Electronic Supplementary Material (ESI) for ChemComm.

Facile synthesis of multicomponent heterobimetallic metallomacrocycles through selective metal-ligand coordination

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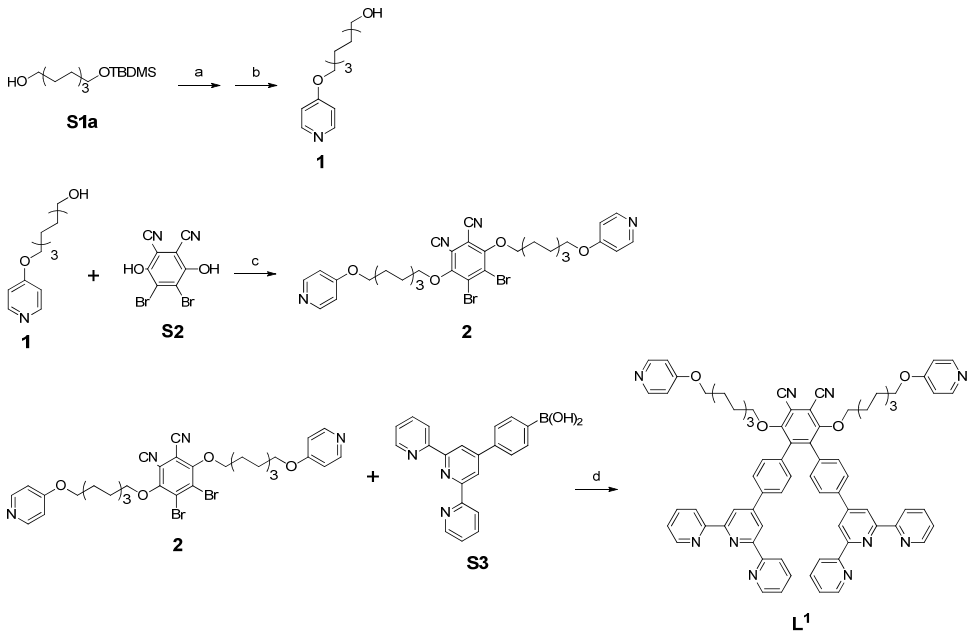
Materials and Methods. Unless otherwise noted, reagents and solvents were used as received from Fisher Scientific and Sigma-Aldrich without further purification. Compounds **S1a**, **S1b**, **S2**, **S3**, **S4**, and **S5** were prepared by following the reported procedures.[1-5] Column chromatography was conducted using silica gel (75-200 μm) from Fuji Silysia GS series or basic Al_2O_3 (50-200 μm) from Acros. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Varian Mercury NMR 400 spectrometer, where chemical shifts (δ in ppm) were determined with respect to the nondeuterated solvents as a reference. ^{31}P and 2D NMR spectra were recorded at 25 °C on a Bruker NMR 500 spectrometer or a Varian Mercury NMR 400 spectrometer. Atomic force microscopy (AFM) was conducted on a Bruker Dimension Icon AFM system with ScanAsyst and the data were processed by NanoScope Analysis version 1.5 (Bruker Software, Inc.). AFM samples were prepared by spin-coating (500 rpm for 1 min) a sample solution (1×10^{-8} M) on a freshly cleaved mica surface. Transmission electron microscope (TEM) images were recorded on a Hitachi Model H-7650 microscope operated at 120 kV. TEM samples were prepared by drop-casting a sample solution (1×10^{-6} M) onto a carbon-coated copper grid and dried *in vacuo* for 24 h.

Mass Spectrometry and Ion Mobility. ESI mass spectrometry and traveling wave ion-mobility (TWIM) experiments were conducted on a Waters Synapt HDMS G2 instrument with a LockSpray ESI using the reported parameters.[6-7] Cold-spray ionization (CSI) experiments were performed on a Thermo Finnigan LCQ Classic LC/MS/MS spectrometer. An in-house fabricated nib was utilized for paper spray and liquid nitrogen was used to cool down the nebulizing gas.[8] All samples were dissolved in MeCN or MeCN/$MeNO_2$ (1:1, v/v) and then infused into the ESI source at a flow rate of 6 μL/min by a syringe pump (KDS-100, KD Scientific). Matrix-assisted laser desorption/ionization coupled with time-of-flight detection mass spectrometry (MALDI-TOF MS) was conducted on a Bruker autoflex™ speed MALDI TOF/TOF mass spectrometer with a 355 nm frequency tripled Nd:YAG SmartBeam® laser. 1 μL of 2,5-dihydroxybenzoic acid (DHB) matrix solution (10 mg/mL in CH_3CN) or 1 μL of α-cyano-4-hydroxycinnamic acid (CHCA) matrix solution (10 mg/mL in a mixture of MeCN/H_2O/TFA = 50/49.9/0.1 wt%) was deposited on a MALDI plate and air-dried. Aliquots of a sample solution (1 mg/mL in $CHCl_3$) were added onto the matrix spots for the measurements acquired in reflection mode.

Molecular Modeling. Energy-minimized structures were obtained following the same settings in the literature.[9] Calculations were proceeded with Anneal and Geometry Optimization functions in Forcite module of Materials Studio version 7.0 program

(Accelrys Software, Inc.). For each structure, 200 conformations after annealing were generated and converted to the corresponding collision cross-sections using projection approximation (PA) and trajectory method (TM) in MOBCAL.[10-11]



Scheme S1. Synthesis of ligand $\mathbf{L^1}$. *Reagents and conditions*: (a) 4-hydroxypyridine, PPh_3, DIAD, 25 °C; (b) TBAF, THF, 0 °C; (c) PPh_3, DIAD, 25 °C; (d) $Pd(PPh_3)_4$, Na_2CO_3, PhMe/H_2O/*t*-BuOH (3:3:1, v/v/v), reflux.

Compound **1**

To a solution of **S1a** (3.0 g, 11.5 mmol), 4-hydroxypyridine (1.4 g, 14.4 mmol), and triphenylphosphine (3.8 g, 14.4 mmol) in anhydrous THF (80 mL), a solution of DIAD (2.9 g, 14.4 mmol) in THF (25 mL) was added dropwise at 0 °C. The resulting dark-green solution was allowed to warm to 25 °C and the mixture was stirred for additional 24 h. The mixture was evaporated to dryness under reduced pressure and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc = 20:1, v/v) to give the crude product, which was dissolved in THF (20 mL). The solution was treated with TBAF (1M in THF, 17.3 mL, 17.3 mmol) at 0 °C and stirred at 25 °C for 2 h. The solvent was removed *in vacuo* and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc = 20:1, v/v) to afford **1** (1.3 g, 5.6 mmol) in 49 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.36 (s, 2H), 6.76 (d, J = 5.3 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 3.60 (t, 2H), 2.25 (s, 1H), 1.82–1.66 (m, 2H), 1.59–1.48 (m, 2H), 1.49–1.37 (m,

2H), and 1.37–1.26 (m, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.34, 151.03, 110.52, 68.08, 62.98, 32.95, 29.50, 29.46, 29.04, 26.05, and 25.90. MALDI-TOF-MS: calcd for $C_{13}H_{22}NO_2$ $[M+H]^+$: *m/z* = 224.1651; found: 224.1627.

Compound **2**

By a similar procedure to that for **1**, **2** was obtained in 29% yield (0.2 g, 0.1 mmol) from **S2** (0.1 g , 0.3 mmol), **1** (0.3 g, 1.4 mmol), triphenylphosphine (0.4 g, 1.4 mmol), and DIAD (0.3 g, 1.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.38 (d, J = 6.2 Hz, 4H), 6.77 (dd, J = 5.1 and 1.2 Hz, 4H), 4.17 (t, J = 6.4 Hz, 4H), 3.98 (t, J = 6.5 Hz, 4H), 1.93–1.83 (m, 4H), 1.83–1.73 (m, 4H), 1.59–1.48 (m, 4H), 1.49–1.42 (m, 4H), and 1.42–1.34 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.39, 156.58, 151.04, 129.87, 112.58, 110.54, 109.46, 76.85, 68.08, 30.14, 29.35, 29.04, 26.05, and 25.78. MALDI-TOF-MS: calcd for $C_{34}H_{41}Br_2N_4O_4$ $[M+H]^+$: *m/z* = 727.1495; found: 727.1489.

Compound $\mathbf{L^1}$

To a degassed two-neck flask containing **2** (0.1 g, 0.2 mmol), 4′-(4-boronophenyl)-2,2′:6′,2″-terpyridine (0.2 g, 0.5 mmol), and Na_2CO_3 (0.1 g, 0.9 mmol), a mixed solvent (350 mL) of toluene/H_2O/*t*-BuOH (3:3:1, v/v/v) was added. After being purged with N_2 for 30 min, $Pd(PPh_3)_4$ (40.0 mg, 33.0 μmol) was added into the mixture, which was then refluxed for 1 day under N_2. After cooling to 25 °C, the mixture was extracted with $CHCl_3$. The combined organic extract was dried over anhydrous $MgSO_4$ and then evaporated to dryness under reduced pressure. The residue was subjected to column chromatography (Al_2O_3, $CHCl_3$) and then recrystallized by $CHCl_3$/MeOH to give $\mathbf{L^1}$ in 51% yield (0.1 g, 0.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.67 (s, 4H), 8.61 (d, J = 4.6 Hz, 4H), 8.57 (d, J = 8.0 Hz, 4H), 8.28 (dd, J = 5.6 and 0.7 Hz, 4H), 7.86–7.75 (m, 8H), 7.28 (dd, J = 4.4 and 3.0 Hz, 4H), 7.20 (d, J = 8.1 Hz, 4H), 6.60 (d, J = 6.3 Hz, 4H), 3.72–3.64 (m, 8H), 1.57–1.40 (m, 8H), 1.26–1.17 (m, 4H), and 1.17–1.01 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.21, 156.92, 156.15, 156.11, 150.94, 149.23, 149.16, 142.33, 138.18, 137.11, 134.46, 131.08, 127.12, 124.13, 121.49, 118.77, 113.56, 110.41, 110.04, 76.01, 67.91, 29.97, 29.34, 29.17, 28.89, 25.92, and 25.63. MALDI-TOF-MS: calcd for $C_{76}H_{69}N_{10}O_4$ $[M+H]^+$: *m/z* = 1185.5503; found: 1185.5525.

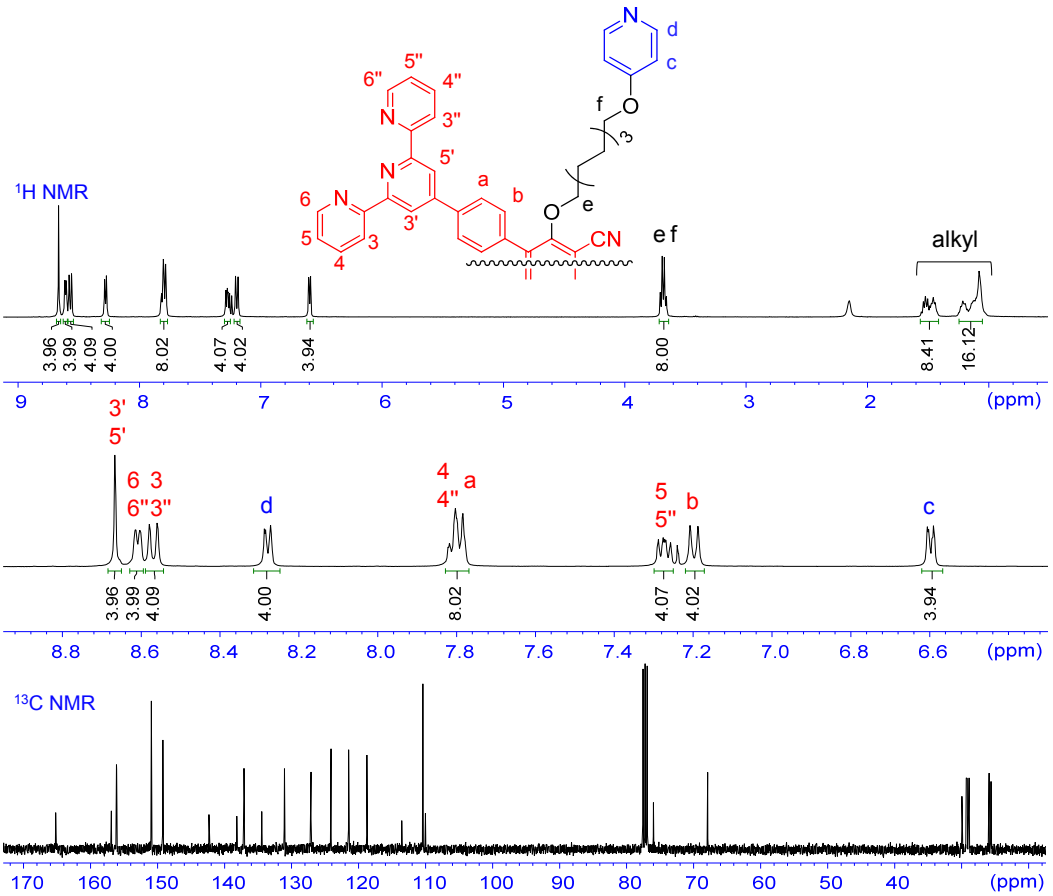


Figure S1. ^{1}H and ^{13}C NMR spectra of **L^{1}**.

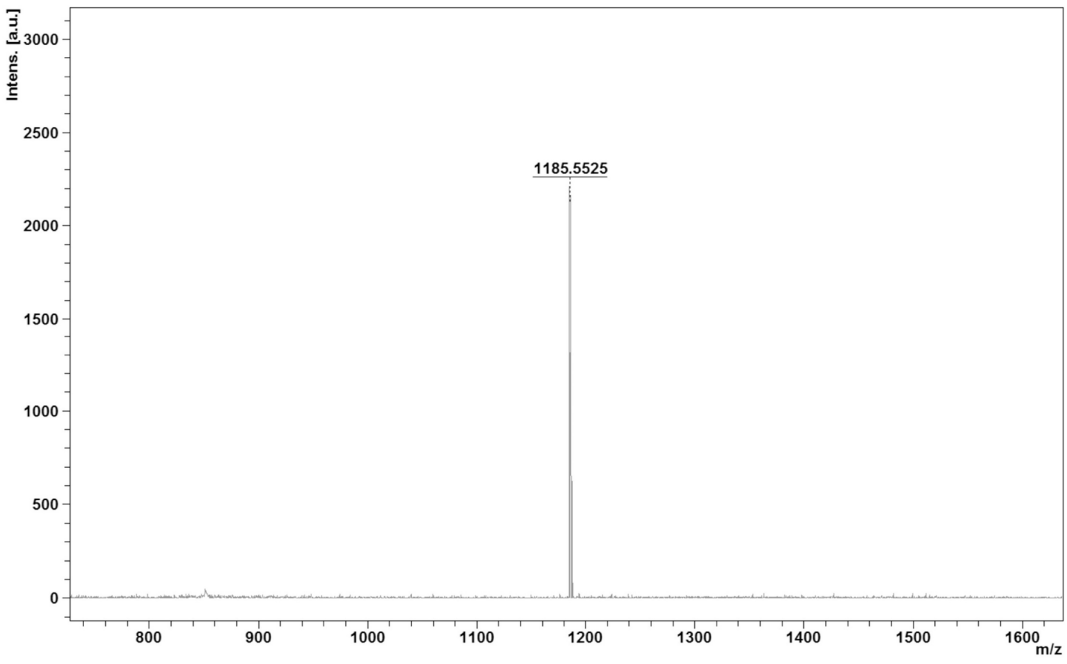
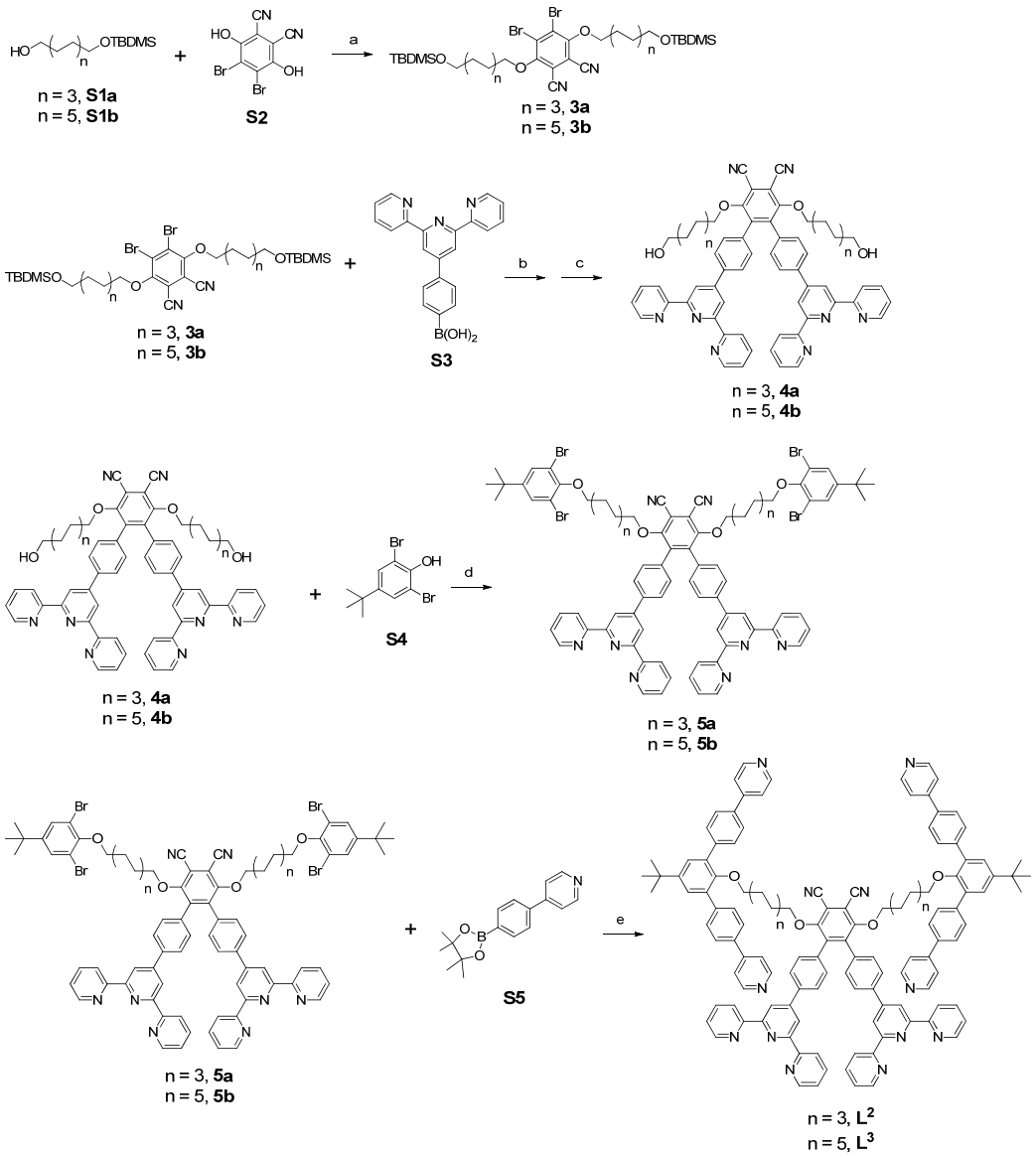


Figure S2. MALDI-TOF MS spectrum of **L^{1}**.



Scheme S2. Synthesis of ligands $\mathbf{L^2}$ and $\mathbf{L^3}$. *Reagents and conditions*: (a) PPh_3, DIAD, 25 °C; (b) $Pd(PPh_3)_4$, Na_2CO_3, PhMe/H_2O/*t*-BuOH (3:3:1, v/v/v), reflux; (c) TBAF, THF, 0 °C; (d) PPh_3, DIAD, 25 °C; (e) $Pd(PPh_3)_4$, Na_2CO_3, PhMe/H_2O/*t*-BuOH (3:3:1, v/v/v), reflux.

Compound **3a**

To a solution of **S1a** (4.9 g, 18.9 mmol), **S2** (2.0 g, 6.3 mmol) and triphenylphosphine (5.0 g, 18.9 mmol) in anhydrous THF (20 mL), a THF solution (20 mL) of DIAD (5.1 g, 25.4 mmol) was then added dropwise at 0 °C. The resulting dark-green solution was allowed to warm to 25 °C and the mixture was stirred for additional 24 h. The solvent

was evaporated under reduced pressure and the residue was purified by column chromatography (SiO_2, EtOAc/hexane = 1/20, v/v) to afford **3a** (1.8 g, 2.3 mmol) in 36% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.16 (t, J = 6.5 Hz, 4H), 3.56 (t, J = 6.5 Hz, 4H), 1.97–1.82 (m, 4H), 1.54–1.44 (m, 8H), 1.41–1.20 (m, 12H), 0.86 (s, 18H), and 0.02 (d, J = 0.7 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.53, 129.79, 112.52, 109.39, 76.87, 63.41, 33.00, 30.13, 29.46, 29.45, 26.18, 25.91, 25.77, 18.55, and -5.05. ESI-MS: calcd for $C_{36}H_{63}Br_2N_2O_4Si_2$ $[M+H]^+$: m/z = 801.2688; found: 801.2650.

Compound **3b**

By a similar procedure to that for **3a**, **3b** was obtained in 45% yield (1.3 g, 1.4 mmol) from **S1a** (3.0 g, 9.4 mmol), **S2** (1.0 g, 3.1 mmol), triphenylphosphine (2.5 g, 9.5 mmol), and DIAD (1.9 g, 9.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.17 (t, J = 6.6 Hz, 4H), 3.58 (t, J = 6.6 Hz, 4H), 1.92–1.78 (m, 4H), 1.53–1.43 (m, 8H), 1.41–1.19 (m, 28H), 0.87 (s, 18H), and 0.03 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.62, 129.87, 112.61, 109.43, 63.59, 33.14, 30.21, 29.87, 29.81, 29.73, 29.69, 29.53, 26.24, 26.05, 25.88, 18.63, and -5.00. ESI-MS: calcd for $C_{44}H_{79}Br_2N_2O_4Si_2$ $[M+H]^+$: m/z = 913.3945; found: 913.3961.

Compound **4a**

To a degassed two-neck flask containing **3a** (0.8 g, 1.0 mmol), 4′-(4-boronophenyl)-2,2′:6′,2″-terpyridine (1.1 g, 3.0 mmol), and Na_2CO_3 (3.2 g, 30.2 mmol), a mixed solvent (350 mL) of toluene/H_2O/*t*-BuOH (3:3:1, v/v/v) was added. After being purged with N_2 for 30 min, $Pd(PPh_3)_4$ (0.2 g, 0.2 mmol) was added into the mixture, which was then refluxed for 1 day under N_2. After cooling to 25 °C, the mixture was extracted with $CHCl_3$. The combined organic extract was dried over anhydrous $MgSO_4$ and then evaporated to dryness under reduced pressure. The residue was subjected to column chromatography (Al_2O_3, $CHCl_3$) and then recrystallized by $CHCl_3$/MeOH to give the crude product, which was dissolved in THF (20 mL). The solution was treated with TBAF (1 M in THF, 4.6 mL, 4.6 mmol) at 0 °C. The resulting solution was allowed to warm to 25 °C and then stirred for 12 h. The solvent was evaporated under reduced pressure and the residue was recrystallized by $CHCl_3$/MeOH to give **4a** as an off-white solid (0.7 g, 0.7 mmol) in 70% yeild. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.64 (s,

4H), 8.62 (d, J = 4.8 Hz, 4H), 8.57 (d, J = 8.0 Hz, 4H), 7.86–7.79 (m, 8H), 7.34–7.26 (m, 4H), 7.19 (d, J = 8.3 Hz, 4H), 3.68 (t, J = 6.2 Hz, 4H), 3.44–3.36 (m, 4H), 2.48 (s, 2H), 1.50–1.40 (m, 4H), 1.35–1.22 (m, 4H), 1.18–1.08 (m, 4H), and 1.08–0.92 (m, 12H).^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.89, 156.22, 156.08, 149.21, 149.03, 142.36, 137.88, 137.22, 134.54, 131.15, 127.05, 124.16, 121.64, 118.80, 113.60, 109.96, 76.02, 62.79, 32.84, 29.89, 29.26, 29.06, 25.74, and 25.54. MALDI-TOF-MS: calcd for $C_{66}H_{63}N_8O_4$ $[M+H]^+$: m/z = 1031.4972; found: 1031.4966.

Compound **4b**

By a similar procedure to that for **4a**, **4b** was obtained in 71% yield (1.1 g, 1.0 mmol) from **3a** (1.2 g, 1.4 mmol), 4′-(4-boronophenyl)-2,2′:6′,2″-terpyridine (1.5 g, 4.2 mmol), and Na_2CO_3 (0.9 g, 8.5 mmol), and $Pd(PPh_3)_4$ (0.3 g, 0.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.65 (s, 4H), 8.62 (d, J = 4.8 Hz, 4H), 8.59 (d, J = 7.9 Hz, 4H), 7.84–7.76 (m, 8H), 7.32–7.26 (m, 4H), 7.19 (d, J = 8.4 Hz, 4H), 3.67 (t, J = 6.4 Hz, 4H), 3.52 (t, J = 6.7 Hz, 4H), 1.81 (s, 2H), 1.50–1.35 (m, 8H), and 1.26–0.99 (m, 32H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.93, 156.25, 156.13, 149.26, 142.34, 138.24, 137.11, 134.48, 131.09, 127.17, 124.09, 121.55, 118.93, 113.62, 110.00, 76.15, 63.19, 32.97, 30.01, 29.64, 29.60, 29.59, 29.50, 29.31, 25.85, and 25.71. MALDI-TOF-MS: calcd for $C_{74}H_{79}N_8O_4$ $[M+H]^+$: m/z = 1143.6224; found: 1143.6341.

Compound **5a**

By a similar procedure to that for **3a**, **5a** was obtained in 60% yield (95.0 mg, 59.0 μmol) from **4a** (0.1 g, 0.1 mmol), **S4** (0.1 g, 0.4 mmol), triphenylphosphine (0.1 g, 0.4 mmol), and DIAD (80.2 mg, 0.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.67 (s, 4H), 8.62 (d, J = 3.9 Hz, 4H), 8.59 (d, J = 7.9 Hz, 4H), 7.84–7.76 (m, 8H), 7.40 (s, 4H), 7.30–7.25 (m, 4H), 7.21 (d, J = 8.3 Hz, 4H), 3.78 (t, J = 6.5 Hz, 4H), 3.67 (t, J = 6.4 Hz, 4H), 1.73–1.59 (m, 4H), 1.54–1.43 (m, 4H), 1.38–1.30 (m, 4H), 1.27–1.19 (m, 22H), and 1.13 (s, 8H).^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.94, 156.26, 156.16, 151.15, 149.71, 149.28, 142.33, 138.32, 137.05, 134.45, 131.09, 129.96, 127.21, 124.06, 121.52, 118.95, 118.06, 113.62, 110.05, 76.13, 73.56, 34.75, 31.38, 30.09, 30.03, 29.48, 29.33, 25.97, and 25.74. MALDI-TOF-MS: calcd for $C_{86}H_{83}Br_4N_8O_4$ $[M+H]^+$: m/z = 1607.3271; found: 1607.3265.

Compound **5b**

By a similar procedure to that for **3a**, **5b** was obtained in 71% yield (1.1 g, 0.6 mmol) from **4b** (1.1 g, 0.9 mmol), **S4** (0.9 g, 2.8 mmol), triphenylphosphine (0.7 g, 2.8 mmol), and DIAD (0.6 g, 2.8 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.67 (s, 4H), 8.63 (d, J = 4.7 Hz, 4H), 8.61 (d, J = 7.9 Hz, 4H), 7.85–7.76 (m, 8H), 7.44 (s, 4H), 7.31–7.25 (m, 4H), 7.20 (d, J = 8.4 Hz, 4H), 3.88 (t, J = 6.7 Hz, 4H), 3.68 (t, J = 6.4 Hz, 4H), 1.49–1.41 (m, 4H), 1.39–1.31 (m, 4H), 1.25 (s, 18H), and 1.20–1.00 (m, 32H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.94, 156.24, 156.13, 151.20, 149.79, 149.25, 142.33, 138.26, 137.06, 134.45, 131.07, 130.01, 127.17, 124.06, 121.50, 118.89, 118.07, 113.60, 110.01, 76.15, 73.72, 34.76, 31.37, 30.21, 30.04, 29.75, 29.72, 29.61, 29.39, 26.02, and 25.76. MALDI-TOF-MS: calcd for $C_{94}H_{99}Br_4N_8O_4$ $[M+H]^+$: m/z = 1719.4523; found: 1719.4465.

Compound $\mathbf{L^2}$

By a similar procedure to that for $\mathbf{L^1}$, $\mathbf{L^2}$ was obtained in 65% yield (0.1 g, 47.2 μmol) from **S5** (0.1 g, 0.4 mmol), **5a** (0.1 g, 72.6 μmol), Na_2CO_3 (0.2 g, 1.9 mmol), and $Pd(PPh_3)_4$ (56.2 mg, 48.6 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.65–8.61 (m, 12H), 8.58 (d, J = 8.5 Hz, 4H), 8.56 (d, J = 8.0 Hz, 4H), 7.81–7.76 (m, 4H), 7.73 (d, J = 8.3 Hz, 4H), 7.71–7.63 (m, 16H), 7.53 (d, J = 6.3 Hz, 8H), 7.35 (s, 4H), 7.28–7.24 (m, 4H), 7.13 (d, J = 8.3 Hz, 4H), 3.51 (t, J = 6.2 Hz, 4H), 3.09 (t, J = 6.1 Hz, 4H), 1.37 (s, 18H), 1.31–1.20 (m, 4H), 1.09–0.99 (m, 4H), 0.95–0.87 (m, 4H), and 0.86–0.68 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.85, 156.17, 156.12, 152.13, 150.35, 149.21, 148.18, 147.10, 142.22, 140.44, 138.15, 137.04, 136.59, 134.70, 130.99, 130.48, 127.68, 127.08, 126.74, 124.04, 121.64, 121.47, 118.86, 110.02, 75.94, 73.54, 34.75, 31.71, 29.90, 29.86, 29.24, 29.09, 25.85, and 25.64. MALDI-TOF-MS: calcd for $C_{130}H_{115}N_{12}O_4$ $[M+H]^+$: m/z = 1907.9164; found: 1907.9126.

Compound $\mathbf{L^3}$

By a similar procedure to that for $\mathbf{L^1}$, $\mathbf{L^3}$ was obtained in 69% yield (0.1 g, 83.5 μmol) from **S5** (0.3 g, 1.1 mmol), **5b** (0.2 g, 0.1 mmol), Na_2CO_3 (0.1 g, 0.9 mmol), and $Pd(PPh_3)_4$ (34.0 mg, 33.6 μmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.66 (s, 4H), 8.63 (d, J = 5.9 Hz, 8H), 8.60 (d, J = 4.5 Hz, 4H), 8.57 (d, J = 8.0 Hz, 4H), 7.80–7.76 (m, 8H), 7.76–7.64 (m, 16H), 7.53 (d, J = 6.0 Hz, 8H), 7.38 (s, 4H), 7.28–7.21 (m, 4H),

7.19 (d, J = 8.1 Hz, 4H), 3.66 (t, J = 6.3 Hz, 4H), 3.18 (t, J = 6.1 Hz, 4H), 1.50–1.40 (m, 8H), 1.38 (s, 18H), and 1.13–0.66 (m, 32H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.94, 156.25, 156.13, 152.19, 150.41, 149.28, 149.25, 148.22, 147.21, 142.33, 140.48, 138.23, 137.03, 136.74, 134.78, 134.49, 131.08, 130.53, 127.77, 127.17, 126.81, 124.03, 121.68, 121.49, 118.92, 113.63, 110.06, 76.15, 73.68, 34.80, 31.75, 30.05, 29.97, 29.93, 29.72, 29.71, 29.69, 29.38, 29.31, 25.97, and 25.76. MALDI-TOF-MS: calcd for $C_{138}H_{131}N_{12}O_4$ $[M+H]^+$: m/z = 2020.0413; found: 2020.0424.

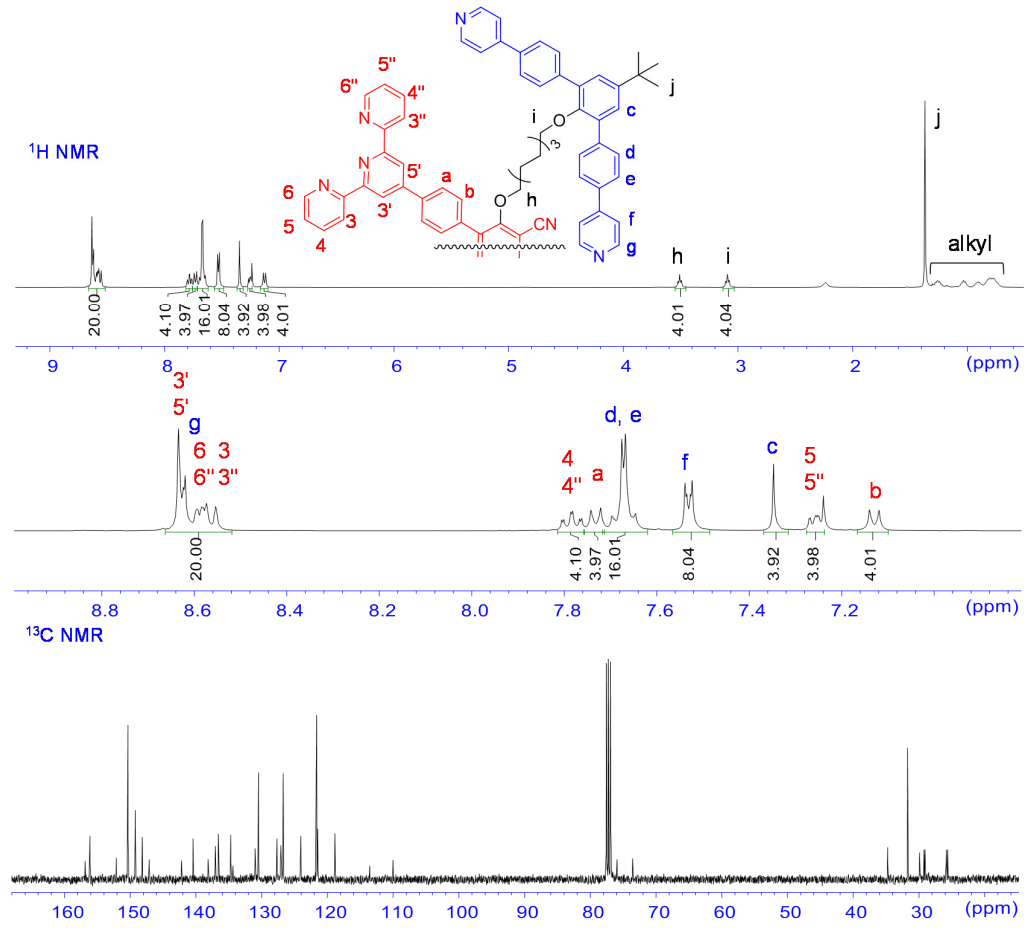


Figure S3. ^{1}H and ^{13}C NMR spectra of **L²**.

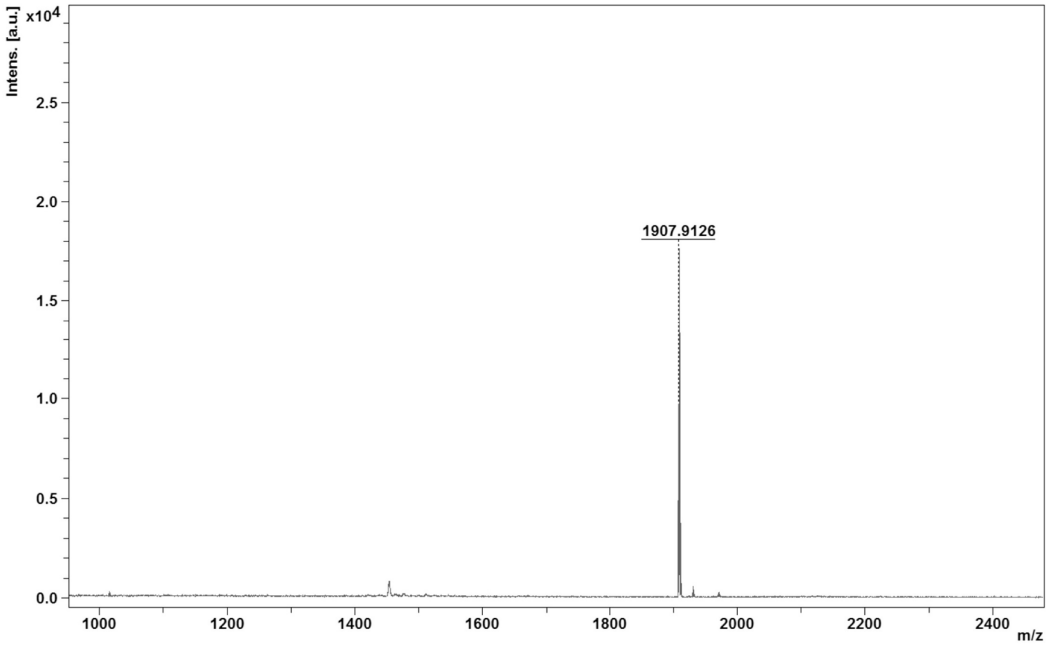


Figure S4. MALDI-TOF MS spectrum of **L²**.

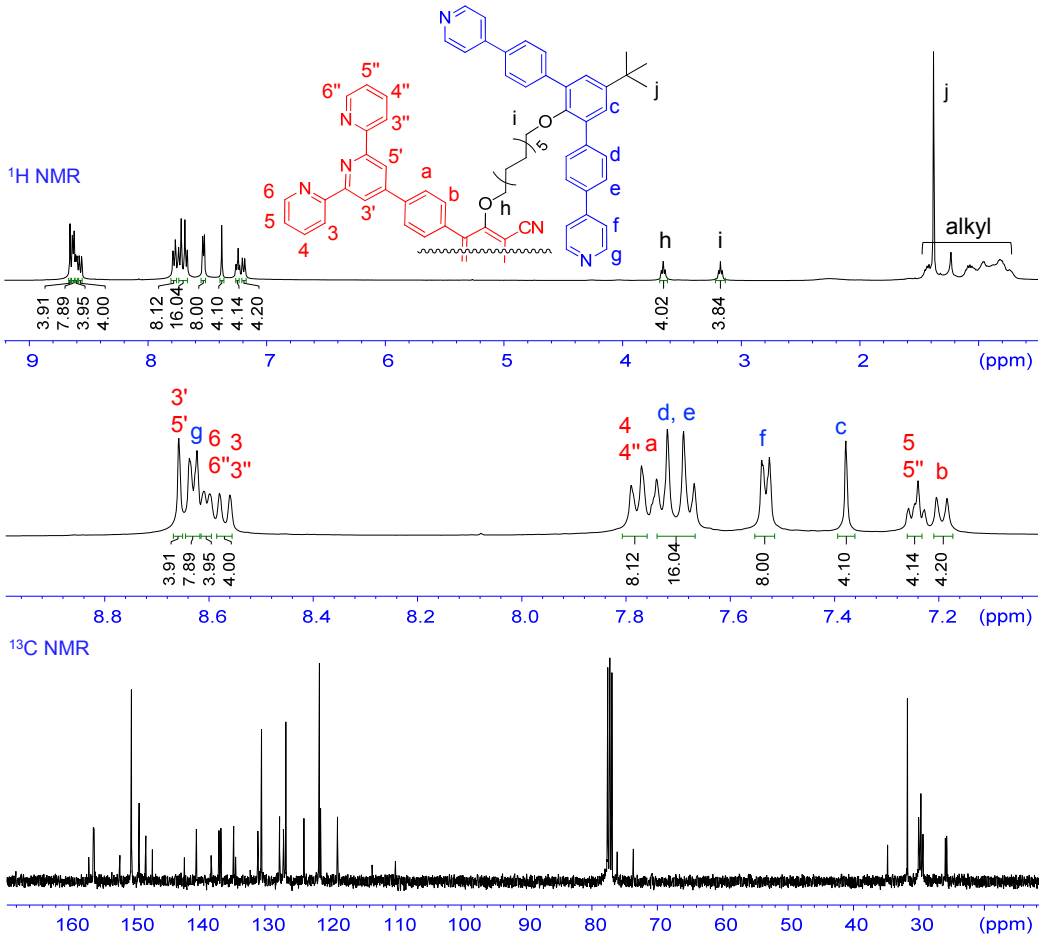


Figure S5. ^{1}H and ^{13}C NMR spectra of **L^{3}**.

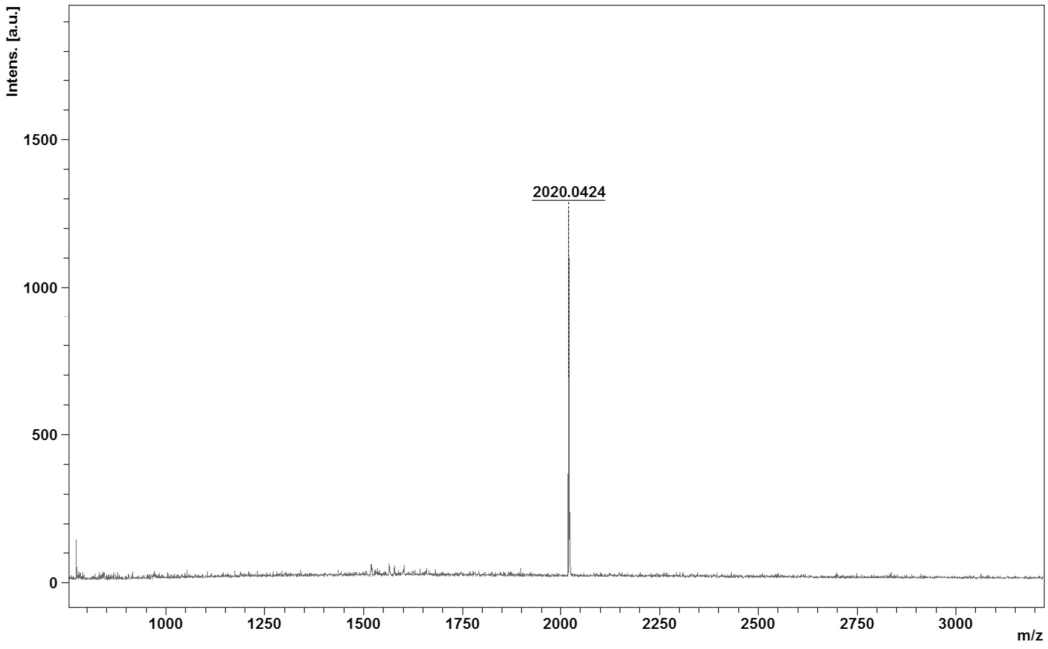
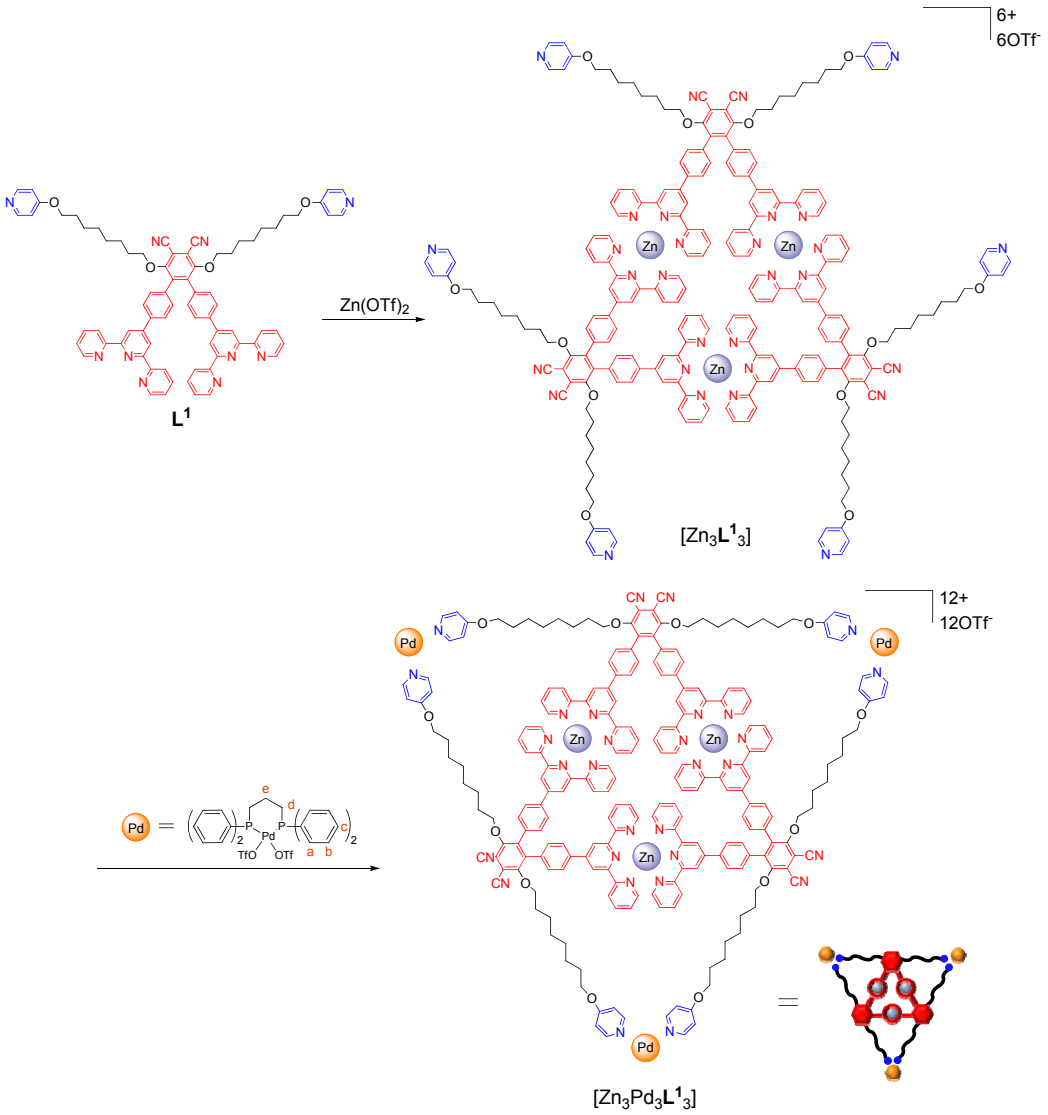


Figure S6. MALDI-TOF MS spectrum of **L^{3}**.

Complex Synthesis



Scheme S3. Synthesis of complexes $[Zn_3\mathbf{L}^1_3]$ and $[Zn_3Pd_3\mathbf{L}^1_3]$.

$[Zn_3\mathbf{L}^1_3]$

To a stirred solution of $\mathbf{L}^1$ (9.2 mg, 7.7 μmol) in $CHCl_3$ (5 mL), a solution of $Zn(OTf)_2$ (3.0 mg, 8.2 μmol) in MeOH (3 mL) was added. The mixture was stirred at 25 ºC for 1 h and then diethyl ether was added to the solution to precipitate the complex. The precipitate was filtered and then washed by H_2O to afford complex $[Zn_3\mathbf{L}^1_3]$ as a white solid (12.0 mg, 2.6 μmol) in 99% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.00 (s, 12H), 8.74 (d, J = 8.2 Hz, 12H), 8.21 (t, J = 7.4 Hz, 24H), 8.01 (t, J = 7.7 Hz, 12H), 7.79 (d, J = 5.0 Hz, 12H), 7.61 (d, J = 8.1 Hz, 12H), 7.32–7.24 (m, 12H), 6.58–6.52 (m,

12H), 3.98 (t, J = 6.0 Hz, 12H), 3.86 (t, J = 6.8 Hz, 12H), 1.66–1.51 (m, 24H), and 1.39–1.07 (m, 48H). ESI-MS (*m/z*): 1399.7247 $[M\text{-}3OTf]^{3+}$ (calcd *m/z* 1399.7606), 1012.4131 $[M\text{-}4OTf]^{4+}$ (calcd *m/z* 1012.3305), and 780.2885 $[M\text{-}5OTf]^{5+}$ (calcd *m/z* 780.2772).

$[Zn_3Pd_3\mathbf{L^1}_3]$ (Stepwise)

To a stirred CD_3CN solution (0.45 mL) of $[Zn_3\mathbf{L^1}_3]$ (6.0 mg, 1.3 μmol), a solution of $Pd(dppp)(OTf)_2$ (3.2 mg, 3.9 μmol) in CD_3CN (0.2 mL) was added. The mixture was stirred at 25 ºC for 3 h. The solvent was evaporated *in vacuo* to afford $[Zn_3Pd_3\mathbf{L^1}_3]$ (9.2 mg, 1.3 μmol) in 99% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.98 (s, 12H), 8.73 (d, J = 8.1 Hz, 12H), 8.27 (br d, J = 5.2 Hz, 12H), 8.20 (d, J = 8.1 Hz, 12H), 7.96 (br t, J = 7.8 Hz, 12H), 7.72 (br, 12H), 7.61 (d, J = 8.2 Hz, 12H), 7.59–7.31 (m, 60H), 7.22 (br, 12H), 6.33 (br, 12H), 3.99 (br t, J = 4.8 Hz, 12H), 3.63 (br, 12H), 3.06 (br, 12H), 2.18 (br, 6H), 1.66–1.50 (m, 12H), 1.43 (br, 12H), 1.17 (br, 36H), and 1.05 (br, 12H). ^{31}P NMR (162 MHz, CD_3CN): δ (ppm) 13.52 (s, 6P). ESI-MS (*m/z*): 2216.7979 $[M\text{-}3OTf]^{3+}$ (calcd *m/z* 2216.7205), 1625.3704 $[M\text{-}4OTf]^{4+}$ (calcd *m/z* 1625.3004), and 1270.4955 $[M\text{-}5OTf]^{5+}$ (calcd *m/z* 1270.4468).

$[Zn_3Pd_3\mathbf{L^1}_3]$ (One-pot)

To a stirred CD_3CN solution (0.45 mL) of $\mathbf{L^1}$ (6.0 mg, 5.1 μmol), a solution of $Pd(dppp)(OTf)_2$ (4.1 mg, 5.1 μmol) and $Zn(OTf)_2$ (1.8 mg, 5.1 μmol) in CD_3CN (0.2 mL) was added. The mixture was stirred at 25 ºC for 3 h. The solvent was evaporated *in vacuo* to afford $[Zn_3Pd_3\mathbf{L^1}_3]$ (11.9 mg, 1.7 μmol) in 99% yield.

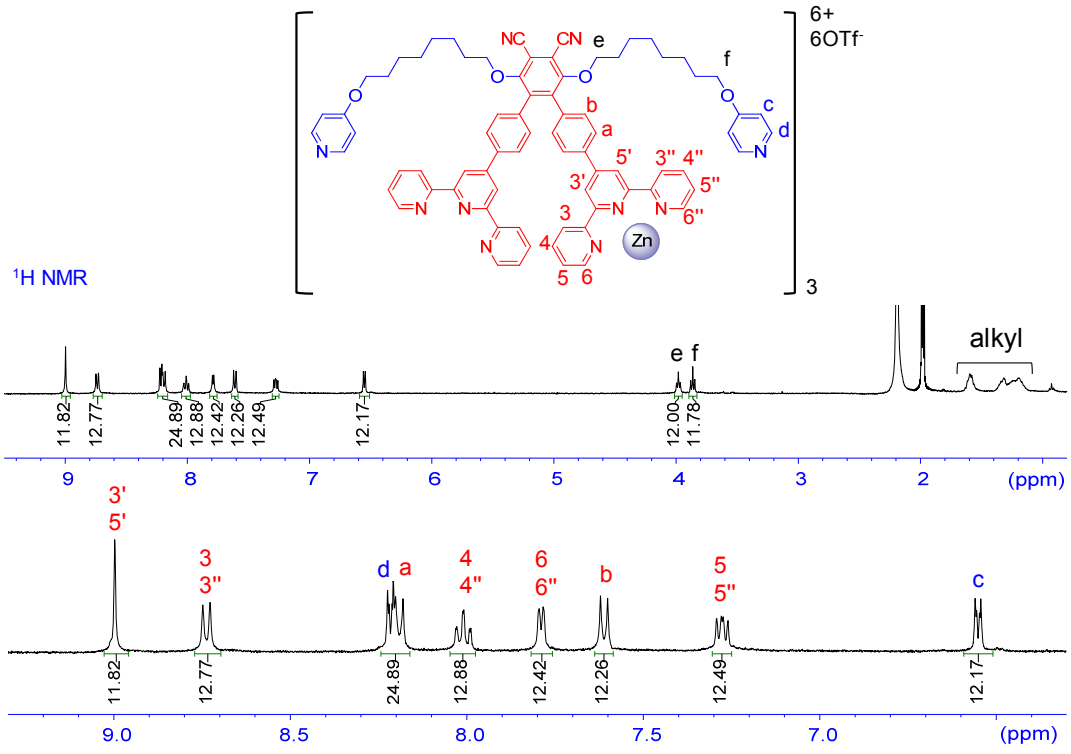


Figure S7. ^{1}H NMR spectra of [Zn_3**L**$^{1}_3$].

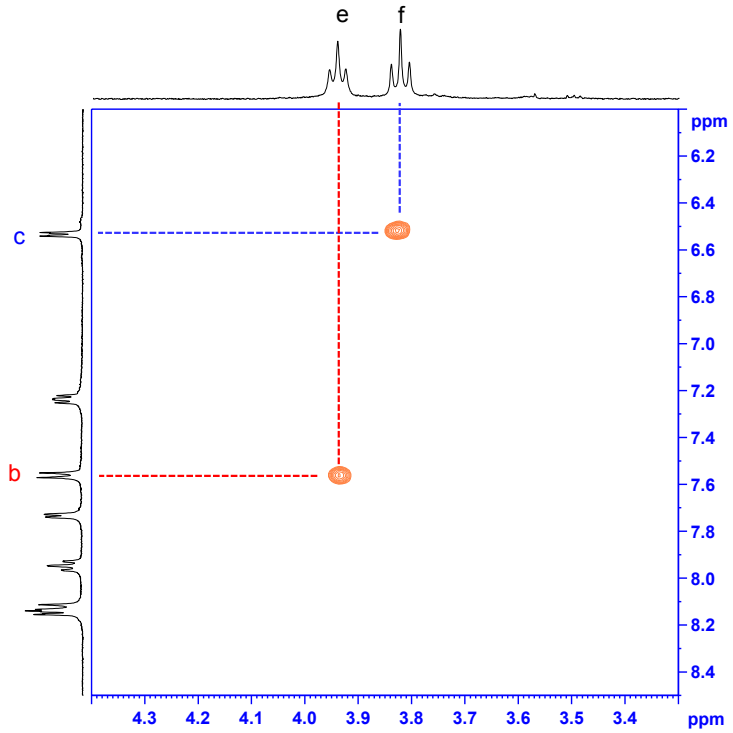


Figure S8. Partial NOESY spectrum of [Zn_3**L**$^{1}_3$].

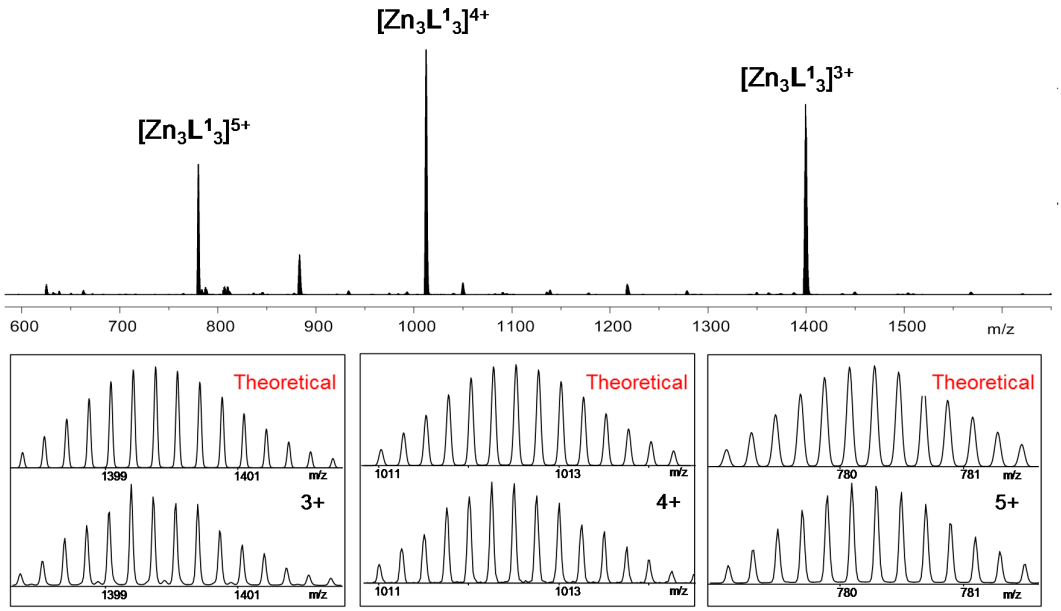


Figure S9. ESI-MS spectrum of [Zn_3**L**$^1_3$] and its experimental and theoretical isotope patterns.

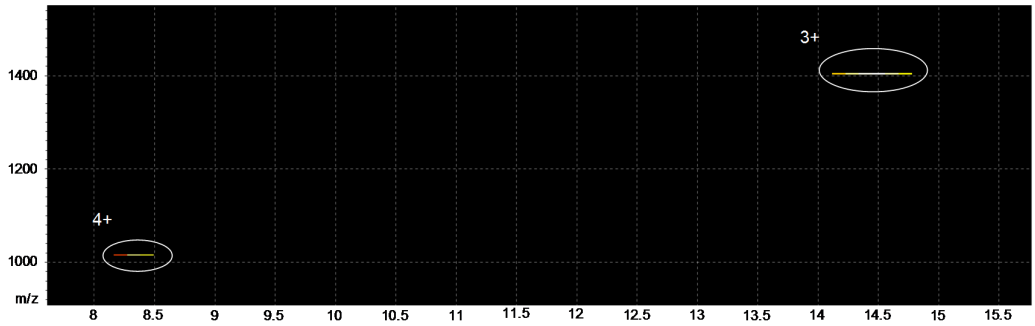


Figure S10. ESI-TWIM-MS plot of [Zn_3**L**$^1_3$].

Table S1. Experimental and calculated collision cross-sections of [Zn_3**L**$^1_3$].

Experimental and Calculated CCSs (Å^2)			
Charge	[Zn_3**L**$^1_3$]$^{3+}$	Charge	[Zn_3**L**$^1_3$]$^{4+}$
3+	667.6	4+	614.1
	Exp.	PA	TM
[Zn_3**L**$^1_3$]	640.9 (26.7)	627.0 (23.5)	733.0 (28.0)

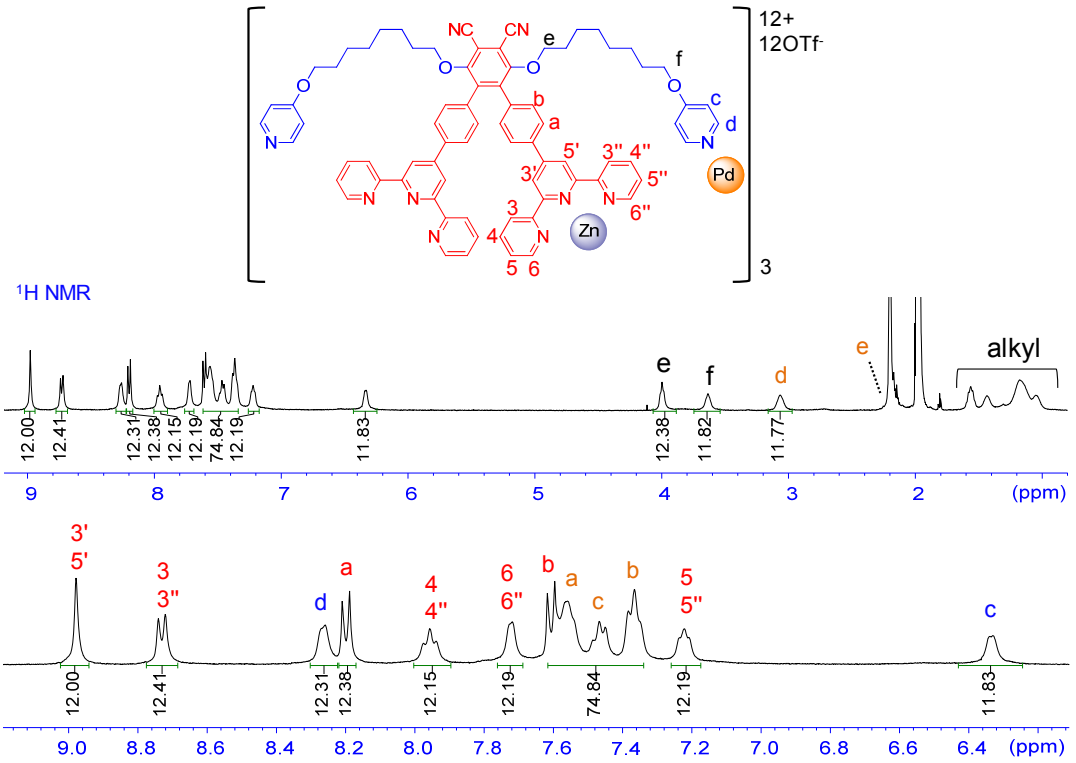


Figure S11. ^{1}H NMR spectra of [$Zn_3Pd_3\mathbf{L}^{1}_3$].

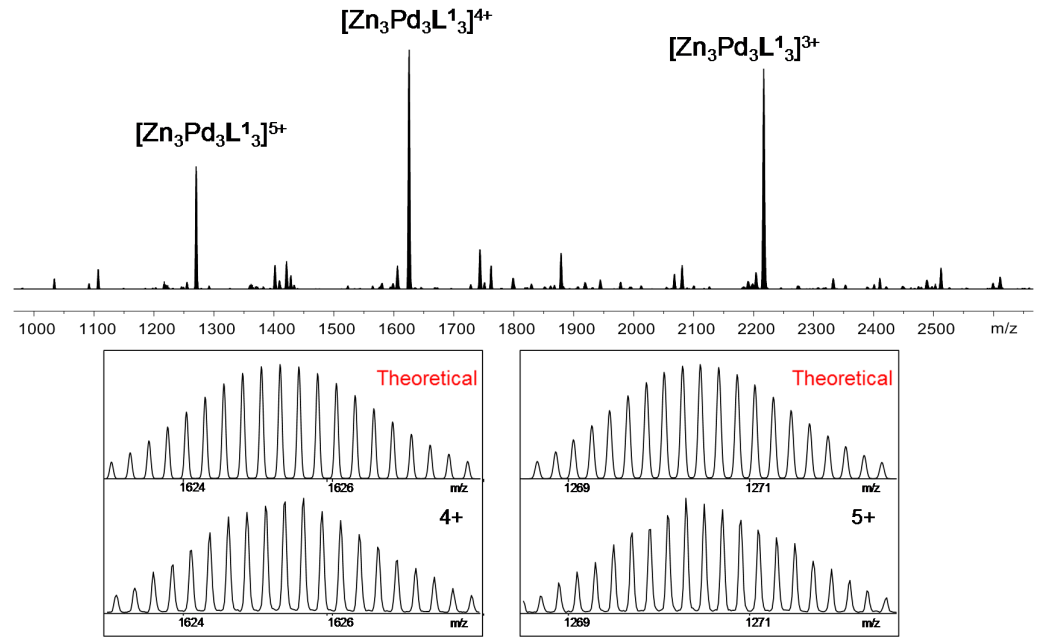


Figure S12. ESI-MS spectra of [$Zn_3Pd_3\mathbf{L}^{1}_3$] and its experimental and theoretical isotope patterns.

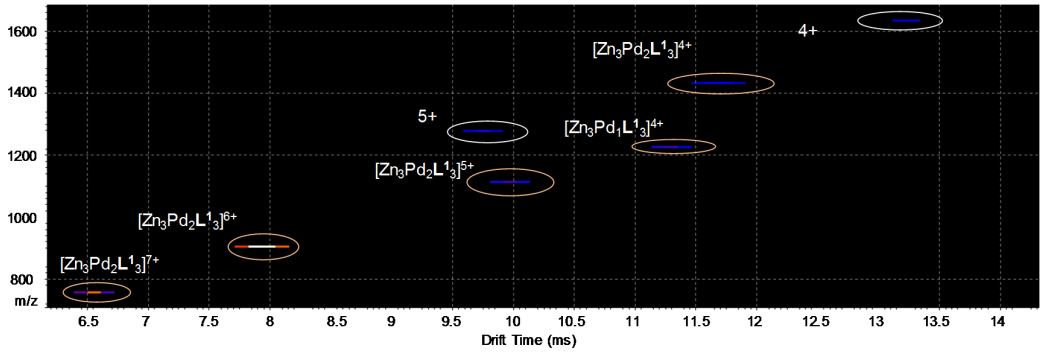


Figure S13. ESI-TWIM-MS plot of $[Zn_3Pd_3\mathbf{L^1}_3]$.

Table S2. Experimental and calculated collision cross-sections of $[Zn_3Pd_3\mathbf{L^1}_3]$.

Experimental and Calculated CCSs (Å^2)			
Charge	$[Zn_3Pd_3\mathbf{L^1}_3]^{4+}$	Charge	$[Zn_3Pd_3\mathbf{L^1}_3]^{5+}$
4+	822.7	5+	838.1
	Exp.	PA	TM
$[Zn_3Pd_3\mathbf{L^1}_3]$	830.4 (7.7)	733.0 (42.5)	878.3 (56.3)

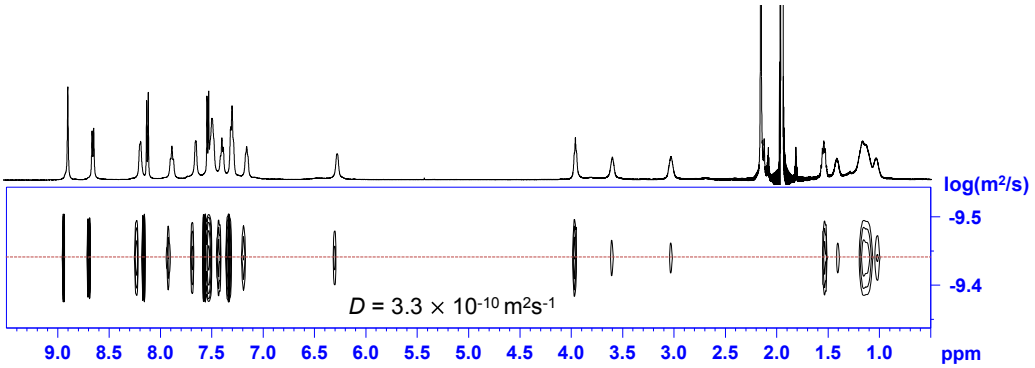


Figure S14. ^{1}H DOSY spectrum of $[Zn_3Pd_3\mathbf{L^1}_3]$ taken in CD_3CN.

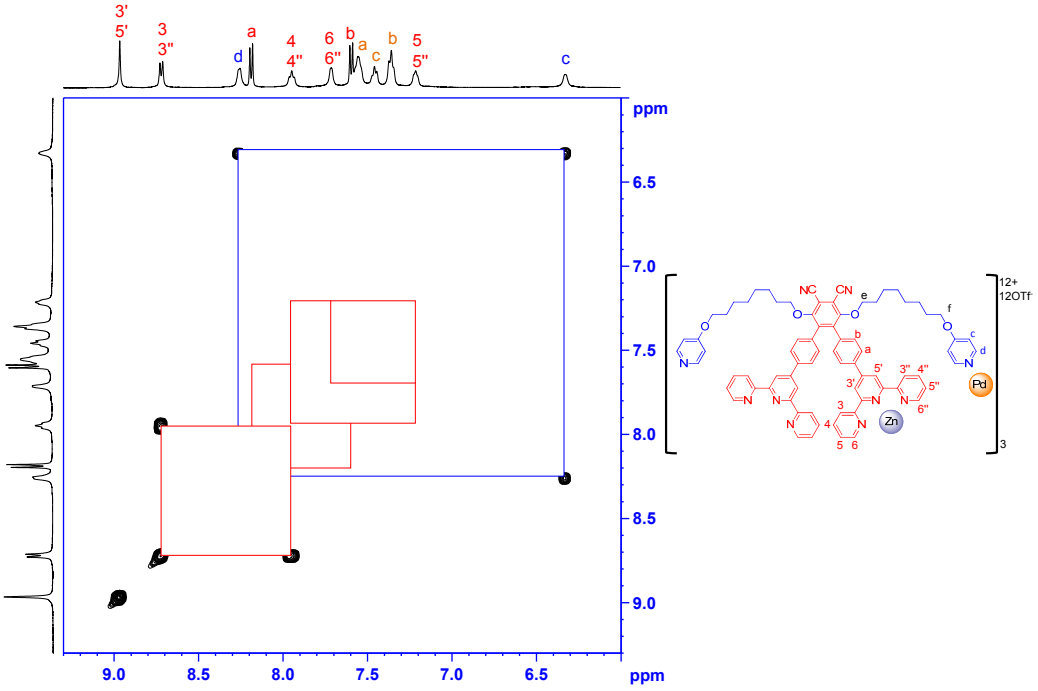


Figure S15. Partial COSY spectrum of $[Zn_3Pd_3\mathbf{L^1}_3]$.

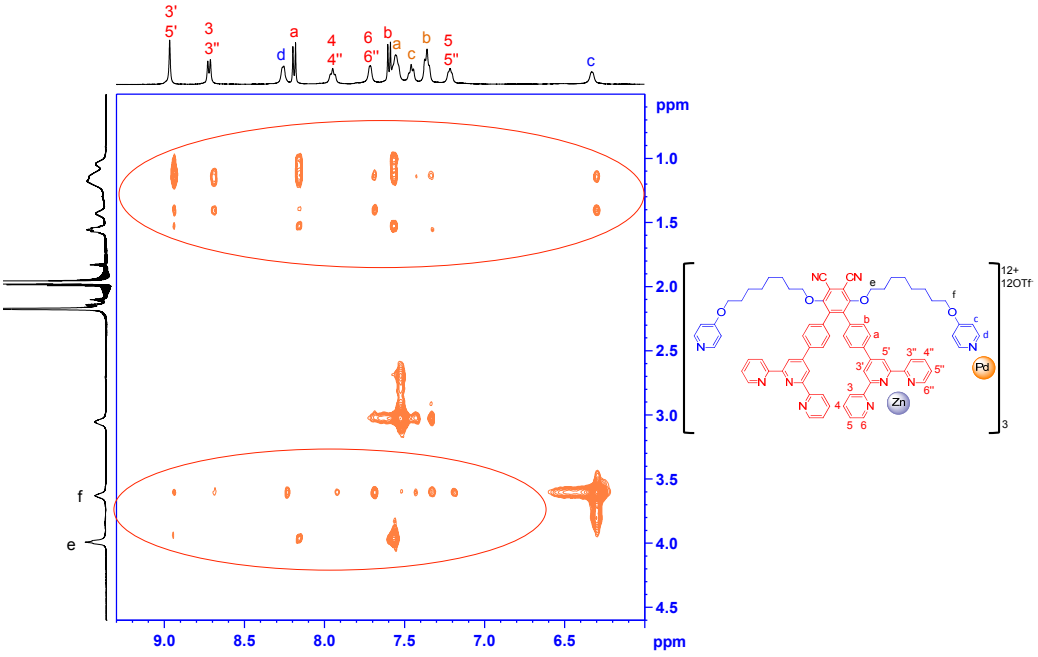
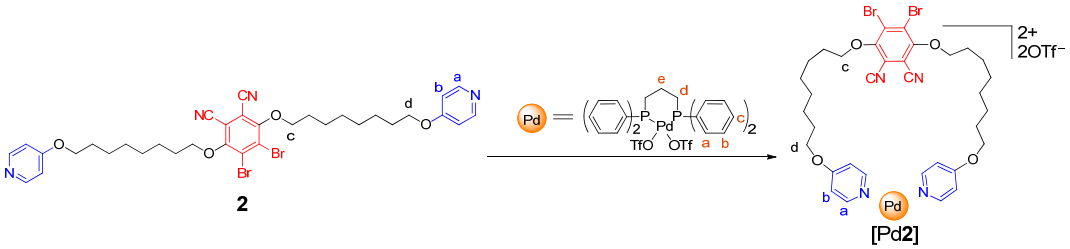


Figure S16. Partial ROESY spectrum of $[Zn_3Pd_3\mathbf{L^1}_3]$. The correlations between the alkyl chains and aromatic rings indicate the inter-ligand connection between pyridines.

Control Experiments



Scheme S4. Synthesis of complex [Pd**2**].

[Pd**2**]

To a stirred CD_3CN solution (0.45 mL) of **2** (5.0 mg, 7.4 μmol), a solution of Pd(dppp)$(OTf)_2$ (6.0 mg, 7.4 μmol) in CD_3CN (0.2 mL) was added. The mixture was stirred at 25 ºC for 3 h, and then the solvent was removed *in vacuo* to afford [Pd**2**] in 99% yield (10.9 mg, 7.4 μmol). ^{1}H NMR (400 MHz, CD_3CN : CD_3NO_2 = 1:1): δ (ppm) 8.29 (br, 4H), 7.67–7.52 (m, 8H), 7.47 (t, J = 7.5 Hz, 4H), 7.37 (t, J = 7.6 Hz, 8H), 6.59 (br, 4H), 4.18 (br, 4H), 3.90 (br, 4H), 3.08 (br, 4H), 2.20–2.16 (m, 2H), 1.86–1.77 (m, 4H), 1.70–1.62 (m, 4H), 1.52–1.42 (m, 4H), and 1.39–1.28 (m, 12H). ^{31}P NMR (162 MHz, CD_3CN : CD_3NO_2 = 1:1): δ (ppm) 13.57 (s, 2P). ESI-MS (*m/z*): 1396.1459 [M-OTf]$^{1+}$ (calcd *m/z* 1396.1487) and 623.5966 [M-2OTf]$^{2+}$ (calcd *m/z* 623.5983).

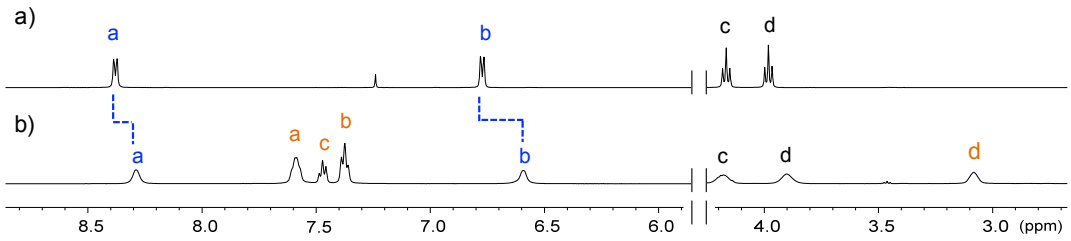


Figure S17. ^{1}H NMR spectra of a) **2** in $CDCl_3$ and b) [Pd**2**] in CD_3CN/CD_3NO_2 (1/1, v/v).

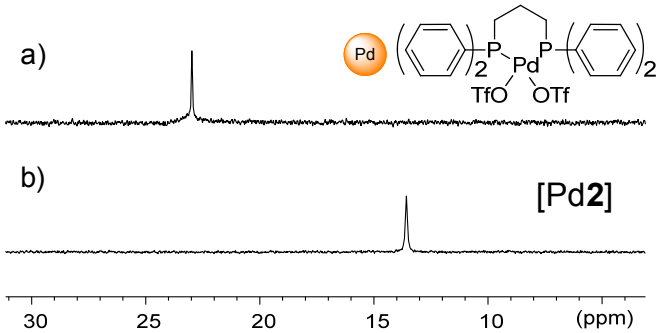


Figure S18. ^{31}P NMR spectra of a) Pd(dppp)$(OTf)_2$ in CD_3CN and b) [Pd**2**] in CD_3CN/CD_3NO_2 (1/1, v/v).

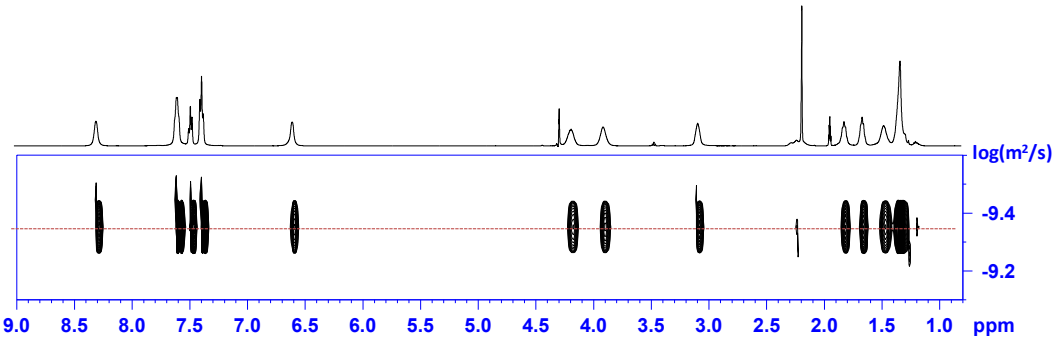


Figure S19. ^{1}H DOSY spectrum of [Pd**2**] in CD_3CN/CD_3NO_2 (1/1, v/v).

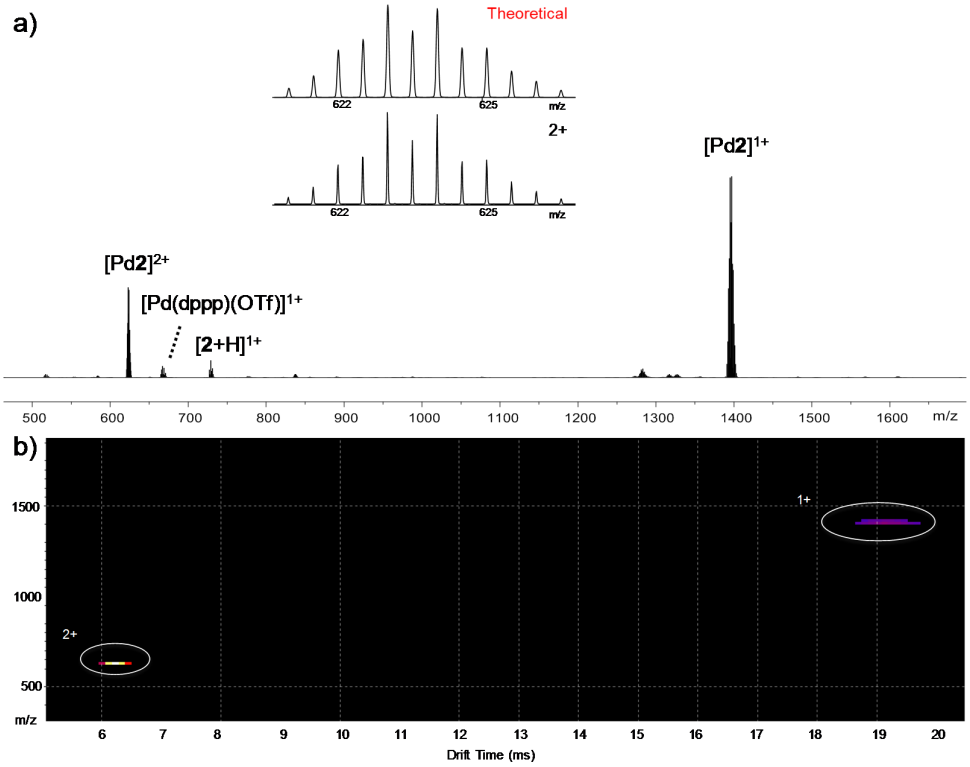
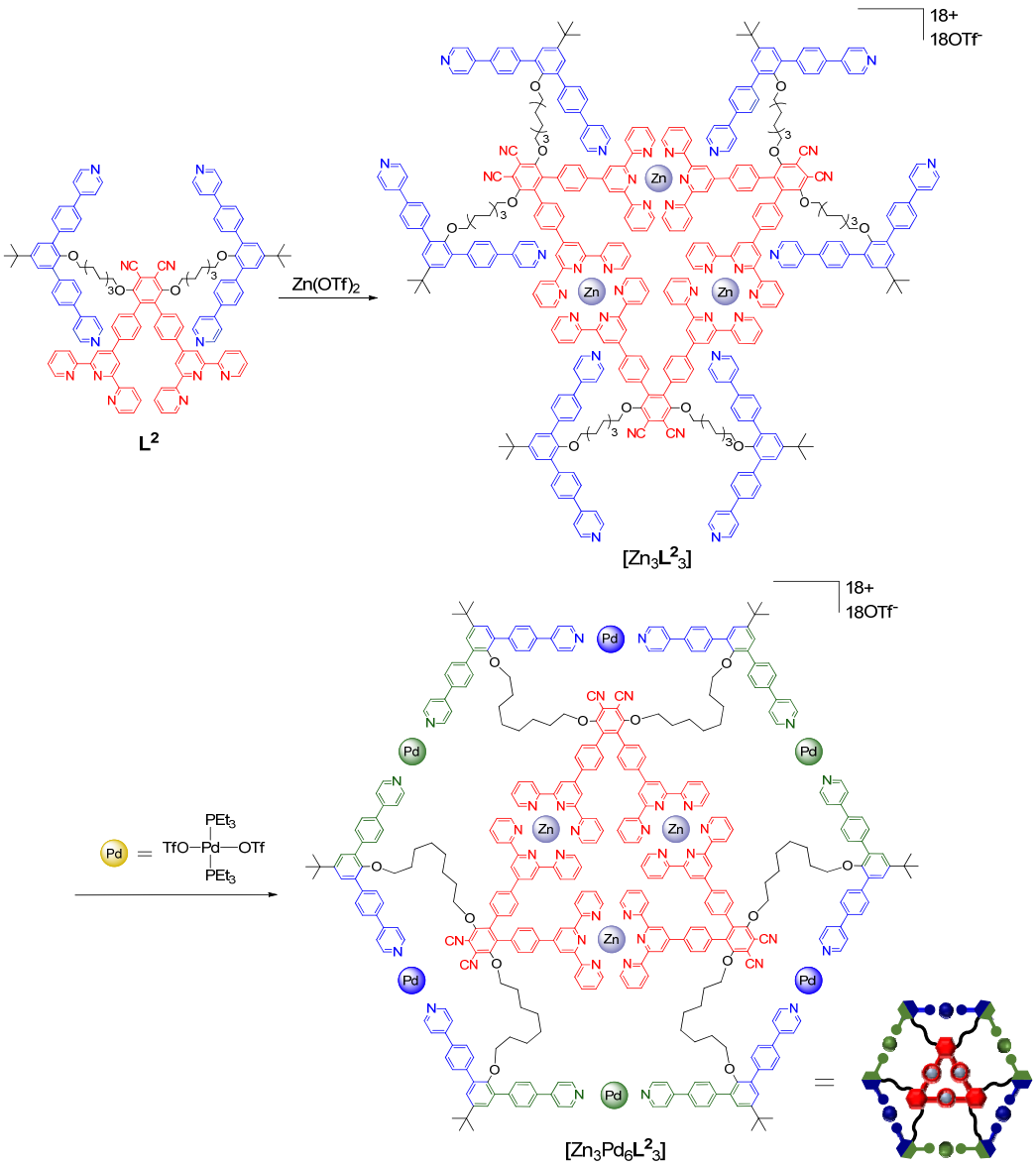


Figure S20. a) ESI-MS spectrum and b) ESI-TWIM-MS plot of [Pd**2**].

Table S3. Experimental and theoretical collision cross-sections of [Pd**2**].

Experimental and Calculated CCSs (Å^2)			
Charge	[Pd**2**]$^{1+}$	Charge	[Pd**2**]$^{2+}$
1+	265.0	2+	244.6
	Exp.	PA	TM
[Pd**2**]	254.8 (10.2)	226.5 (10.9)	245.7 (11.9)



Scheme S5. Synthesis of complexes $[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]$ and $[Zn_3Pd_6\mathbf{L}^{\mathbf{2}}{}_3]$.

$[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]$

To a stirred solution of $\mathbf{L}^{\mathbf{2}}$ (51.0 mg, 26.7 μmol) in $CHCl_3$ (7 mL), a solution of $Zn(OTf)_2$ (9.9 mg, 27.3 μmol) in MeOH (7 mL) was added. The mixture was stirred at 25 ºC for 1 h and then diethyl ether was added to the solution to precipitate the complex. The precipitate was filtered and then washed by H_2O to afford complex $[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]$ as a white solid (60.2 mg, 8.8 μmol) in 99% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.94 (s, 12H), 8.66 (d, J = 8.3 Hz, 12H), 8.65–8.58 (m, 24H), 8.15 (d, J = 7.9 Hz, 12H), 7.93 (t, J = 7.9 Hz, 12H), 7.78 (d, J = 8.4 Hz, 24H), 7.71 (d, J = 8.5 Hz, 24H), 7.66 (d, J = 5.1

Hz, 12H), 7.67–7.59 (m, 24H), 7.54 (d, J = 7.9 Hz, 12H), 7.40 (s, 12H), 7.22–7.13 (m, 12H), 3.76 (t, J = 6.2 Hz, 12H), 3.06 (t, J = 5.6 Hz, 12H), 1.36 (s, 54H), 1.07–0.99 (m, 12H), 0.98–0.80 (m, 48H), and 0.79–0.71 (m, 12H). ESI-MS (*m/z*): 2122.7888 [M-3OTf]$^{3+}$ (calcd *m/z* 2122.8350), 1554.8350 [M-4OTf]$^{4+}$ (calcd *m/z* 1554.8555), and 1214.1444 [M-5OTf]$^{5+}$ (calcd *m/z* 1214.0925).

[Zn_3Pd_6**L²**$_3$] (Stepwise)

To a stirred CD_3CN solution (0.5 mL) of [Zn_3**L²**$_3$] (5.7 mg, 0.8 mmol), a solution of *trans*-$Pd(PEt_3)_2(OTf)_2$ (3.2 mg, 5.0 mmol) in CD_3CN (0.20 mL) was added. The mixture was stirred at 25 ºC for 3 h, and then the solvent was evaporated *in vacuo* to afford [Zn_3Pd_6**L²**$_3$] (8.9 mg, 0.8 mmol) in 99% yield. ^{1}H NMR (500 MHz, CD_3CN : CD_3NO_2 = 1:1) δ (ppm) 9.13 (d, J = 5.7 Hz, 12H), 9.07 (s, 12H), 8.95 (d, J = 6.3 Hz, 12H), 8.79 (d, J = 8.2 Hz, 12H), 8.27–8.20 (m, 36H), 8.10–7.93 (m, 60H), 7.89 (d, J = 5.0 Hz, 12H), 7.72–7.64 (m, 18H), 7.64–7.60 (m, 6H), 7.33 (t, J = 6.3 Hz, 12H), 3.98 (br t, J = 6.2 Hz, 12H), 3.29 (br, 12H), 1.69–1.60 (m, 36H), and 1.55–0.76 (m, 270H). ^{31}P NMR (162 MHz, CD_3CN) δ 20.90 (s, 6P) and 20.31 (s, 6P). ESI-MS (*m/z*): 1373.8236 [M-7OTf]$^{7+}$ (calcd *m/z* 1373.7898), 1183.4886 [M-8OTf]$^{8+}$ (calcd *m/z* 1183.4452), 1035.5345 [M-9OTf]$^{9+}$ (calcd *m/z* 1035.5148), 916.9948 [M-10OTf]$^{10+}$ (calcd *m/z* 916.9658), and 820.0613 [M-11OTf]$^{11+}$ (calcd *m/z* 820.0879).

[Zn_3Pd_6**L²**$_3$] (One-pot)

To a stirred CD_3CN solution (0.45 mL) of **L²** (5.0 mg, 2.6 μmol), a solution of *trans*-$Pd(PEt_3)_2(OTf)_2$ (3.4 mg, 5.2 μmol) and $Zn(OTf)_2$ (1.0 mg, 2.6 μmol) in CD_3CN (0.2 mL) was added. The mixture was stirred at 25 ºC for 3 h, and then the solvent was evaporated *in vacuo* to afford [Zn_3Pd_6**L²**$_3$] (9.4 mg, 0.9 μmol) in 99% yield.

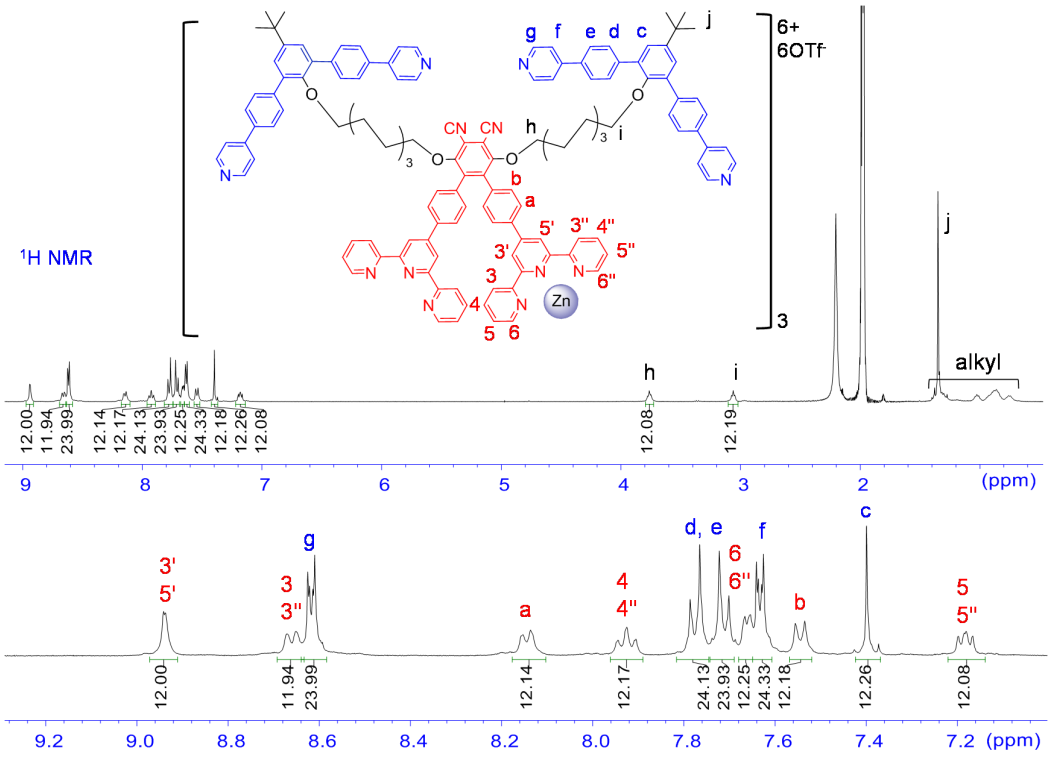


Figure S21. ^{1}H NMR spectra of [$Zn_3\mathbf{L}^{2}_3$].

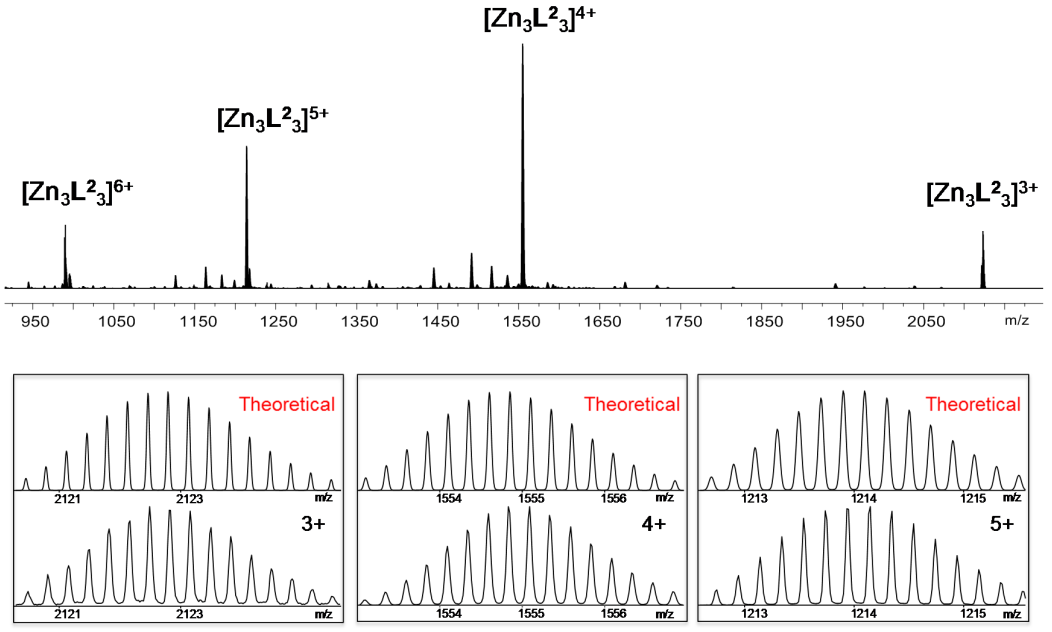


Figure S22. ESI-MS spectra of [$Zn_3\mathbf{L}^{2}_3$] and its experimental and theoretical isotope patterns.

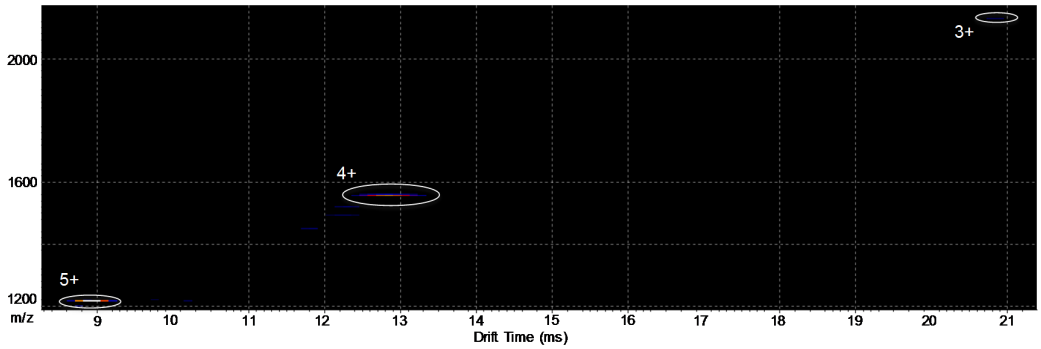


Figure S23. ESI-TWIM-MS plot of $[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]$.

Table S4. Experimental and calculated collision cross-sections of $[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]$.

Experimental and Calculated CCSs (Å^2)			
Charge 3+	$[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]^{3+}$ 832.0	Charge 4+	$[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]^{4+}$ 804.3
Charge 5+	$[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]^{5+}$ 784.4		
	Exp.	PA	TM
$[Zn_3\mathbf{L}^{\mathbf{2}}{}_3]$	806.9 (19.5)	825.3 (56.9)	984.5 (61.3)

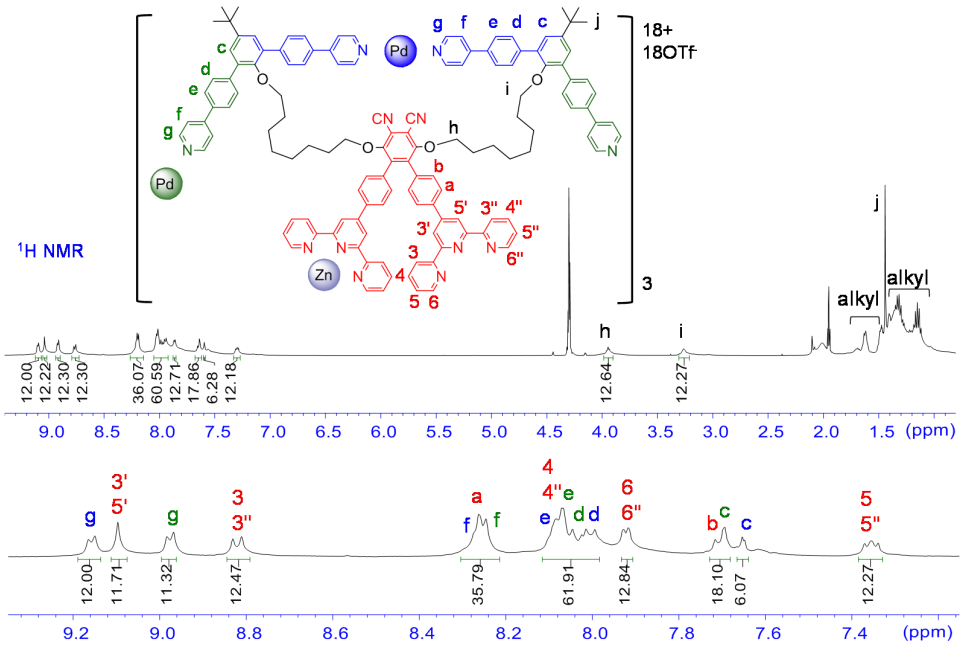


Figure S24. ^{1}H NMR spectra of $[Zn_3Pd_6\mathbf{L}^{\mathbf{2}}{}_3]$ taken in CD_3CN/CD_3NO_2 (1/1, v/v).

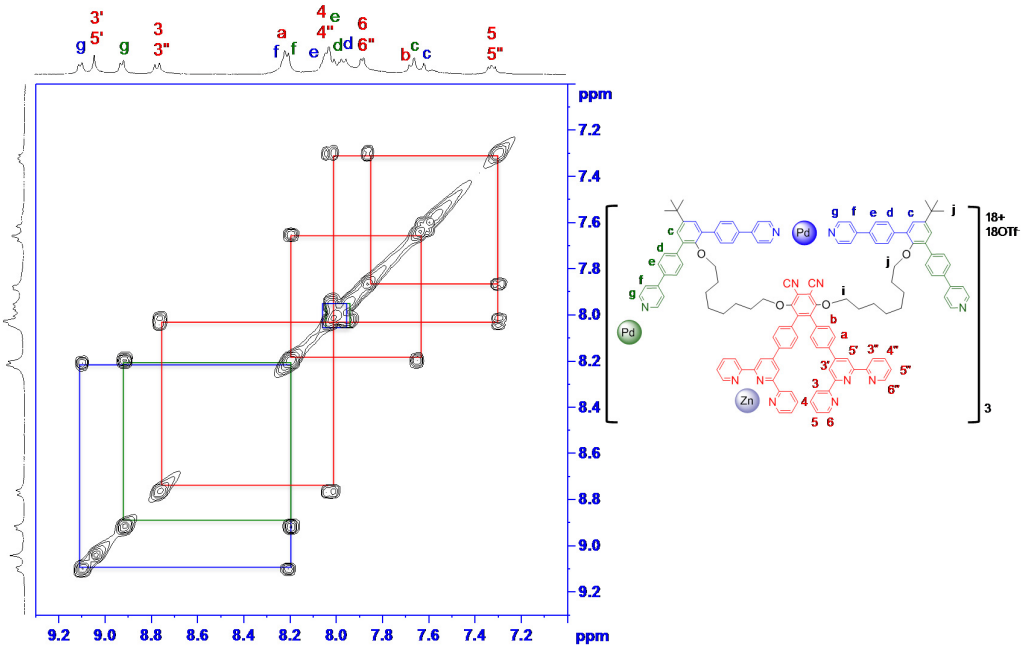


Figure S25. Partial COSY spectrum of [$Zn_3Pd_6\mathbf{L^2}_3$].

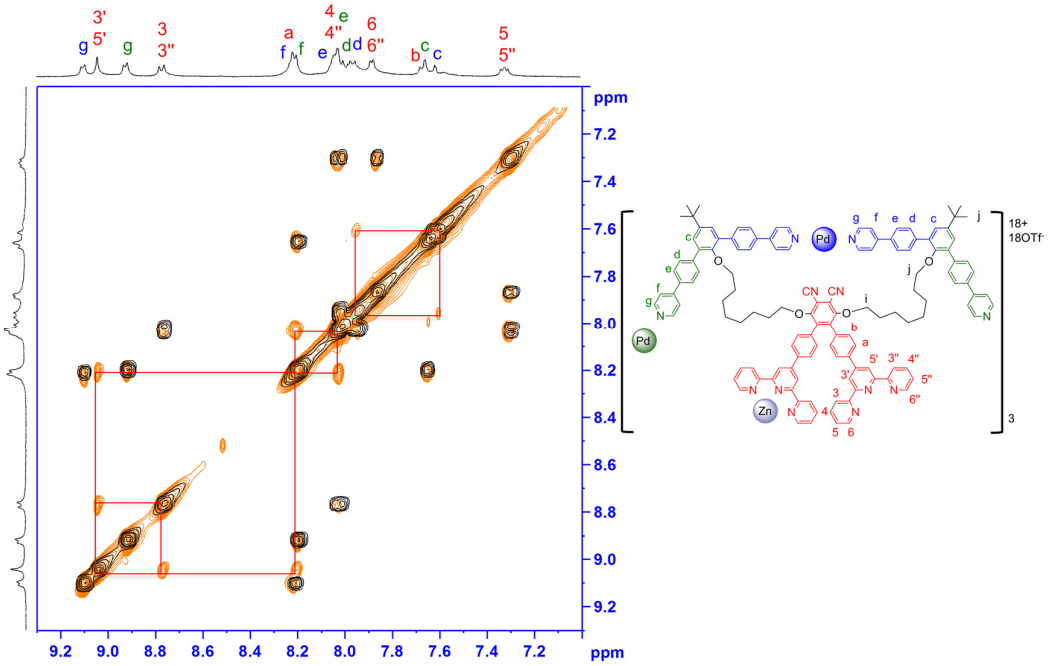


Figure S26. Partial ROESY spectrum of [$Zn_3Pd_6\mathbf{L^2}_3$] (brown: ROESY signals, black: COSY signals).

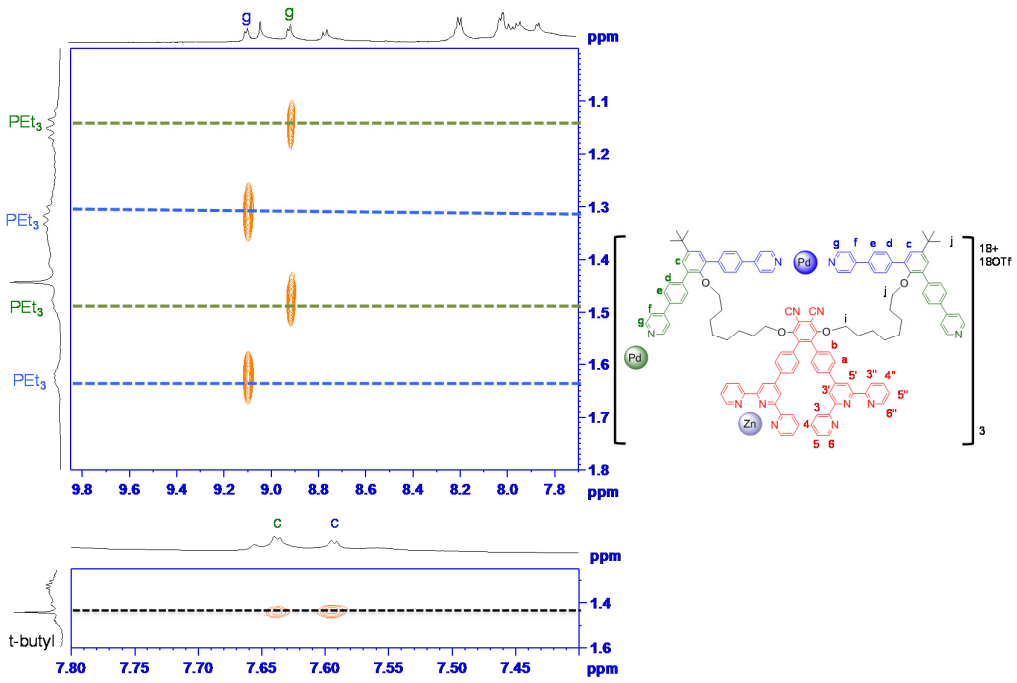


Figure S27. Partial ROESY spectra of [$Zn_3Pd_6\mathbf{L^2}_3$].

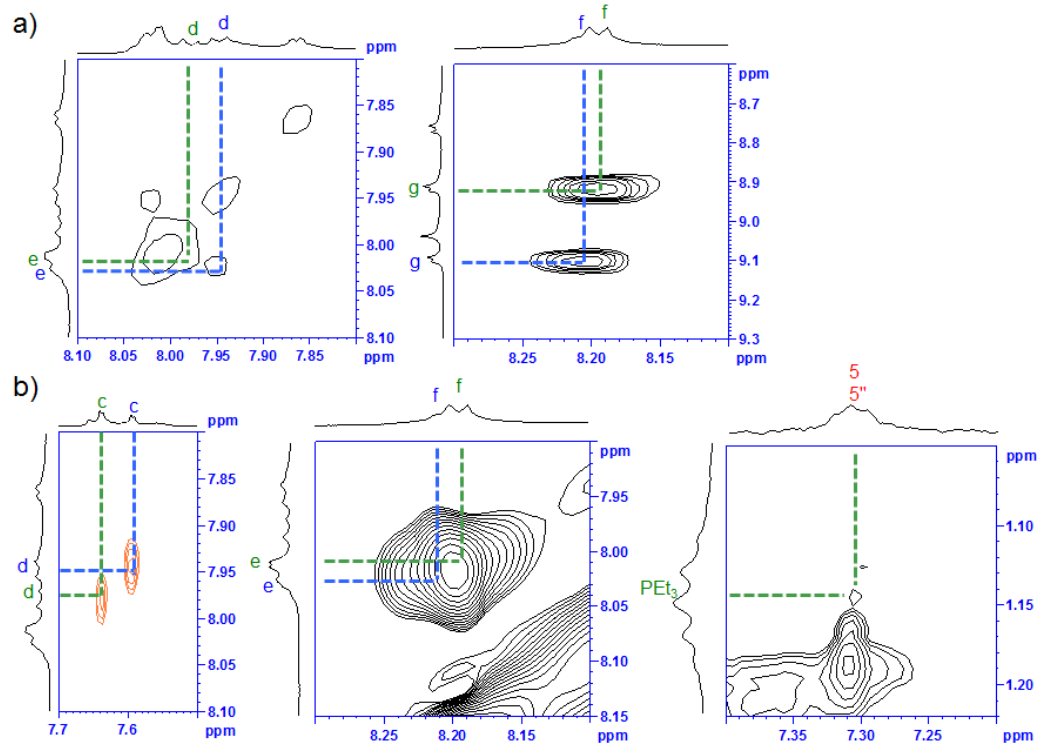


Figure S28. Partial a) COSY and b) ROESY spectra of [$Zn_3Pd_6\mathbf{L^2}_3$].

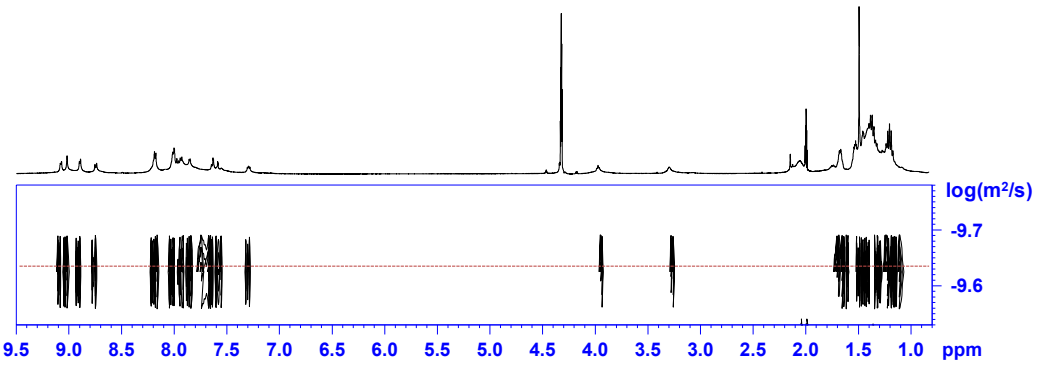


Figure S29. ^{1}H DOSY spectrum of $[Zn_3Pd_6\mathbf{L^2}_3]$ in CD_3CN/CD_3NO_2 (1/1, v/v).

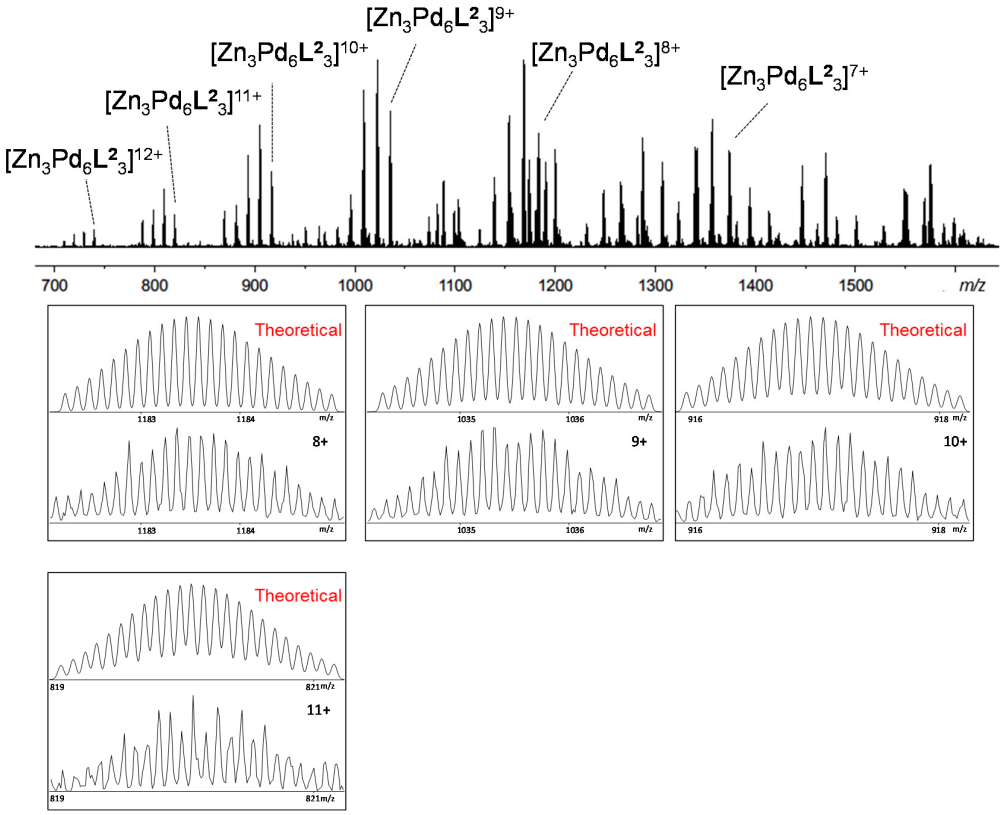


Figure S30. ESI-MS spectra of $[Zn_3Pd_6\mathbf{L^2}_3]$ and its experimental and theoretical isotope patterns.

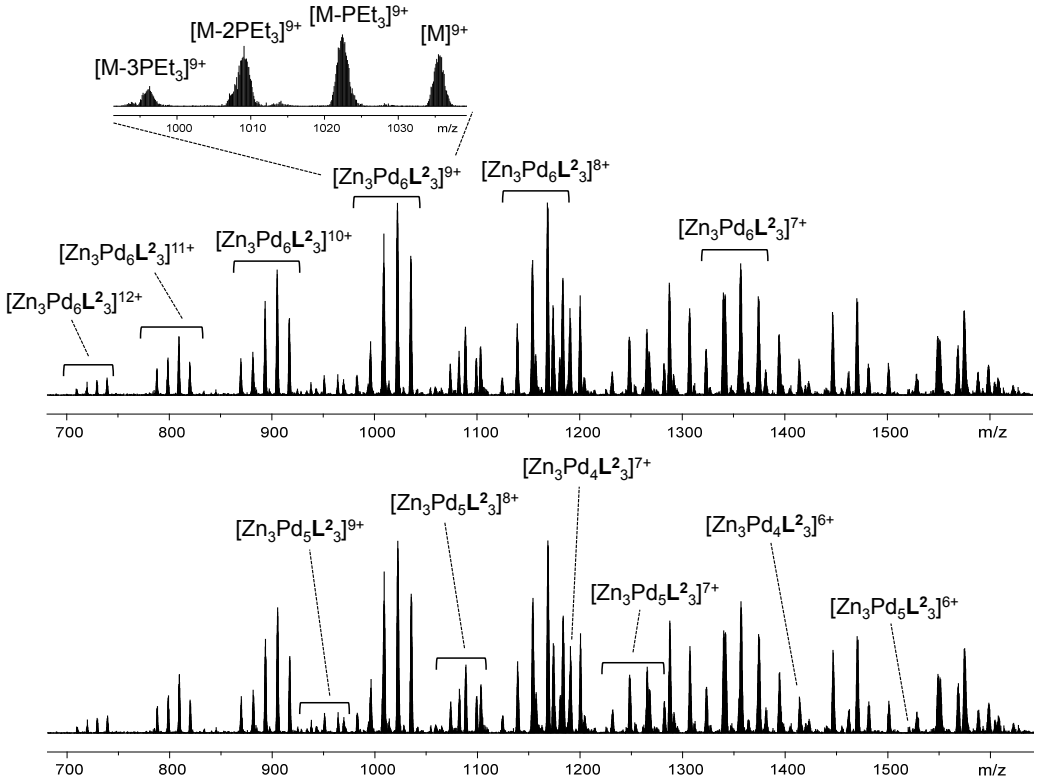
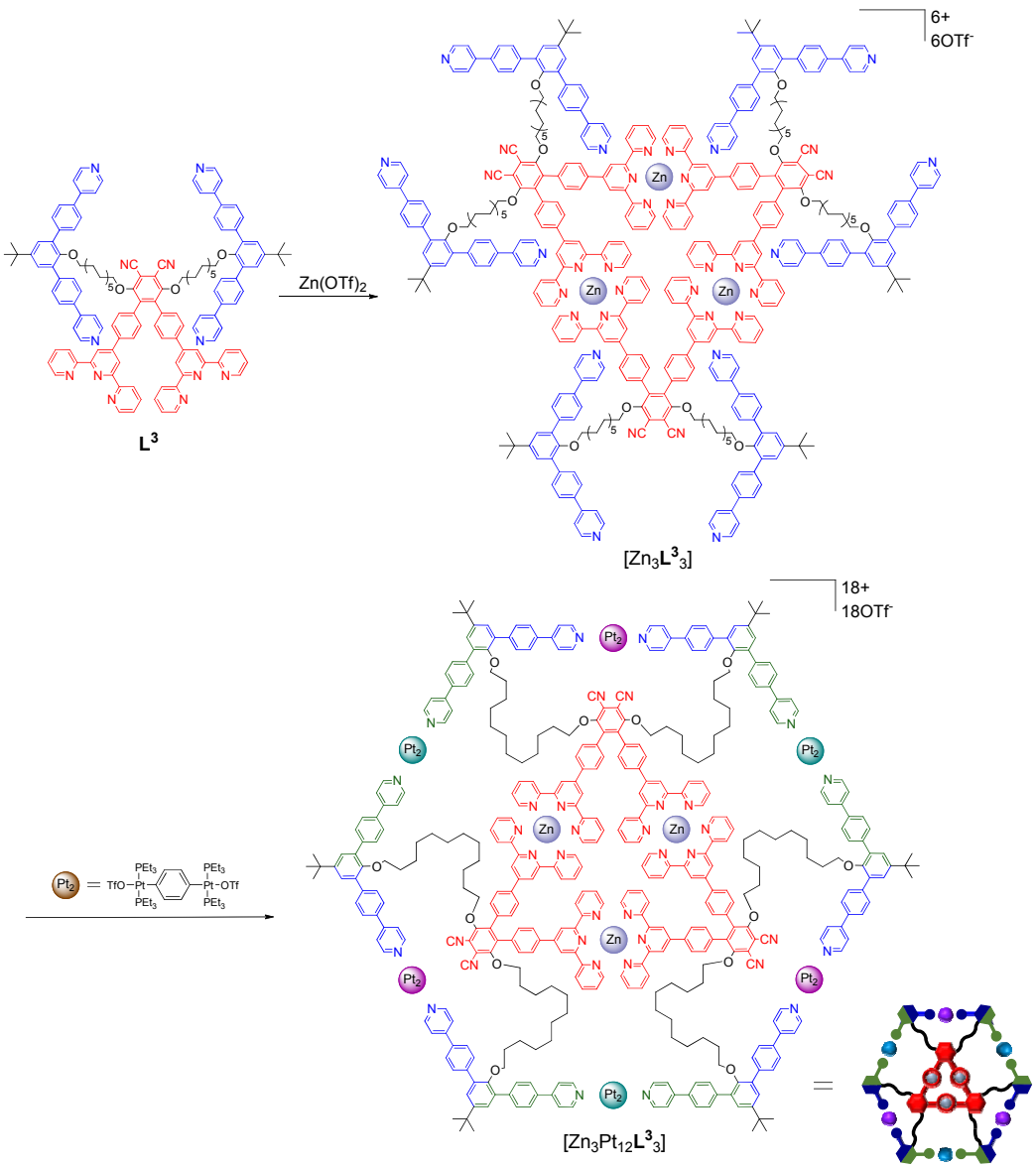


Figure S31. Fragmentation assignments for the ESI-MS spectra of [$Zn_3Pd_6\mathbf{L^2}_3$].



Scheme S6. Synthesis of complexes $[Zn_3\mathbf{L}^3{}_3]$ and $[Zn_3Pt_{12}\mathbf{L}^3{}_3]$.

$[Zn_3\mathbf{L}^3{}_3]$

To a stirred solution of $\mathbf{L}^3$ (51.5 mg, 25.5 μmol) in $CHCl_3$ (7 mL), a solution of $Zn(OTf)_2$ (9.5 mg, 26.0 μmol) in MeOH (7 mL) was added. The mixture solution was stirred at 25 ºC for 1 h and then diethyl ether was added to the solution to precipitate the complex. The precipitate was filtered and then washed by H_2O to afford $[Zn_3\mathbf{L}^3{}_3]$ as a white solid in (61.0 mg, 8.5 μmol) in 99% yield. ^{1}H NMR (400 MHz, CD_3NO_2): δ (ppm) 8.99 (s, 12H), 8.64 (d, J = 8.0 Hz, 12H), 8.60–8.52 (m, 24H), 8.20 (d, J = 7.5 Hz, 12H), 7.95 (t,

J = 7.6 Hz, 12H), 7.85–7.72 (m, 60H), 7.68 (d, *J* = 7.9 Hz, 12H), 7.64–7.59 (m, 24H), 7.49 (s, 12H), 7.21 (t, *J* = 6.4 Hz, 12H), 4.00 (t, *J* = 5.7 Hz, 12H), 3.12 (t, *J* = 5.6 Hz, 12H), 1.65–1.50 (m, 24H), 1.38 (s, 54H), 1.17–0.60 (m, 84H), and 0.50 (br, 12H). ESI-MS (*m/z*): 2234.8413 $[M\text{-}3OTf]^{3+}$ (calcd *m/z* 2234.9219), 1638.9307 $[M\text{-}4OTf]^{4+}$ (calcd *m/z* 1638.9495), and 1281.3573 $[M\text{-}5OTf]^{5+}$ (calcd *m/z* 1281.3676).

$[Zn_3Pt_{12}\mathbf{L^3}_3]$ (Stepwise)

To a stirred CD_3NO_2 solution (0.5 mL) of $[Zn_3\mathbf{L^3}_3]$ (5.4 mg, 0.8 μmol), a solution of 1,4-bis(*trans*-$Pt(PEt_3)_2(OTf)$)benzene (5.6 mg, 4.8 μmol) in CD_3NO_2 (0.20 mL) was added. The mixture was stirred at 25 ºC for 3 h, and then the solvent was evaporated *in vacuo* to afford $[Zn_3Pt_{12}\mathbf{L^3}_3]$ (11.0 mg, 0.8 μmol) in 99% yield. ^{1}H NMR (400 MHz, CD_3NO_2): δ (ppm) 9.04 (br, 12H), 8.92 (br, 12H), 8.86 (br, 12H), 8.74 (br d, *J* = 8.1 Hz, 12H), 8.19 (br, 12H), 8.13–7.98 (m, 60H), 7.95–7.85 (m, 42H), 7.61 (br, 18H), 7.28 (br, 24H), 7.19 (br, 12H), 3.85 (br, 12H), 3.22 (br, 12H), 1.57 (br, 84H), 1.53–1.38 (m, 138H), and 1.37–0.82 (m, 312H). ^{31}P NMR (162 MHz, CD_3NO_2): δ (ppm) 17.15 (s, 12P, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 2752.89 Hz) and 17.05 (s, 12P, ^{195}Pt satellites, $^1J_{Pt\text{-}P}$ = 2752.89 Hz). ESI-MS (*m/z*): 1308.3623 $[M\text{-}10OTf]^{10+}$ (calcd *m/z* 1308.3457), 1175.7887 $[M\text{-}11OTf]^{11+}$ (calcd *m/z* 1175.7725), 1065.3892 $[M\text{-}12OTf]^{12+}$ (calcd *m/z* 1065.3820), and 972.0563 $[M\text{-}13OTf]^{13+}$ (calcd *m/z* 972.0469).

$[Zn_3Pt_{12}\mathbf{L^3}_3]$ (One-pot)

To a stirred CD_3NO_2 solution (0.45 mL) of $\mathbf{L^3}$ (8.0 mg, 4.0 μmol), a solution of 1,4-bis(*trans*-$Pt(PEt_3)_2(OTf)$)benzene (9.8 mg, 7.9 μmol) and $Zn(OTf)_2$ (1.4 mg, 4.0 μmol) in CD_3CN (0.2 mL) was added. The mixture was stirred at 25 ºC for 3 h, and then the solvent was evaporated *in vacuo* to afford $[Zn_3Pt_{12}\mathbf{L^3}_3]$ (19.2 mg, 1.3 μmol) in 99% yield.

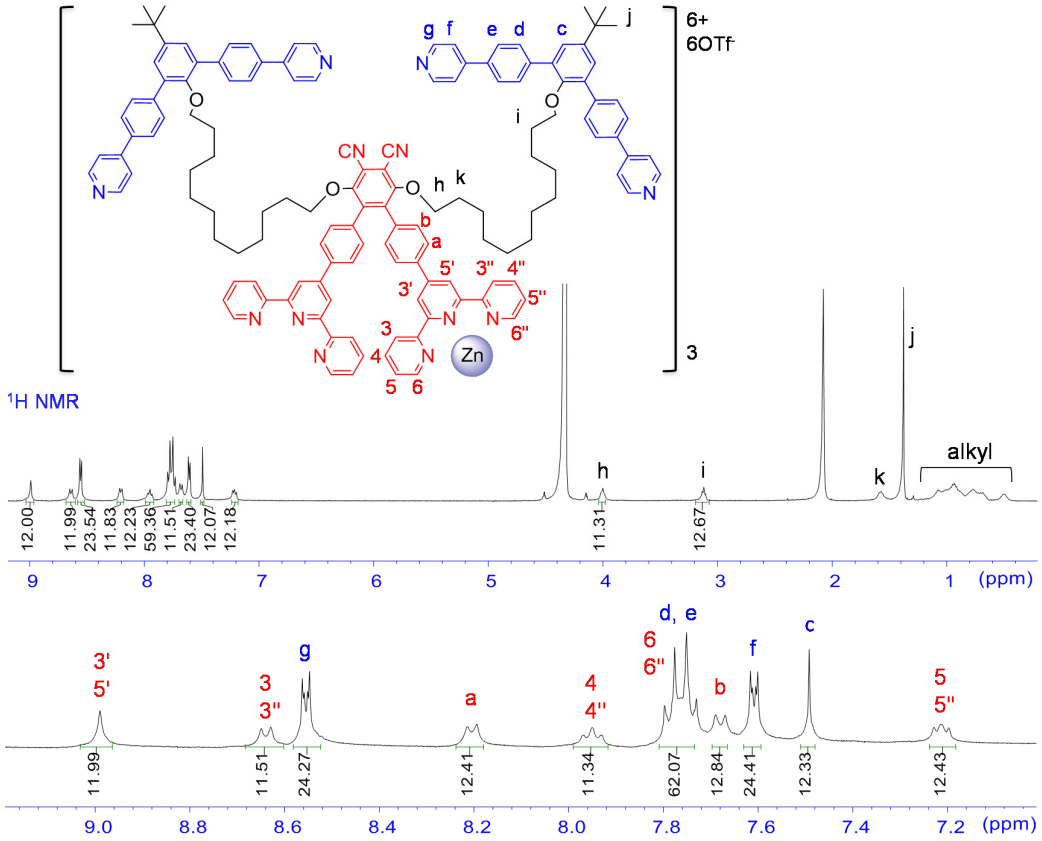


Figure S32. ^{1}H NMR spectra of [Zn_3**L**$^{3}_3$].

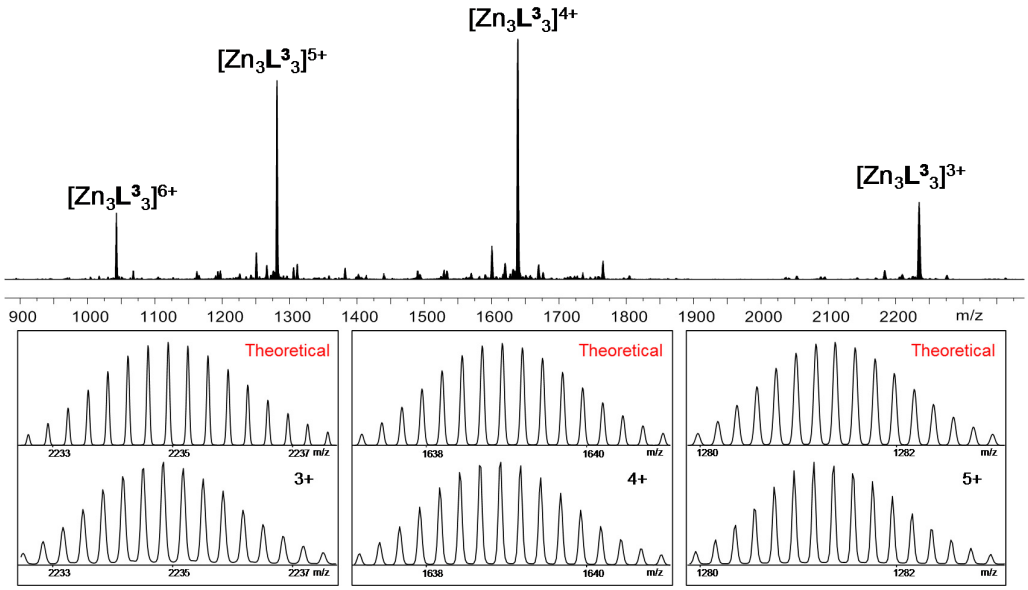


Figure S33. ESI-MS spectra of [Zn_3**L**$^{3}_3$] and its experimental and theoretical isotope patterns.

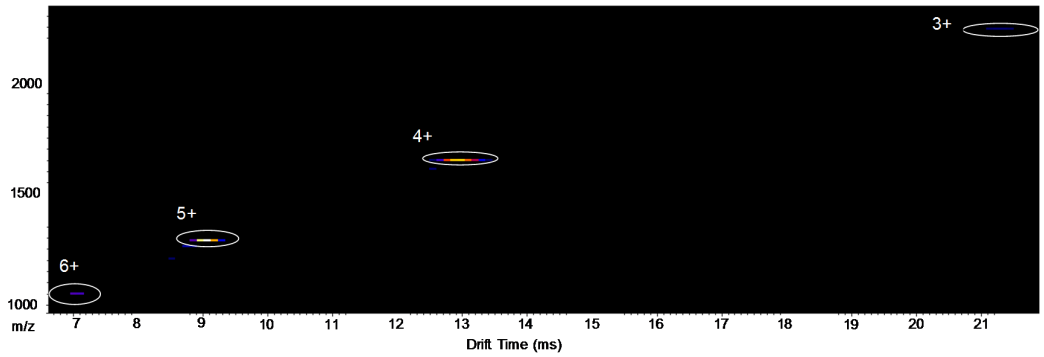


Figure S34. ESI-TWIM-MS plot of $[Zn_3\mathbf{L}^{\mathbf{3}}_3]$.

Table S5. Experimental and calculated collision cross-sections of $[Zn_3\mathbf{L}^{\mathbf{3}}_3]$.

Experimental and Calculated CCSs (Å^2)			
Charge	$[Zn_3\mathbf{L}^{\mathbf{3}}_3]^{3+}$	Charge	$[Zn_3\mathbf{L}^{\mathbf{3}}_3]^{4+}$
3+	851.6	4+	813.5
Charge	$[Zn_3\mathbf{L}^{\mathbf{3}}_3]^{5+}$	Charge	$[Zn_3\mathbf{L}^{\mathbf{3}}_3]^{6+}$
5+	797.9	6+	793.4
	Exp.	PA	TM
$[Zn_3\mathbf{L}^{\mathbf{3}}_3]$	814.1 (22.9)	868.6 (56.1)	1029.2 (61.2)

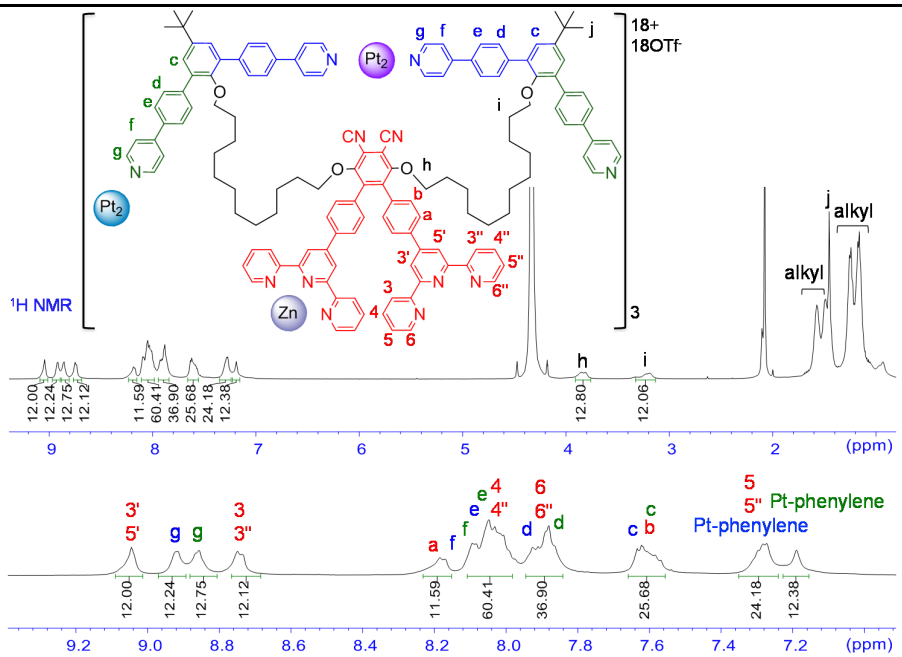


Figure S35. ^{1}H NMR spectra of $[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}_3]$.

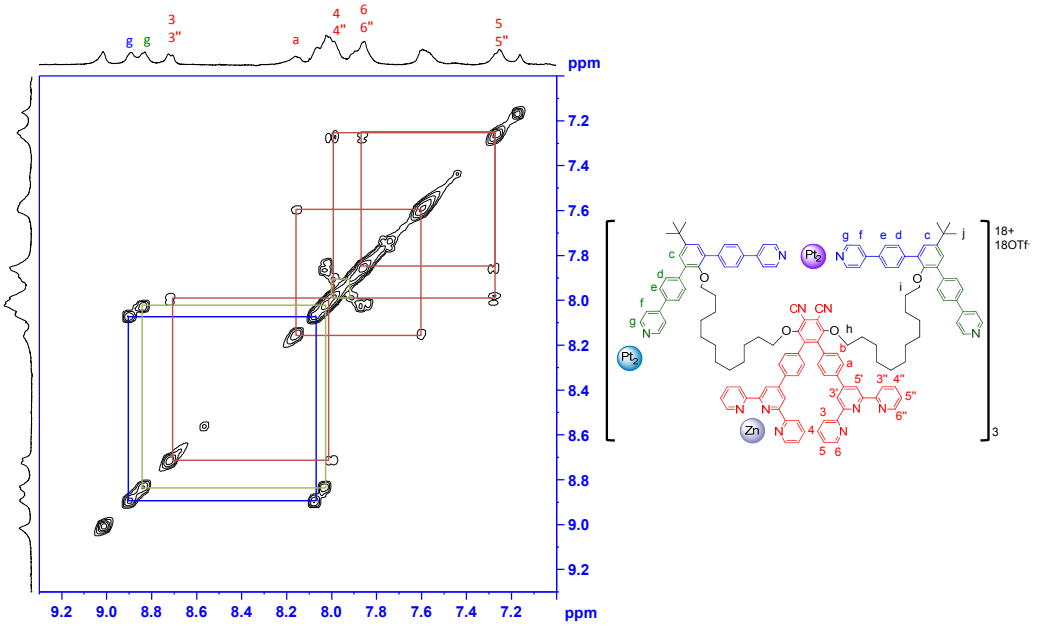


Figure S36. Partial COSY spectrum of $[Zn_3Pt_{12}\mathbf{L}^3_3]$.

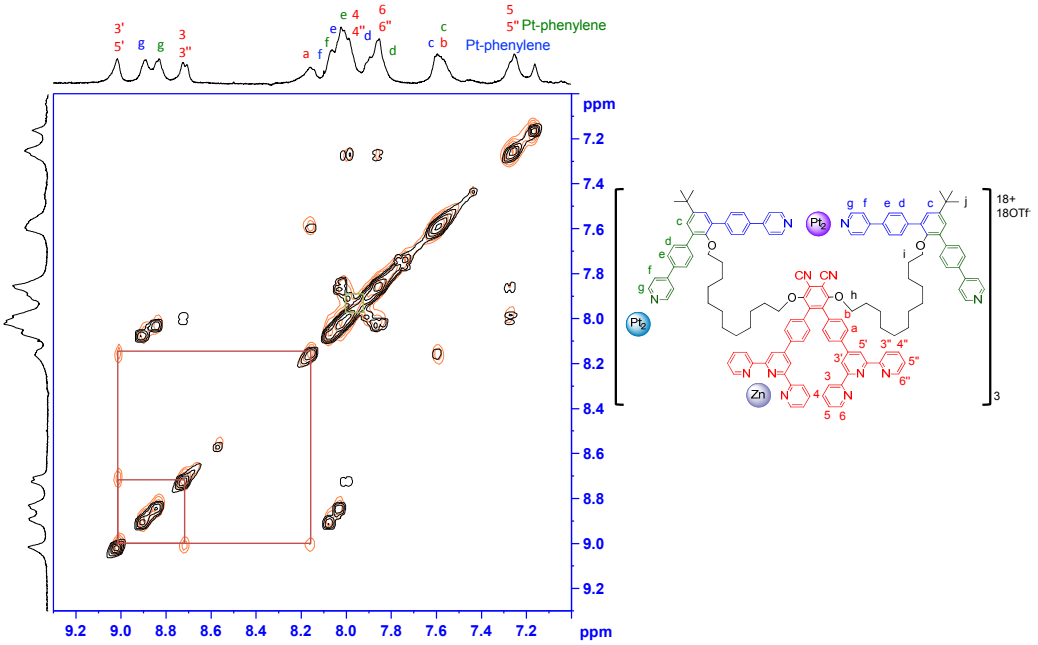


Figure S37. Partial NOESY spectrum of $[Zn_3Pt_{12}\mathbf{L}^3_3]$ (brown: NOESY signals, black: COSY signals).

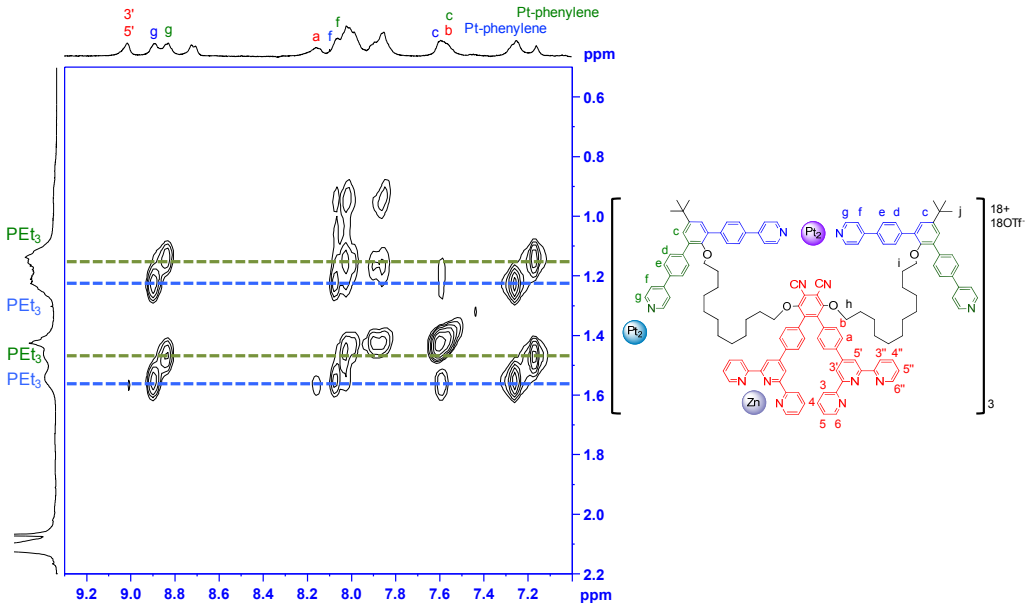


Figure S38. Partial NOESY spectrum of [$Zn_3Pt_{12}\mathbf{L}^3_3$].

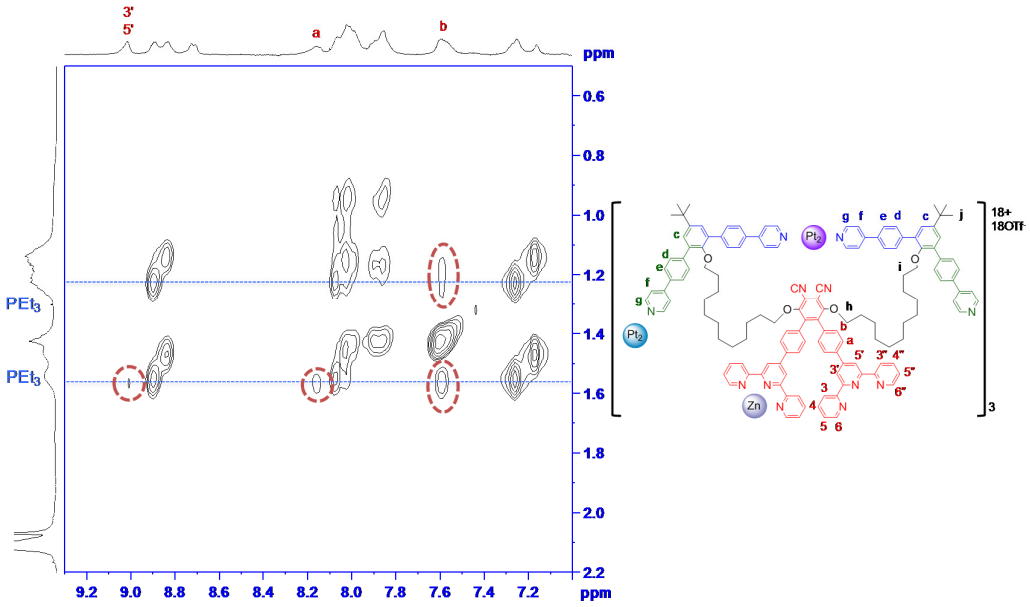


Figure S39. Partial NOESY spectrum of [$Zn_3Pt_{12}\mathbf{L}^3_3$].

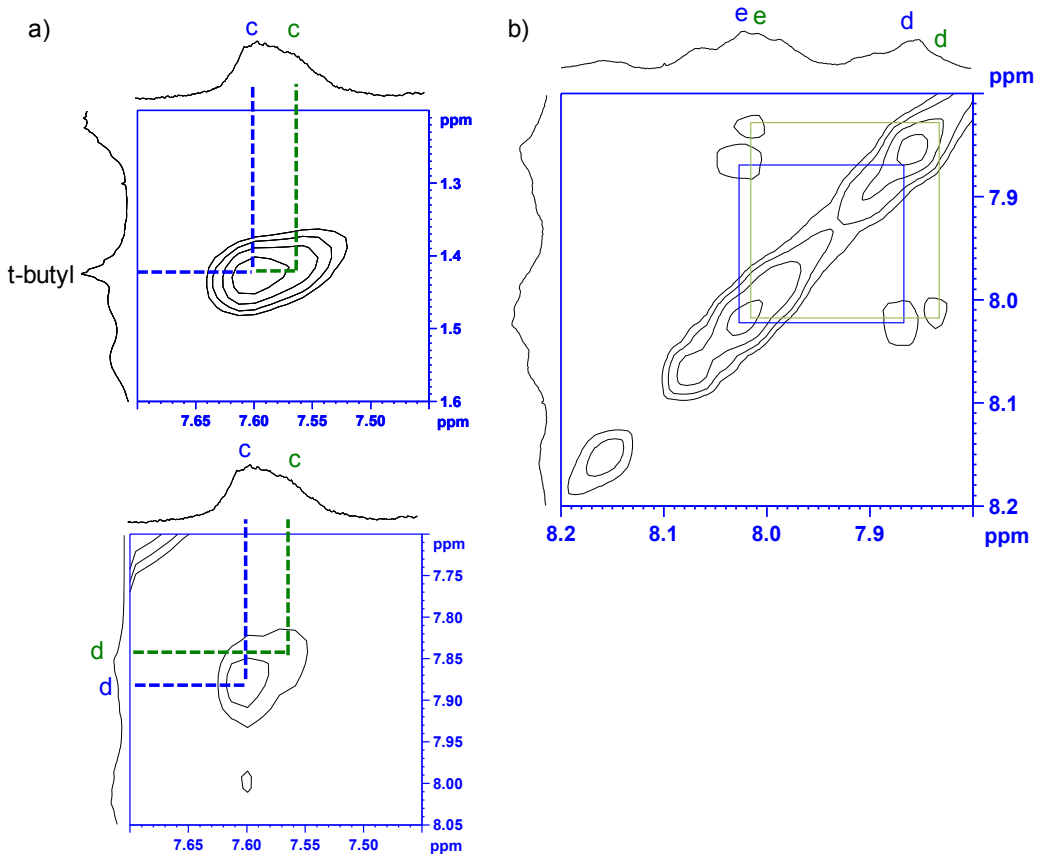


Figure S40. Partial a) NOESY and b) COSY spectra of $[Zn_3Pt_{12}\mathbf{L}^3_3]$.

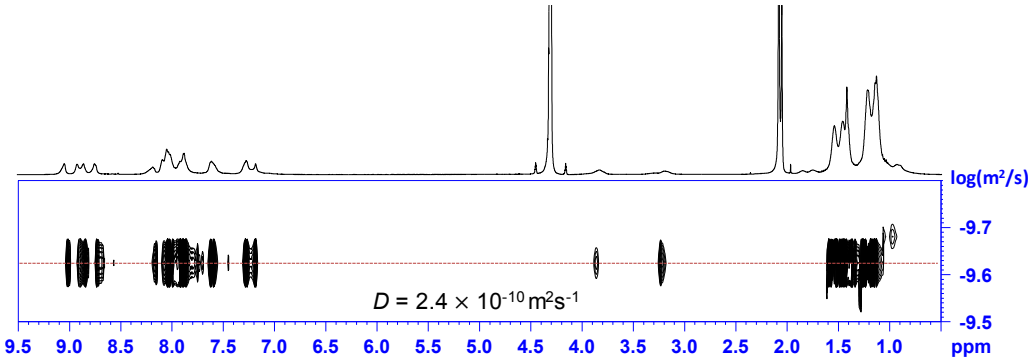


Figure S41. ^{1}H DOSY spectrum of $[Zn_3Pt_{12}\mathbf{L}^3_3]$ taken in CD_3NO_2.

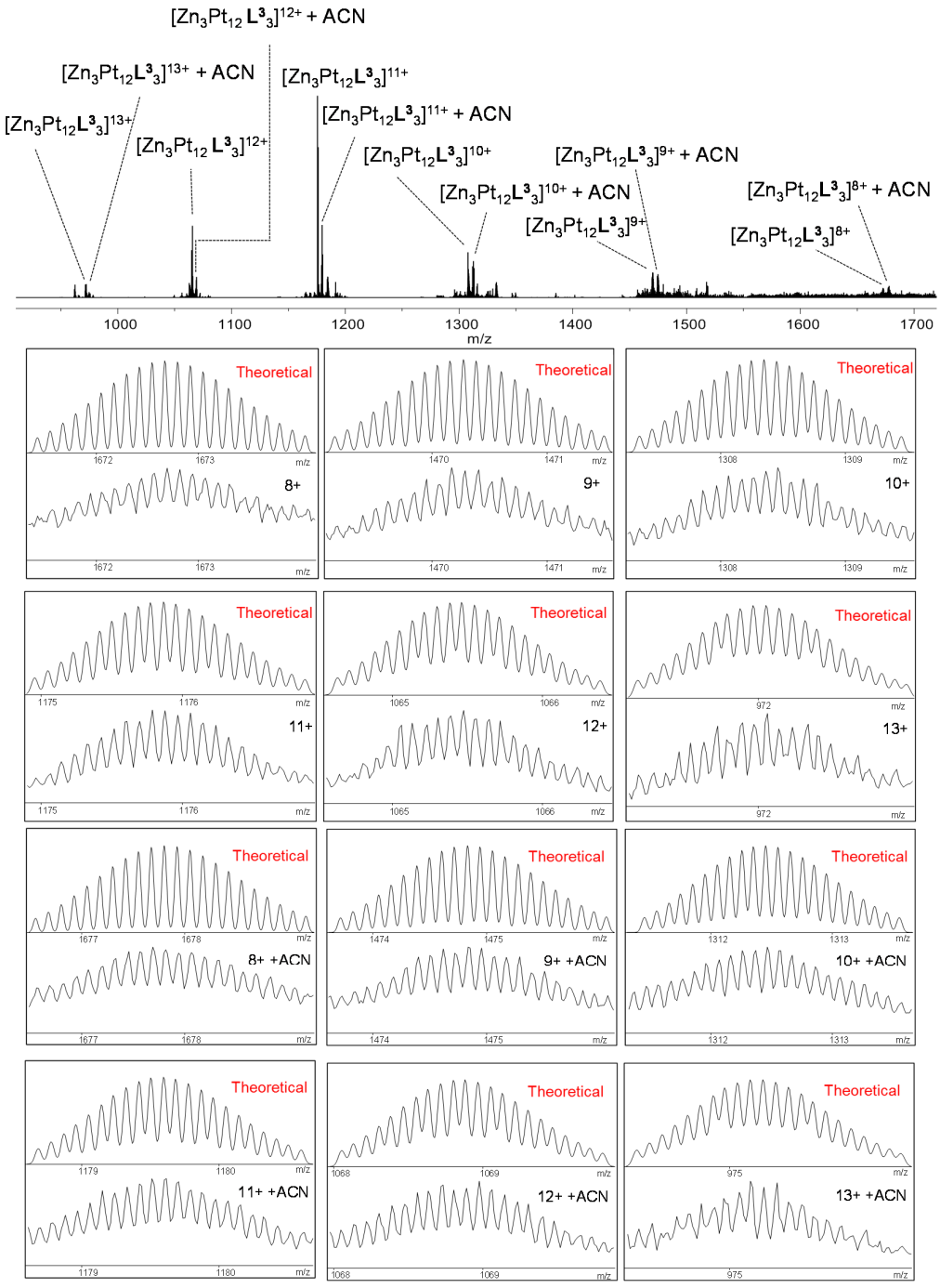


Figure S42. ESI-MS spectrum of $[Zn_3Pt_{12}\mathbf{L^3}_3]$ and its experimental and theoretical isotope patterns.

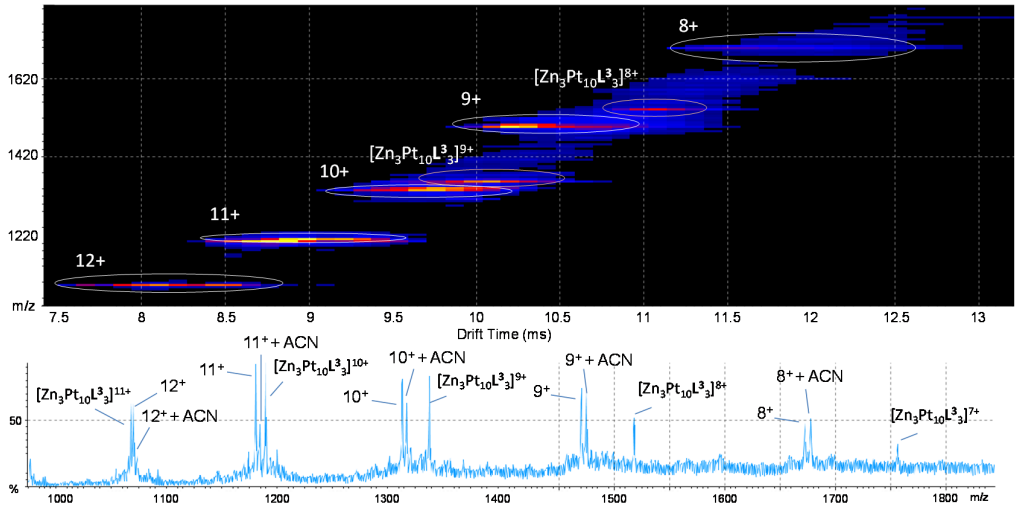
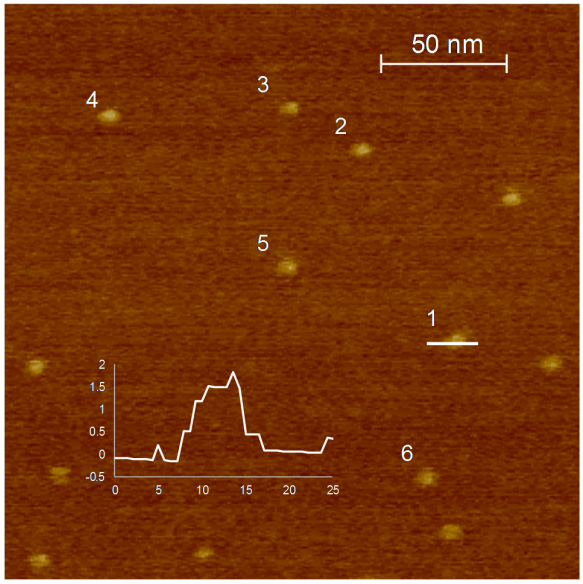


Figure S43. ESI-TWIM-MS plot of $[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}{}_3]$.

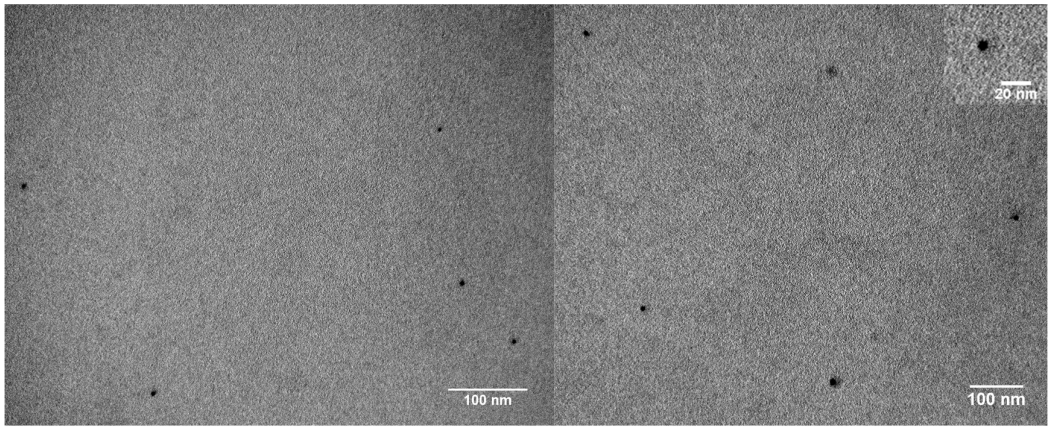
Table S6. Experimental and calculated collision cross-sections of $[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}{}_3]$.

Experimental and Calculated CCSs (Å^2)			
Charge 8+	$[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}{}_3]^{8+}$ 1527.5	Charge 9+	$[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}{}_3]^{9+}$ 1583.2
Charge 10+	$[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}{}_3]^{10+}$ 1694.5	Charge 11+	$[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}{}_3]^{11+}$ 1745.8
Charge 12+	$[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}{}_3]^{12+}$ 1871.6		
	Exp.	PA	TM
$[Zn_3Pt_{12}\mathbf{L}^{\mathbf{3}}{}_3]$	1684.5 (121.5)	1429.6 (104.7)	1705.5 (142.4)



	Height
1	1.73
2	1.78
3	1.75
4	1.72
5	1.65
6	1.73
nm	1.73 ± 0.04

Figure S44. AFM image of [$Zn_3Pt_{12}\mathbf{L}^3_3$] and the statistical analysis for the height.



Average = 7.0 ± 0.9 nm

Figure S45. TEM images of [$Zn_3Pt_{12}\mathbf{L}^3_3$] and the statistical analysis for the diameter.

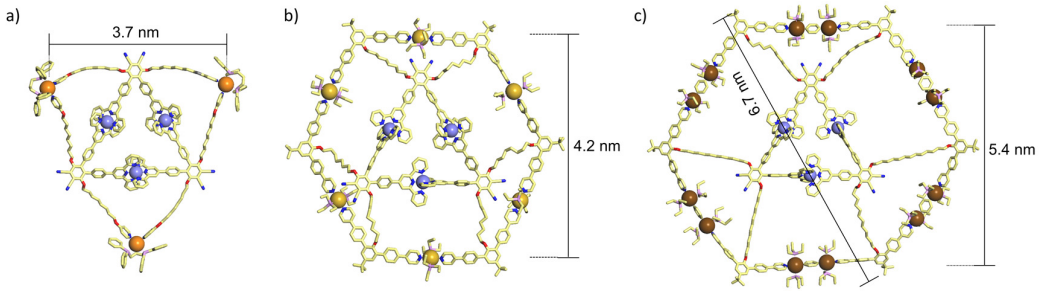


Figure S46. Energy-minimized structures of a) [$Zn_3Pd_3\mathbf{L}^1_3$], b) [$Zn_3Pd_6\mathbf{L}^2_3$], and c) [$Zn_3Pt_{12}\mathbf{L}^3_3$].

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