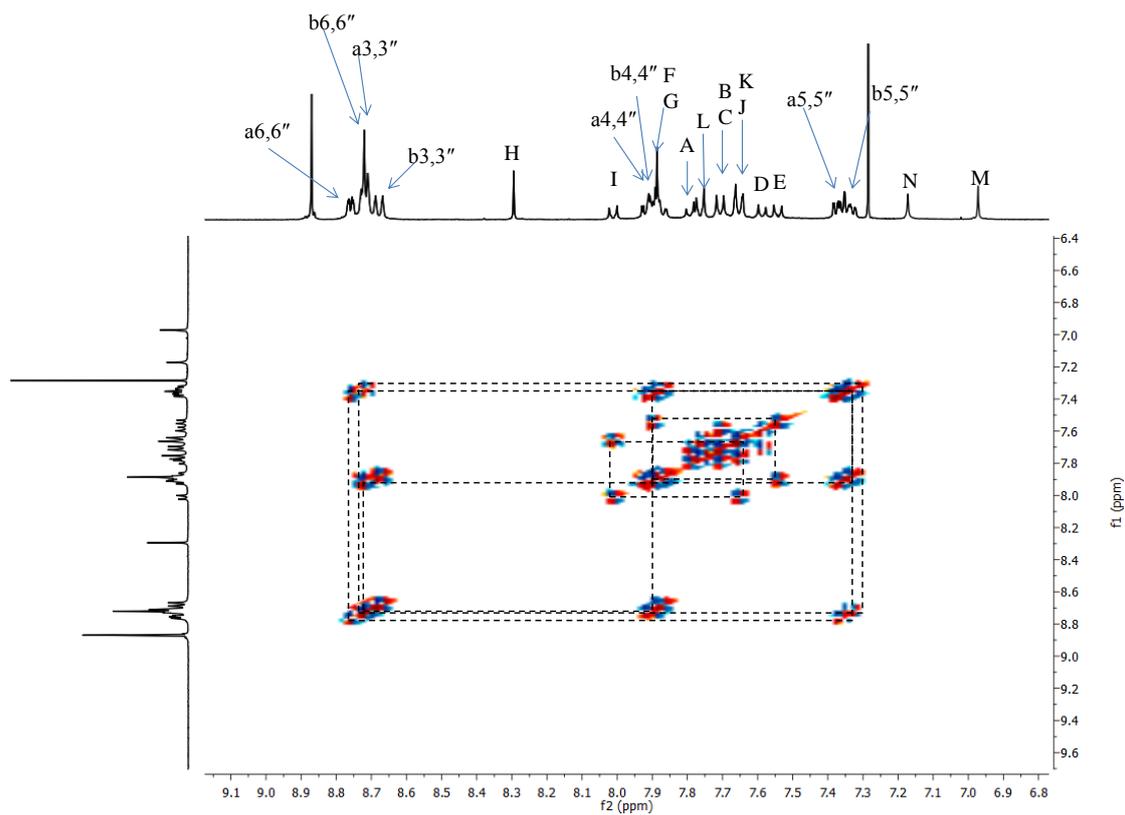


Figure S24. 2D COSY NMR (400 MHz) spectrum of ligand **LD** (aromatic region).

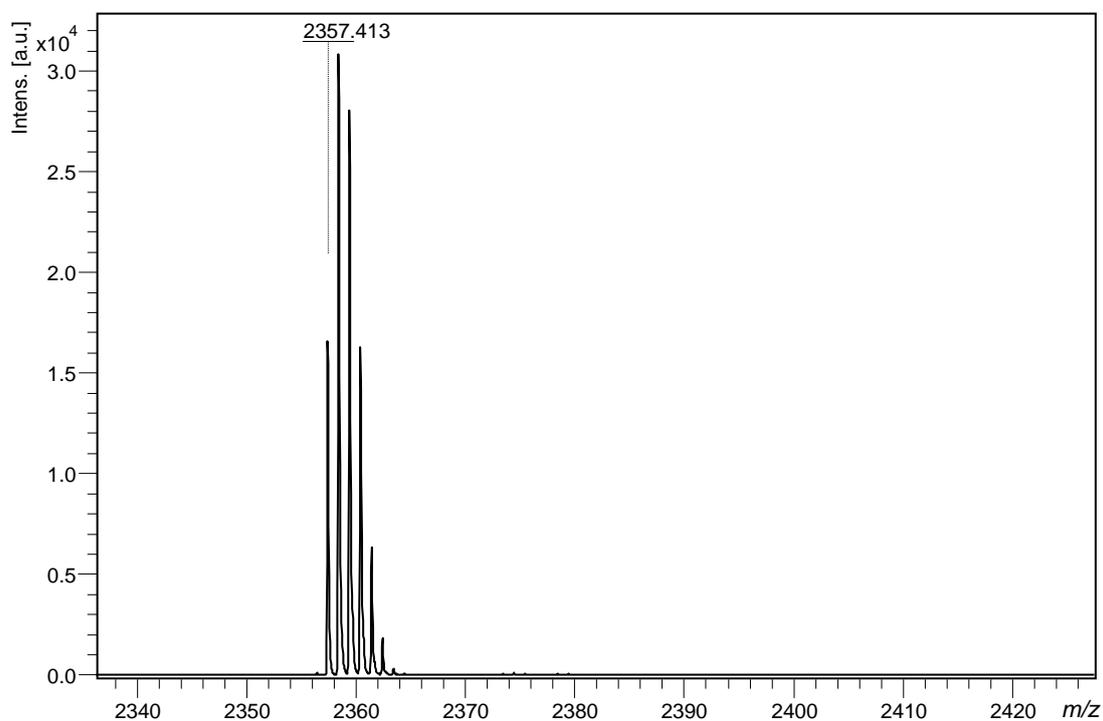


Figure S25. MALDI-TOF mass spectrum of ligand **LD**.

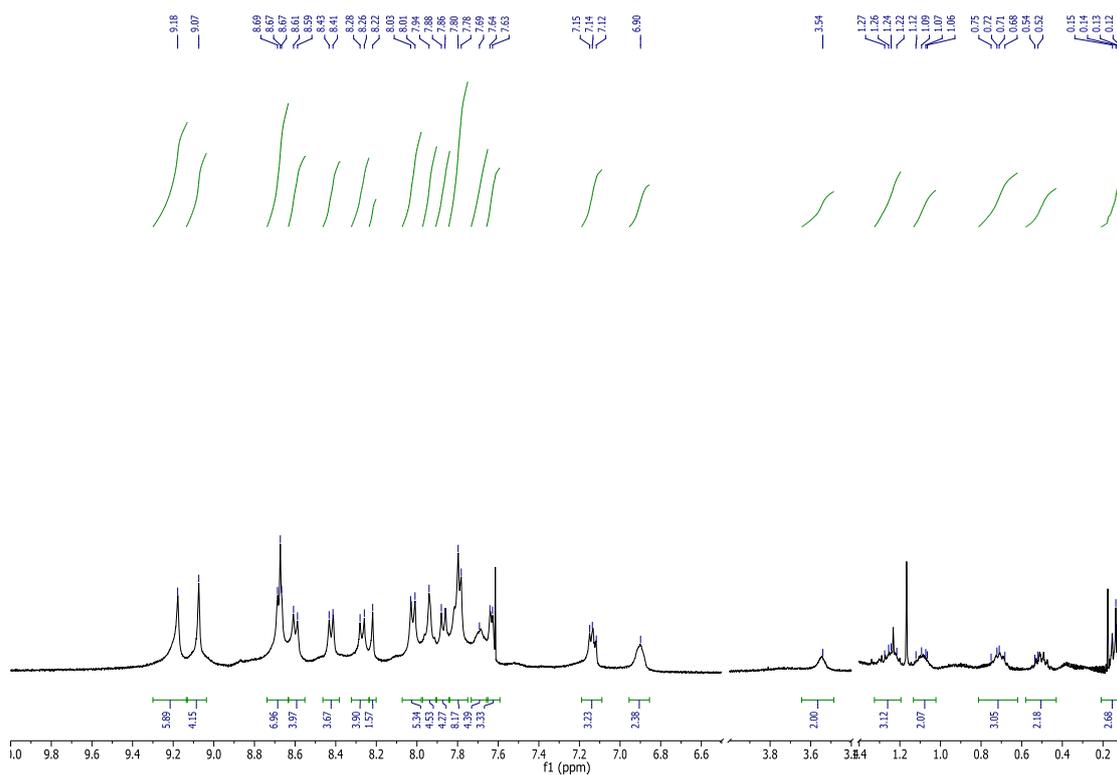


Figure S26. ^1H NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LB}_6]$.

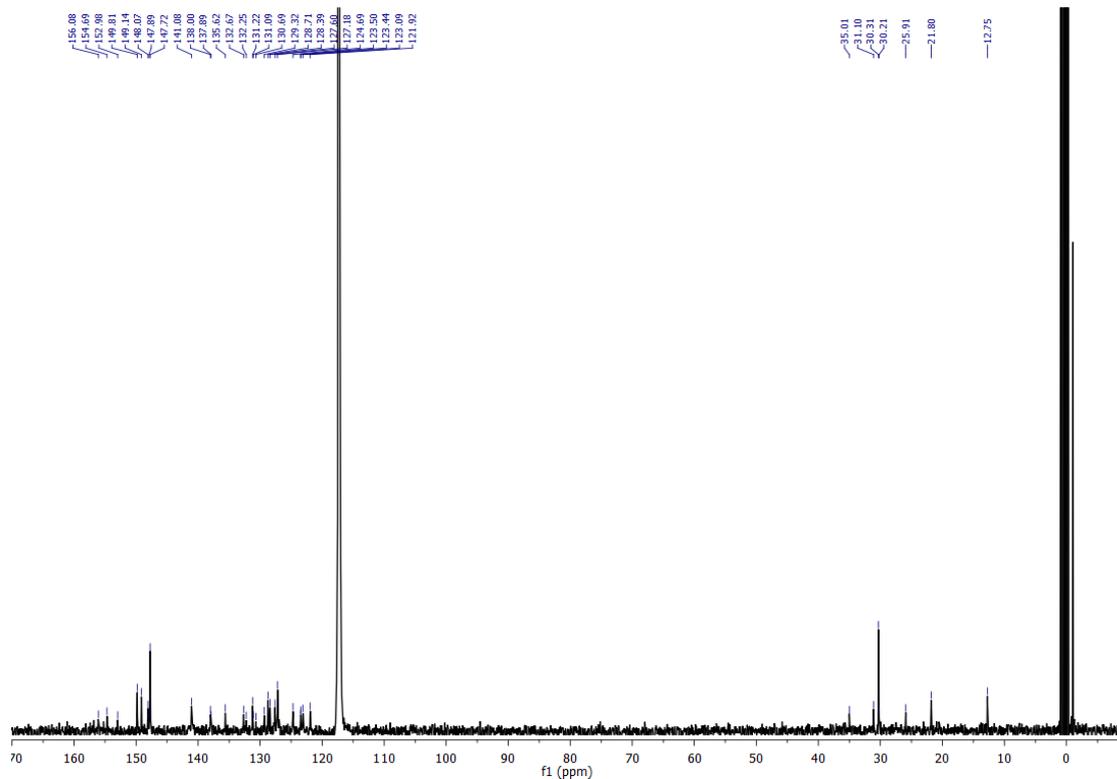


Figure S27. ^{13}C NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LB}_6]$.

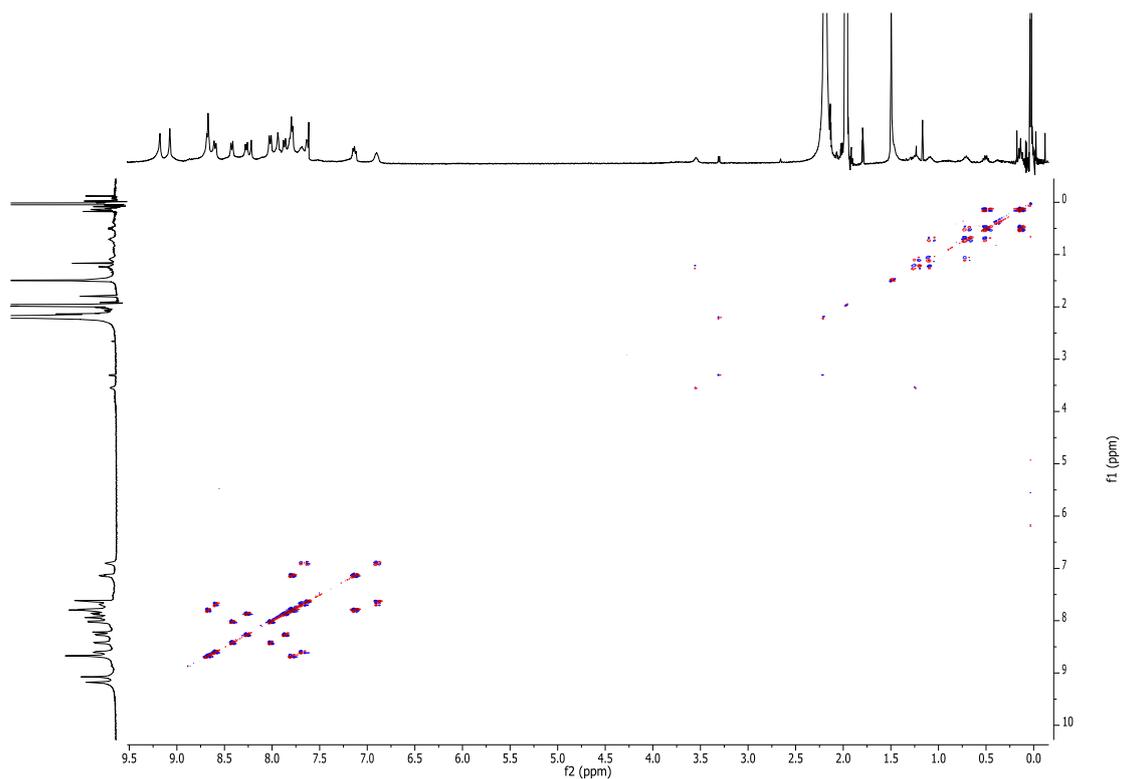


Figure S28. 2D COSY NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LB}_6]$.

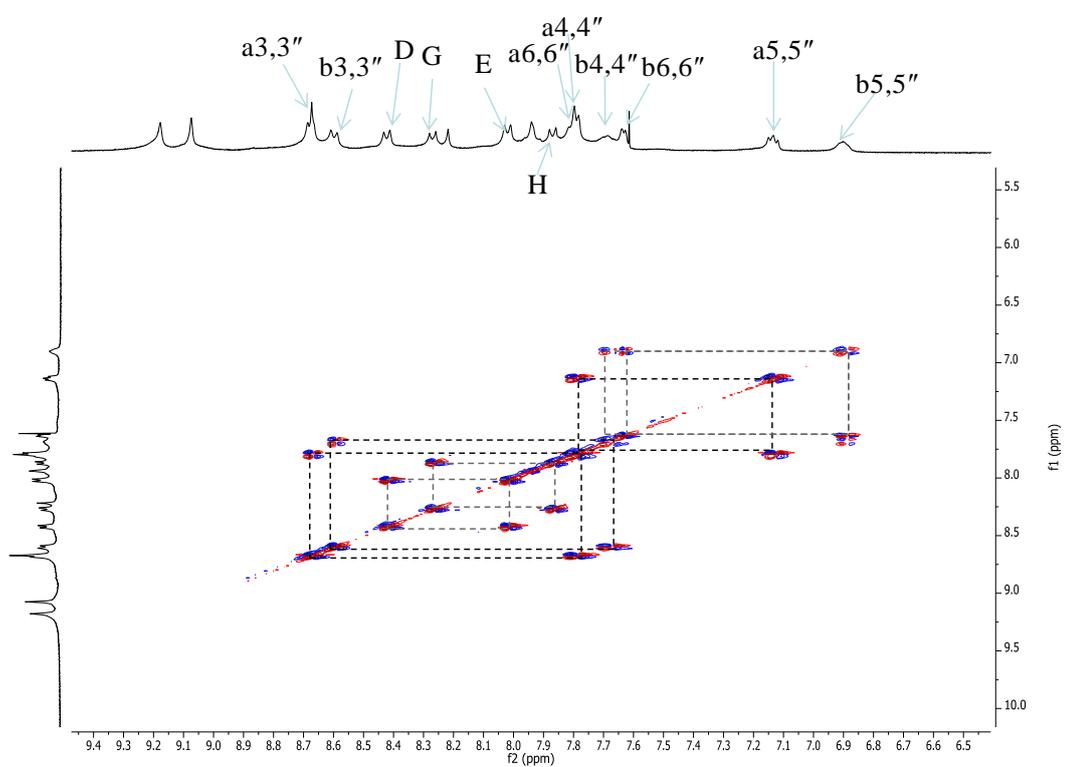


Figure S29. 2D COSY NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LB}_6]$ (aromatic region).

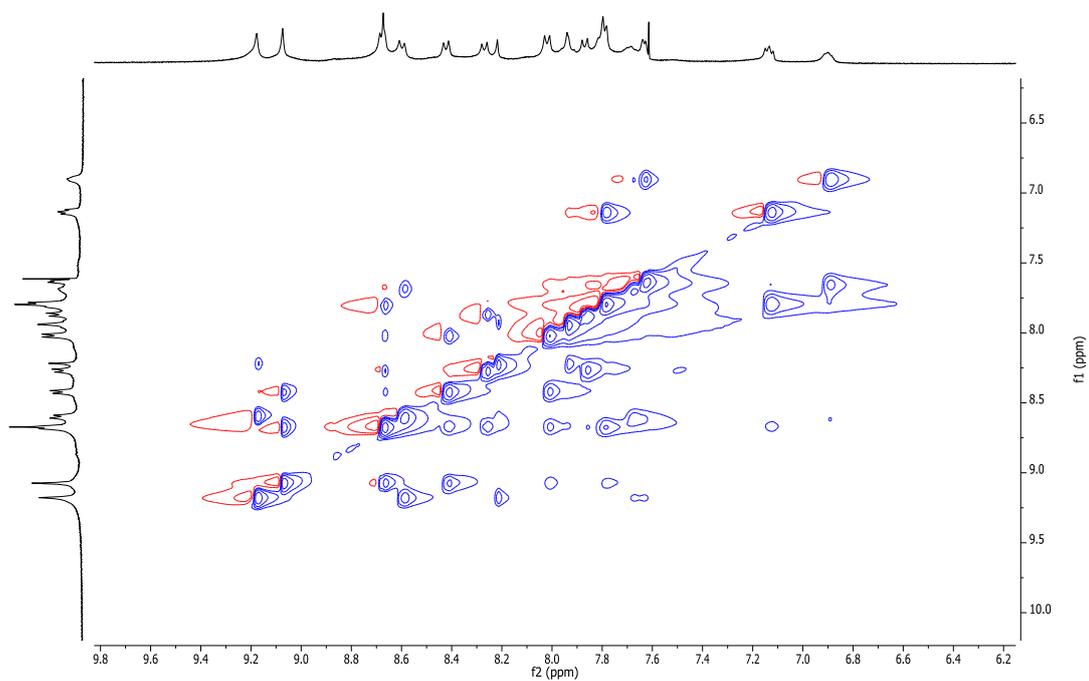


Figure S30. 2D NOESY NMR (400 MHz) spectrum of complex [Zn₁₂LB₆] (aromatic region).

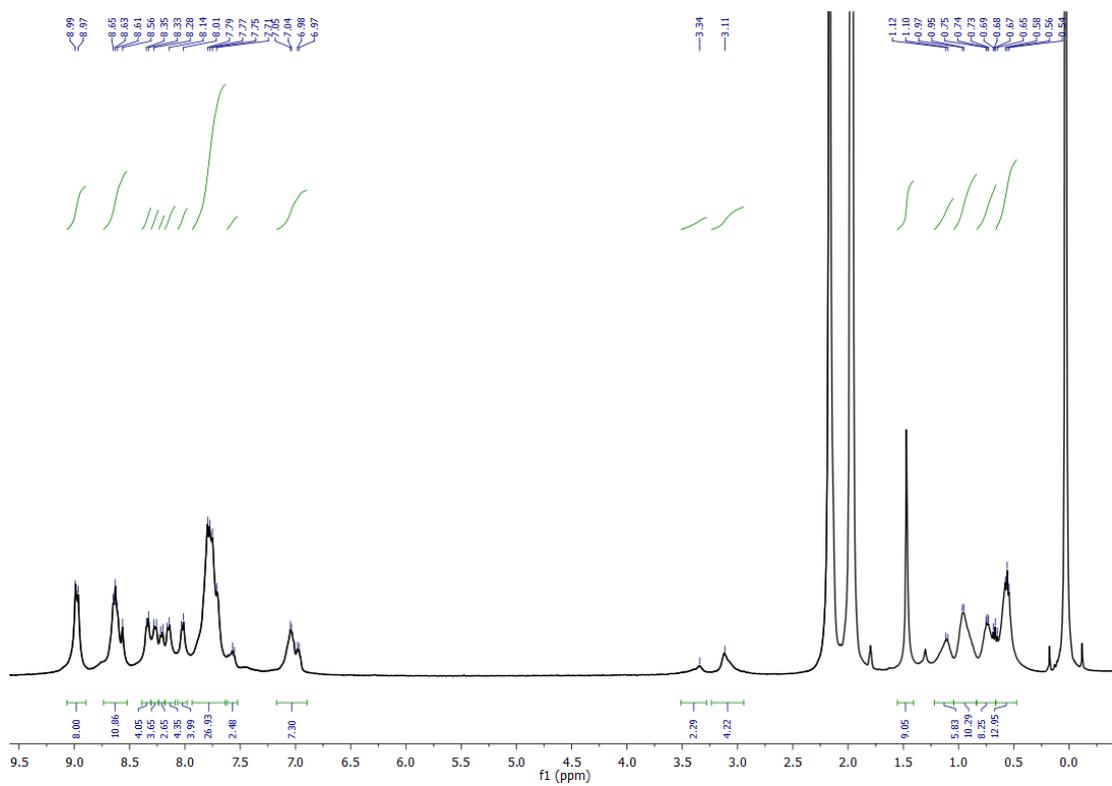


Figure S31. ¹H NMR (400 MHz) spectrum of complex [Zn₁₂LC₆].

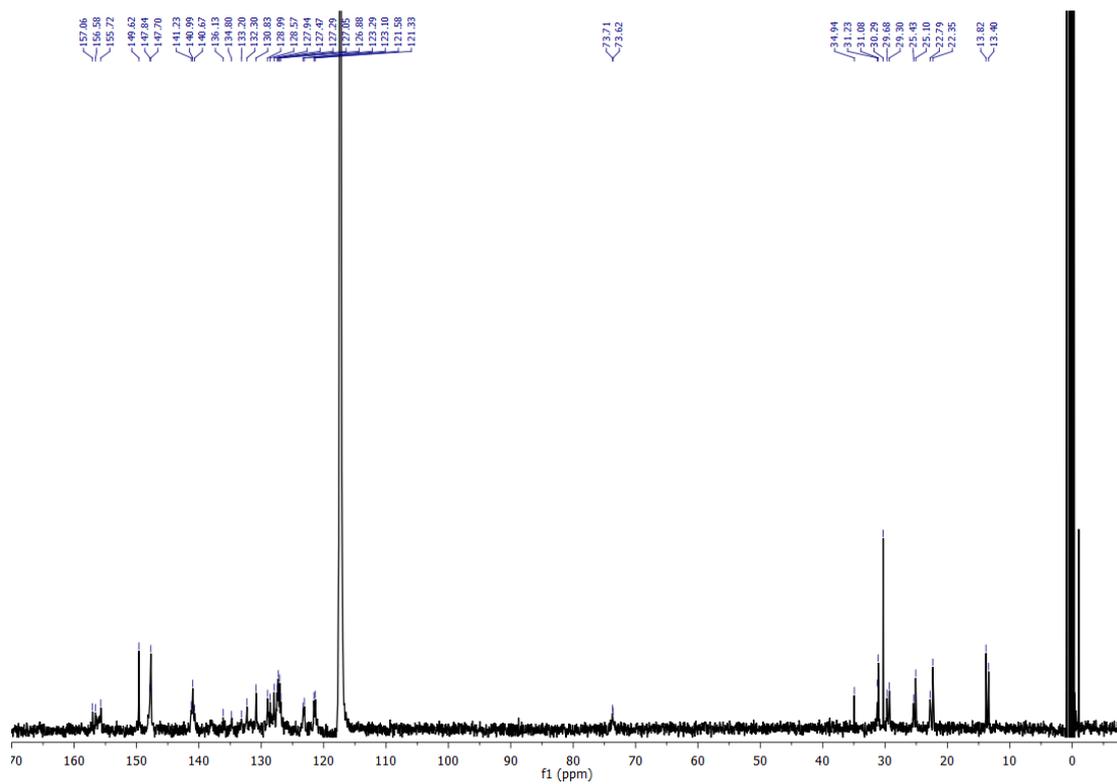


Figure S32. ^{13}C NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LC}_6]$.

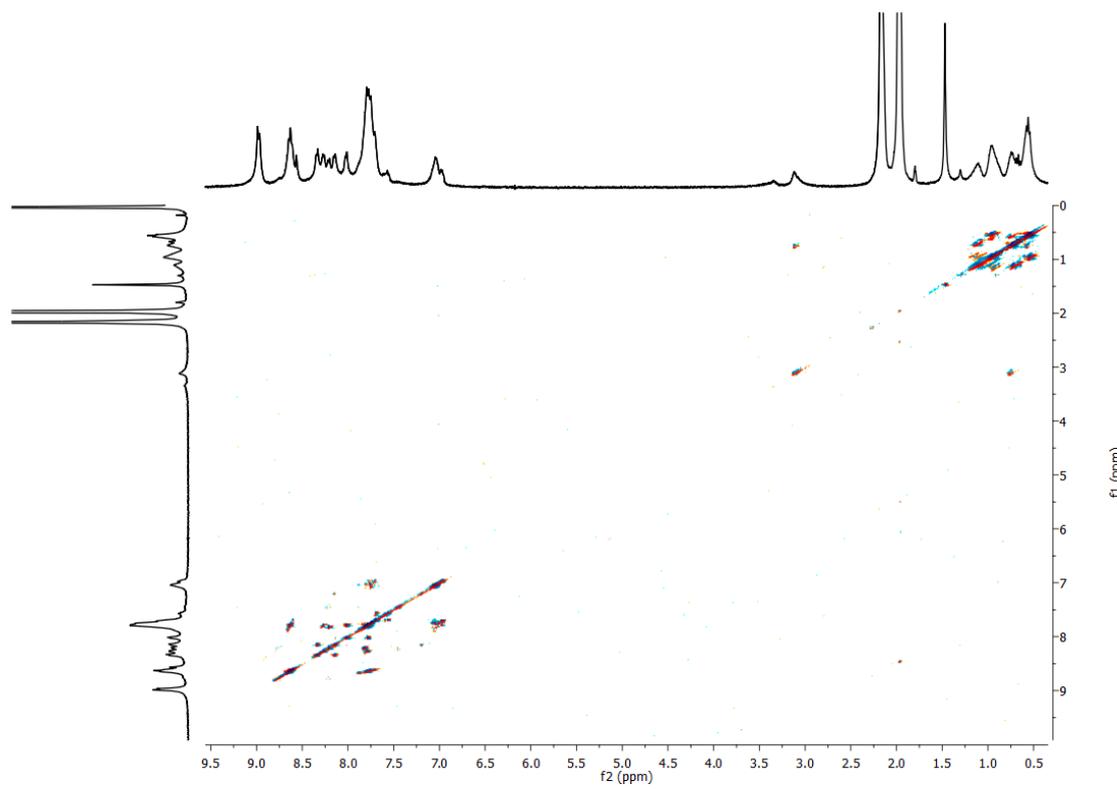


Figure S33. 2D COSY NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LC}_6]$.

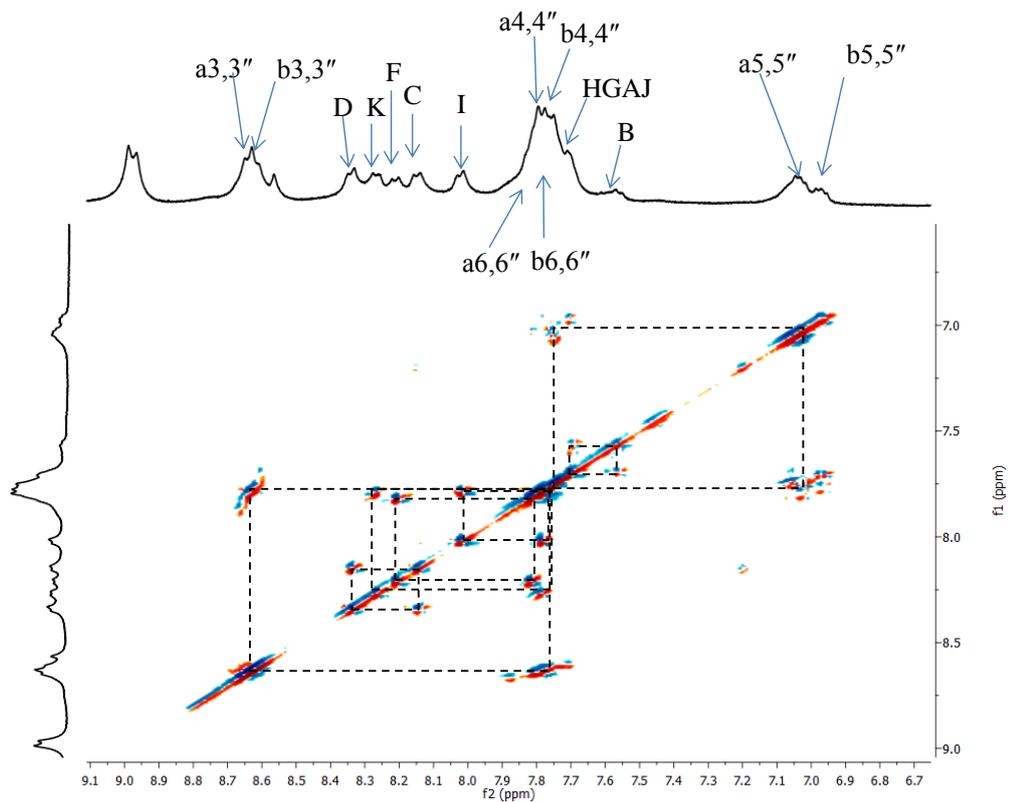


Figure S34. 2D COSY NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LC}_6]$ (aromatic region).

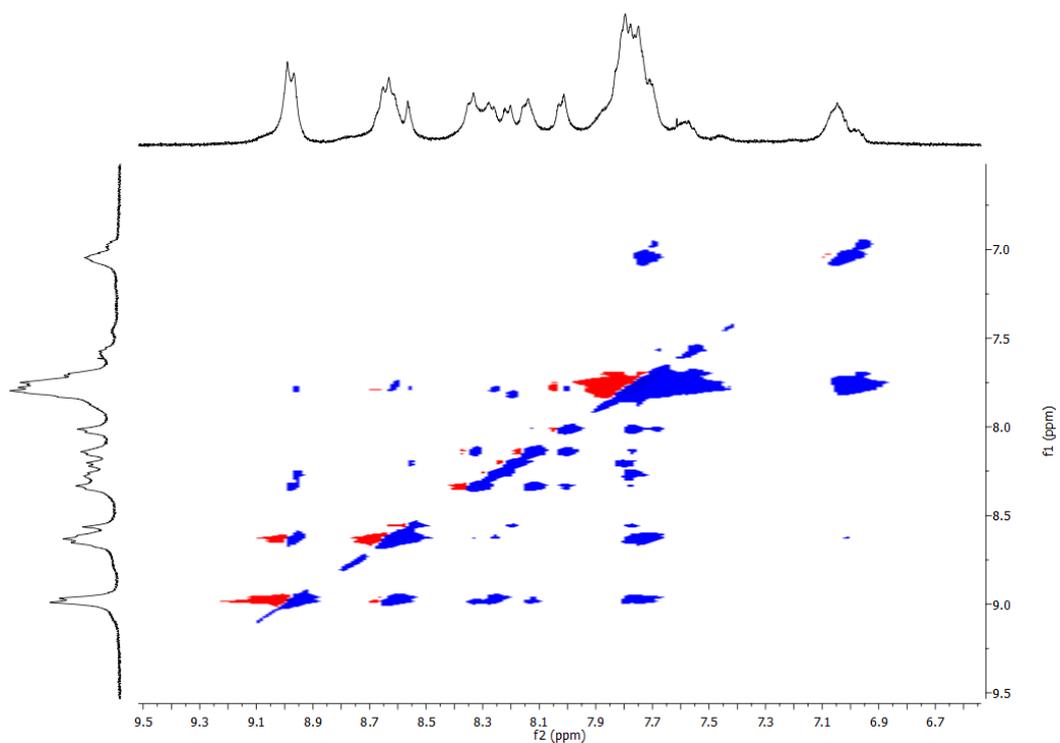


Figure S35. 2D NOESY NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LC}_6]$ (aromatic

region).

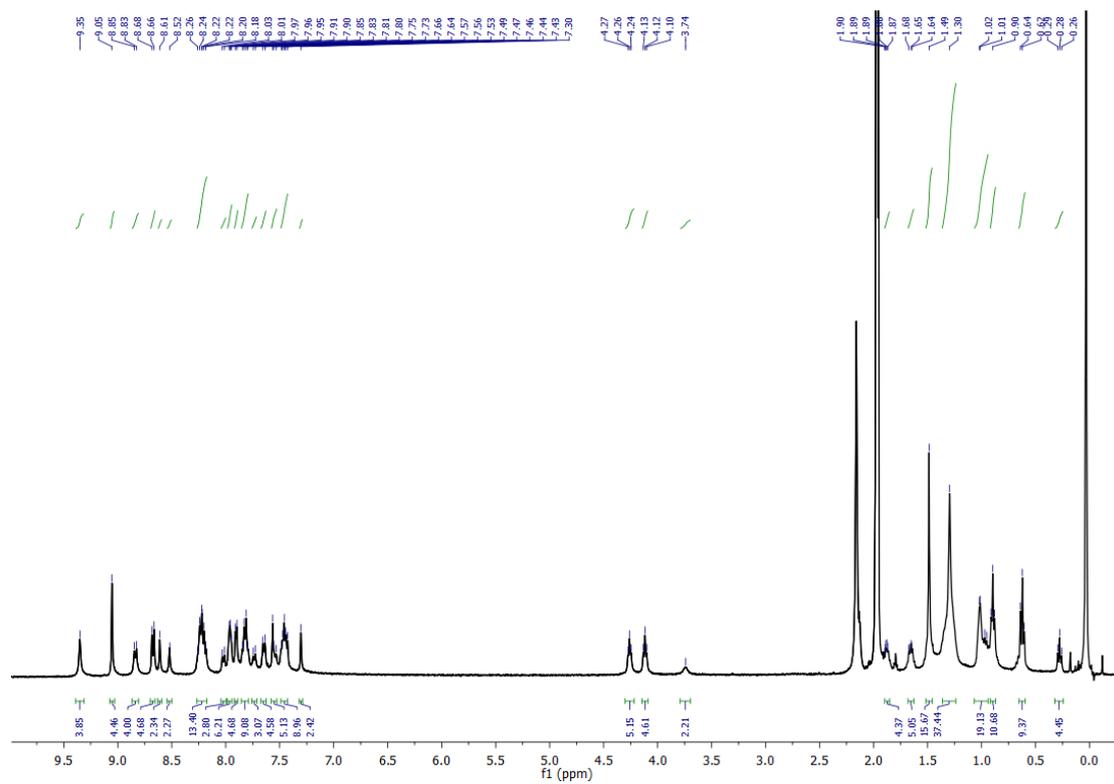


Figure S36. ¹H NMR (400 MHz) spectrum of complex [Zn₁₂LD₆].

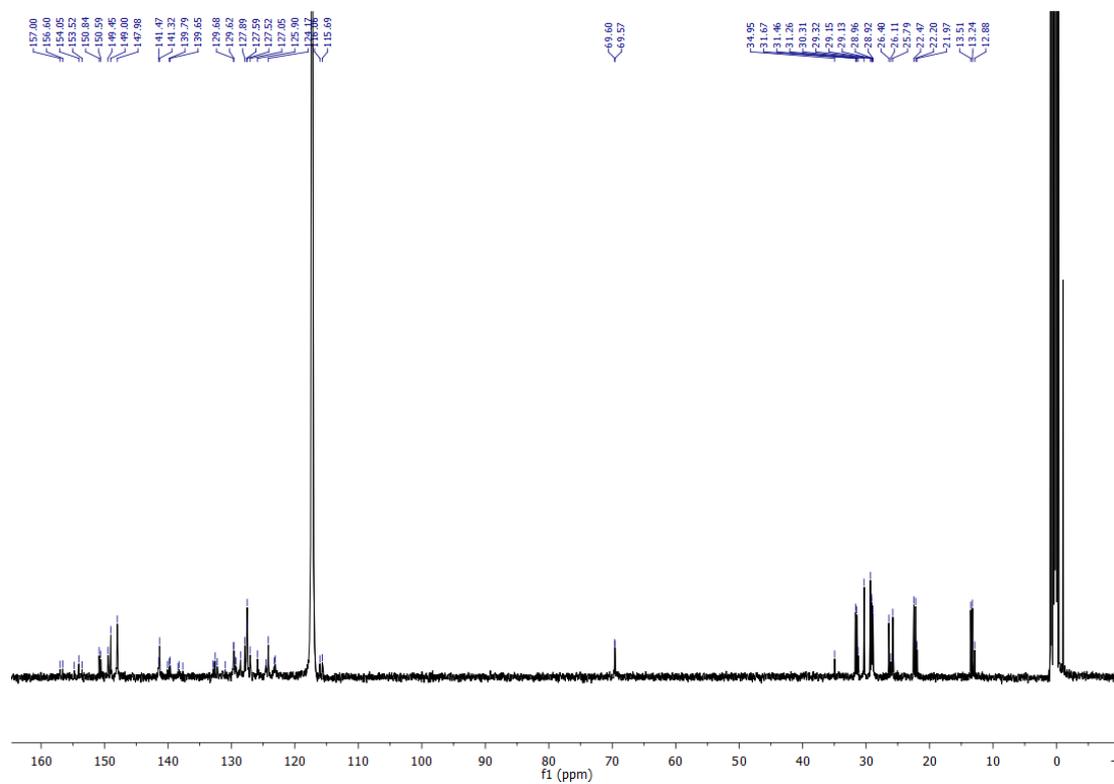


Figure S37. ¹³C NMR (400 MHz) spectrum of complex [Zn₁₂LD₆].

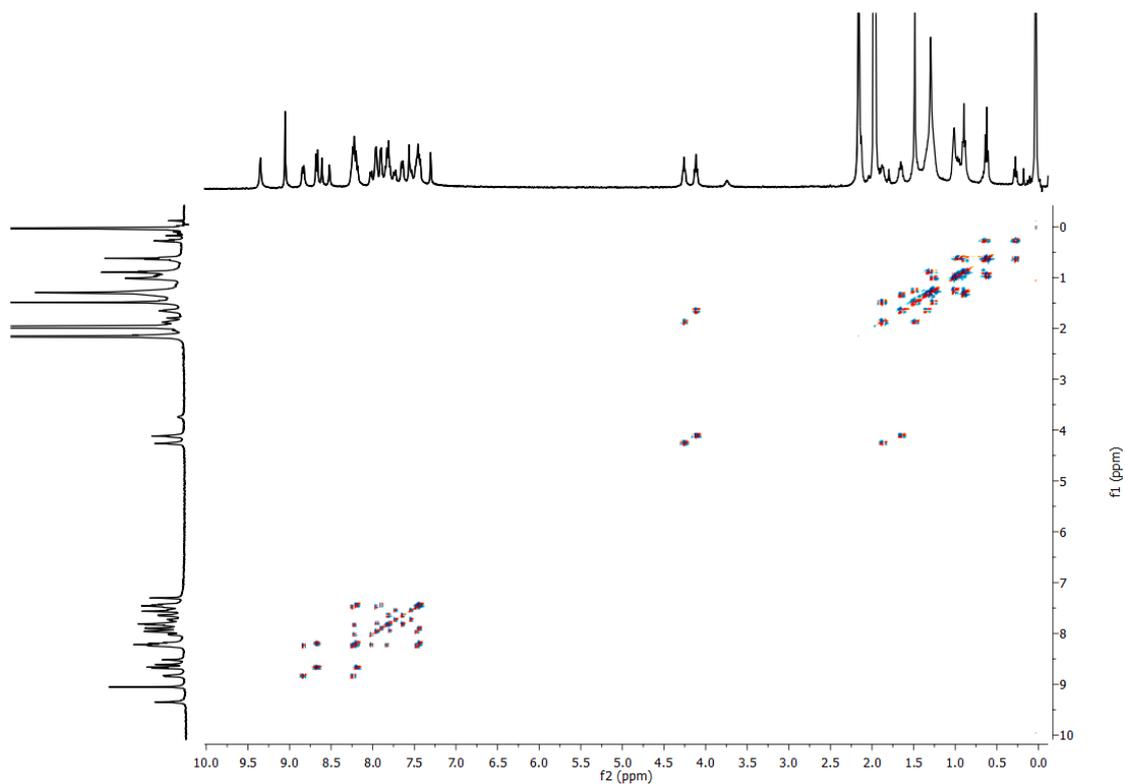


Figure S38. 2D COSY NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LD}_6]$.

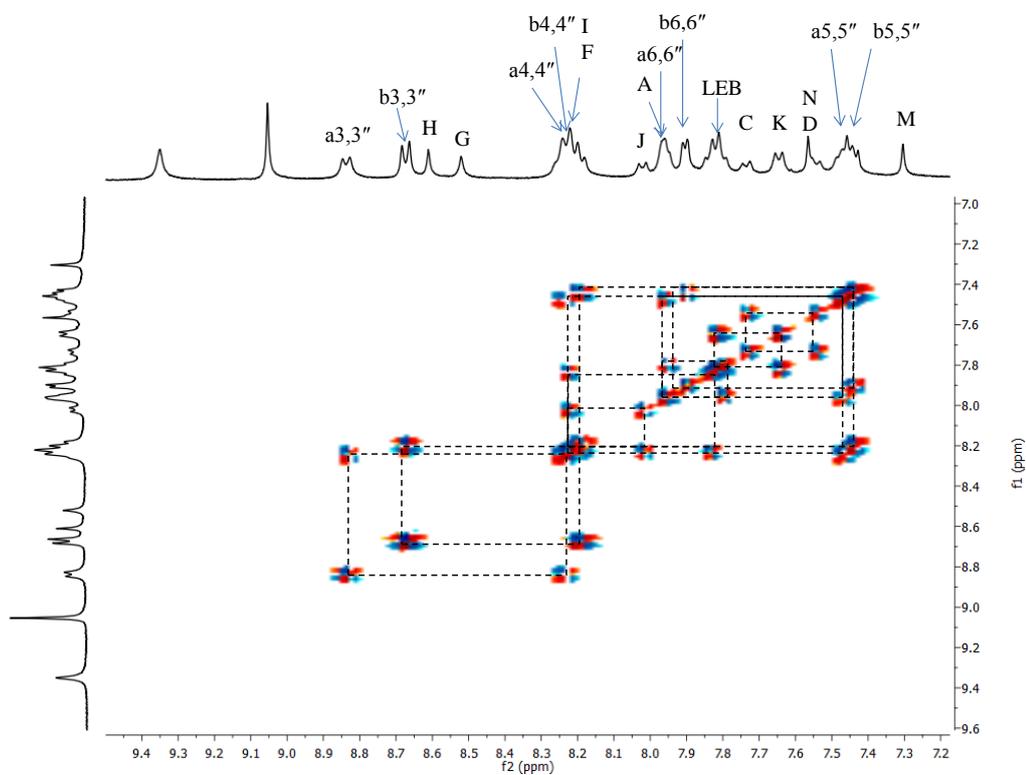


Figure S39. 2D COSY NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LD}_6]$ (aromatic region).

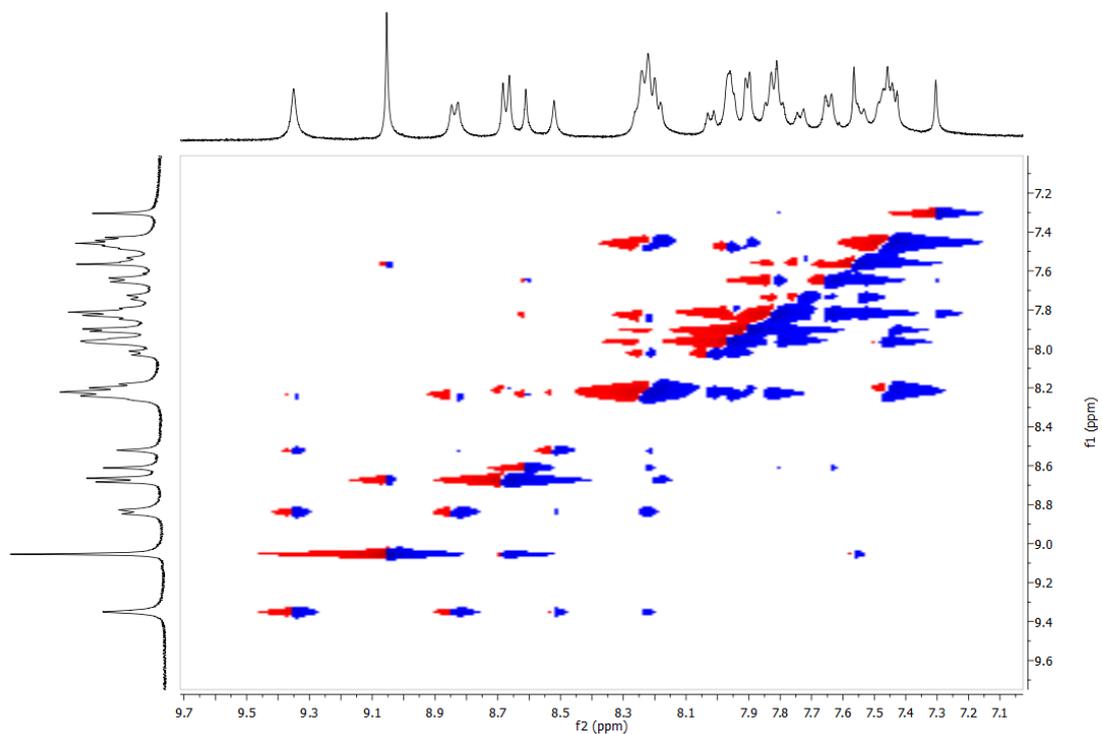


Figure S40. 2D NOESY NMR (400 MHz) spectrum of complex $[\text{Zn}_{12}\text{LD}_6]$ (aromatic region).

9. ESI-MS of multiple macrocycles assembled by ditopic tpy ligand **6** with Zn^{2+} .

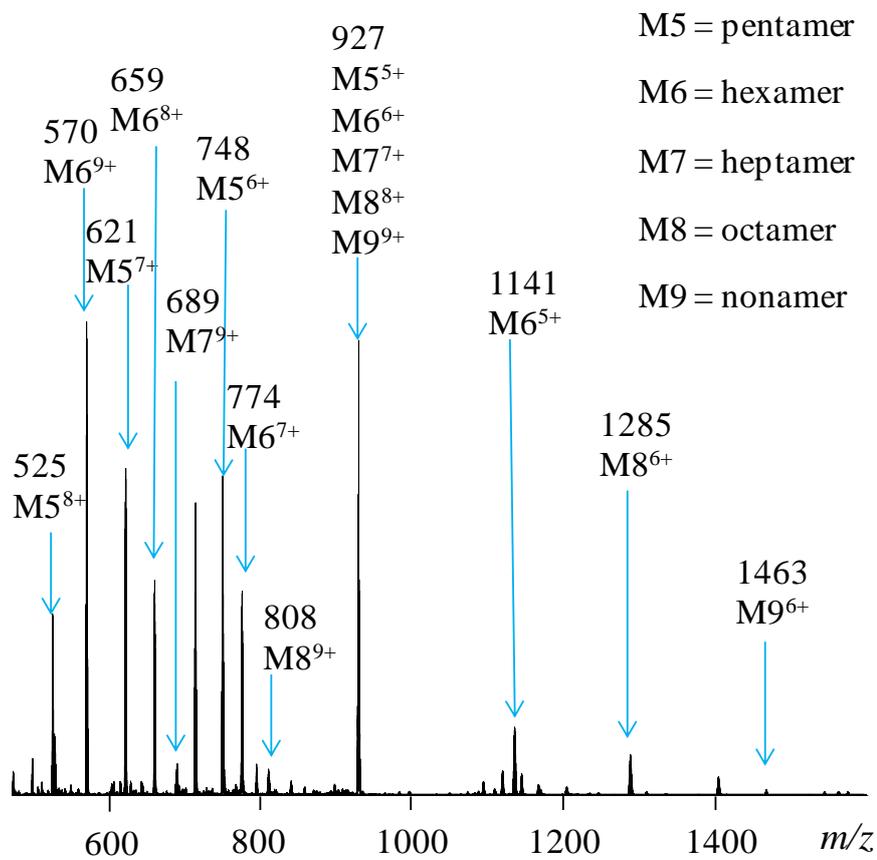


Figure S41. ESI-MS of multiple macrocycles assembled by ditopic tpy ligand **6** with Zn^{2+} .

10. STM images.

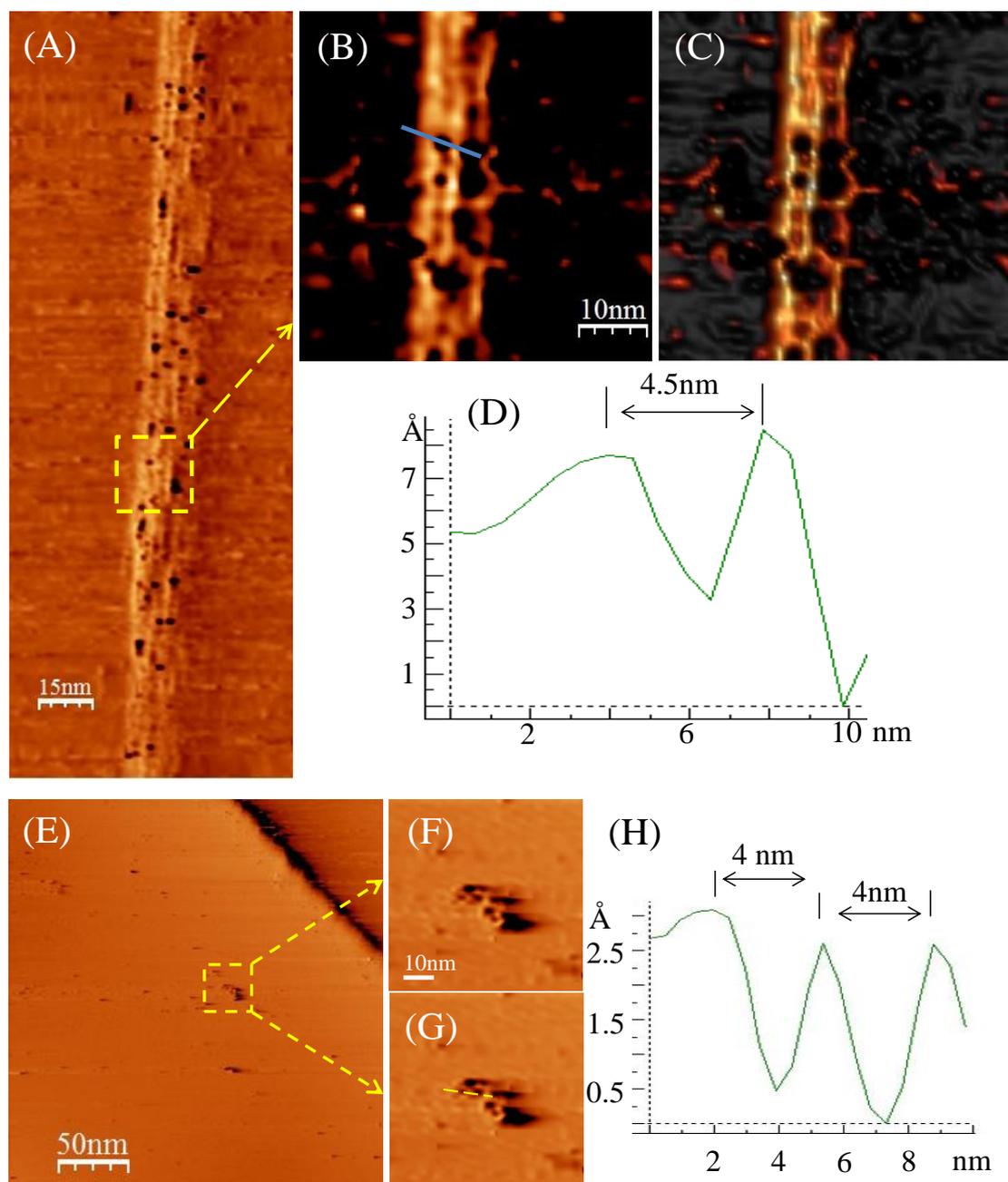


Figure S42. STM images of complex $[\text{Zn}_{12}\text{LC}_6]$ on HOPG.

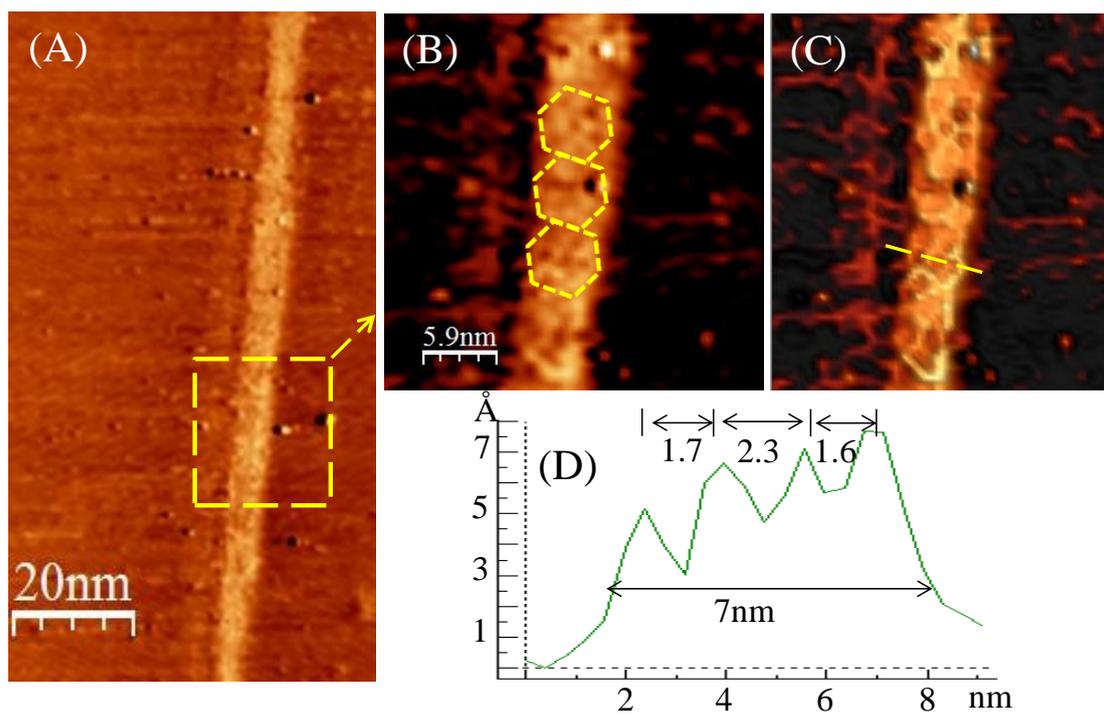


Figure S43. STM images of complex $[\text{Zn}_{12}\text{LD}_6]$ on HOPG.

11. TEM images.

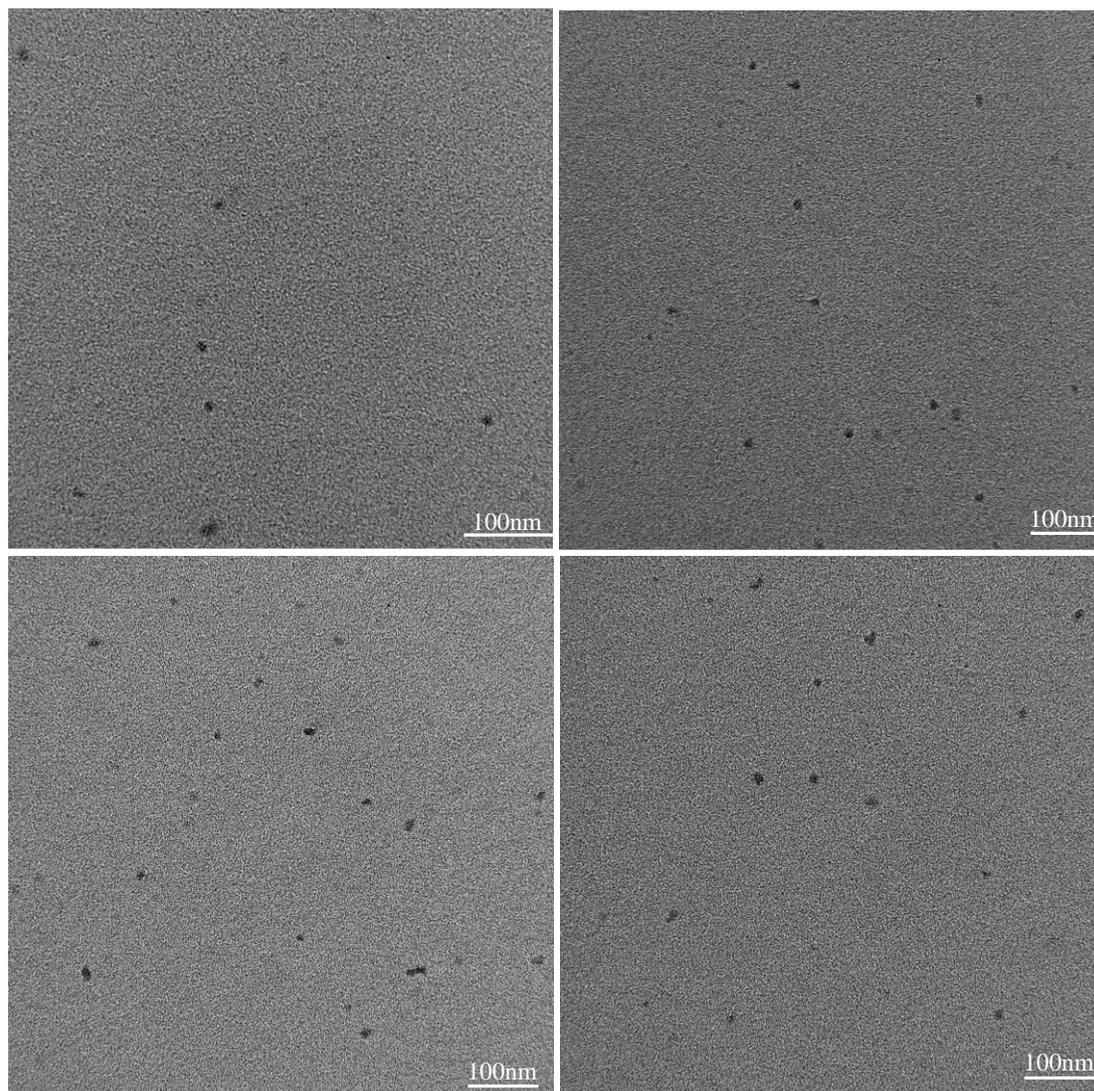


Figure S44. TEM images of complex $[\text{Zn}_{12}\text{LB}_6]$.

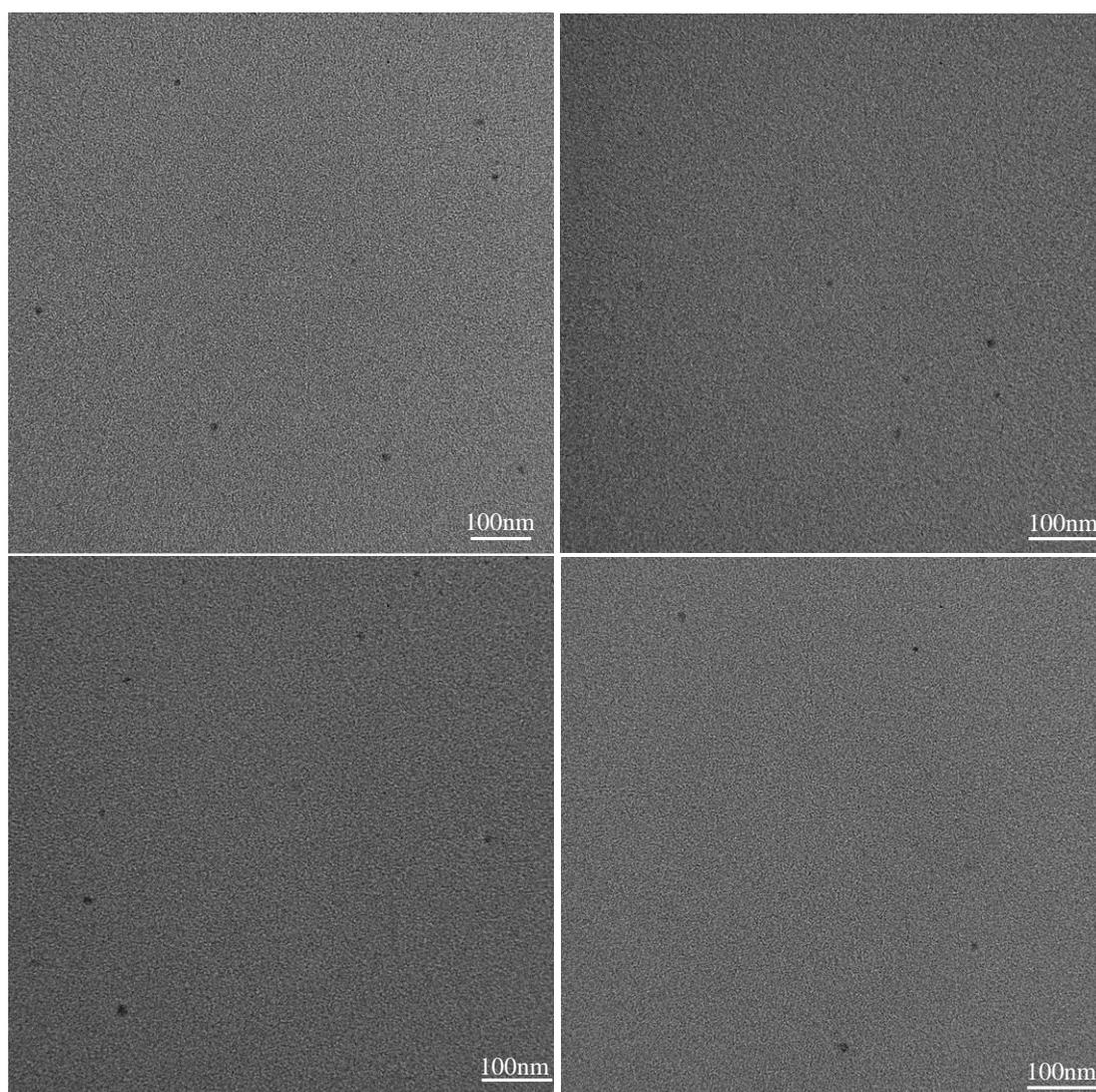


Figure S45. TEM images of complex $[\text{Zn}_{12}\text{LC}_6]$.

12. Reference

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