Supporting Information

Stepwise construction of a metallocatenane based on non-labile bis(terpyridine)-Cd^{II} complexes

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Materials and general methods. Unless noted, reagents and solvents were purchased from Fisher Scientific, AK Scientific, and Sigma-Aldrich without further purification. Column chromatography was conducted using silica gel (45-75 μm) from Fuji Silysia GS series and basic Al_2O_3 (50-200 μm) from Acros. ^1H and ^{13}C NMR spectra were recorded at 25 °C on Bruker DPX-400, Bruker AVIII-400, and Bruker AVIII-500 NMR spectrometers, where chemical shifts (δ in ppm) were determined with respect to the nondeuterated solvents as a reference. 2D COSY, DOSY, and ROESY spectra were recorded at 25 °C on a Bruker AVIII-500 NMR spectrometer. Atomic force microscopy (AFM) images were recorded on a Bruker Dimension Icon AFM system with ScanAsyst and the data were processed by NanoScope Analysis version 1.5 (Bruker Software, Inc.). Samples for AFM were prepared by spin-coating (500 rpm for 1 min) a sample solution (1×10^{-5} M) on a freshly cleaved mica surface. Transmission electron microscopy (TEM) was conducted on a JEOL 1200 EX microscope (80 kV) and a Philips Tecnai F30 Field Emission Gun Transmission Microscope (300 kV). TEM samples were prepared by drop-casting a sample solution (1×10^{-5} 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 source using the literature parameters.[1] Matrix-assisted laser desorption/ionization coupled with a time-of-flight detector (MALDI-TOF) mass spectrometry 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 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 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 settings in the literature.[1, 2] Calculations were proceeded with Geometry Optimization and followed by Anneal in Forcite module of Materials Studio version 7.0 program (Accelrys Software, Inc.). 200 conformations were generated after annealing and converted into the corresponding collision cross-sections (CCSs) using projection approximation (PA) in DriftScope 2.0 from Waters and trajectory method (TM) in MOBCAL.[3]

X-ray crystallography. Single-crystal X-ray data were collected on an Oxford Diffraction Gemini A CCD diffractometer and processed with CrysAlisPro software (Agilent Technologies). Graphite monochromated Cu-Kα radiation (λ = 1.54178 Å) at 200(2) K was used in the diffraction data collection. Empirical absorption correction was done by spherical harmonics from SCALE3 ABSPACK.[4] The structure was solved and refined by applying SHELXS-97[5] and SHELXL-97[6] programs. The structure was deposited at the Cambridge Crystallographic Data Center with the deposition number of CCDC 2363052.

Synthesis of [CdL^a_2].

L^a was synthesized according to the literature procedure.[7]

Complex [CdL^a_2]. $Cd(NO_3)_2 \cdot 4H_2O$ (5.4 mg, 17.5 μmol) in MeOH (1 mL) was mixed with L^a (20.0 mg, 34.3 μmol) in $CHCl_3$ (1 mL). After refluxing for 8 h, NH_4PF_6 (56.0 mg, 343.8 μmol) was added into the mixture, which then was stirred for additional 1 h at room temperature. The mixture was precipitated by Et_2O, filtered, washed with Et_2O, and dried under reduced pressure to give [CdL^a_2] as a white solid (25.6 mg, 16.3 μmol) in 95% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.49 (d, J = 7.4 Hz, 4H), 8.38 (s, 4H), 8.13 (d, J =7.4 Hz, 4H), 8.05 (t, J = 7.4 Hz, 4H), 7.84–7.75 (m, 6H), 7.07 (d, J = 8.2 Hz, 4H), 6.77 (t, J = 8.2 Hz, 4H), 5.99 (d, J = 8.9 Hz, 8H), and 2.85 (s, 24H). ESI-MS (m/z): 638.2808 $[M - 2PF_6]^{2+}$ (calcd m/z = 638.2847).

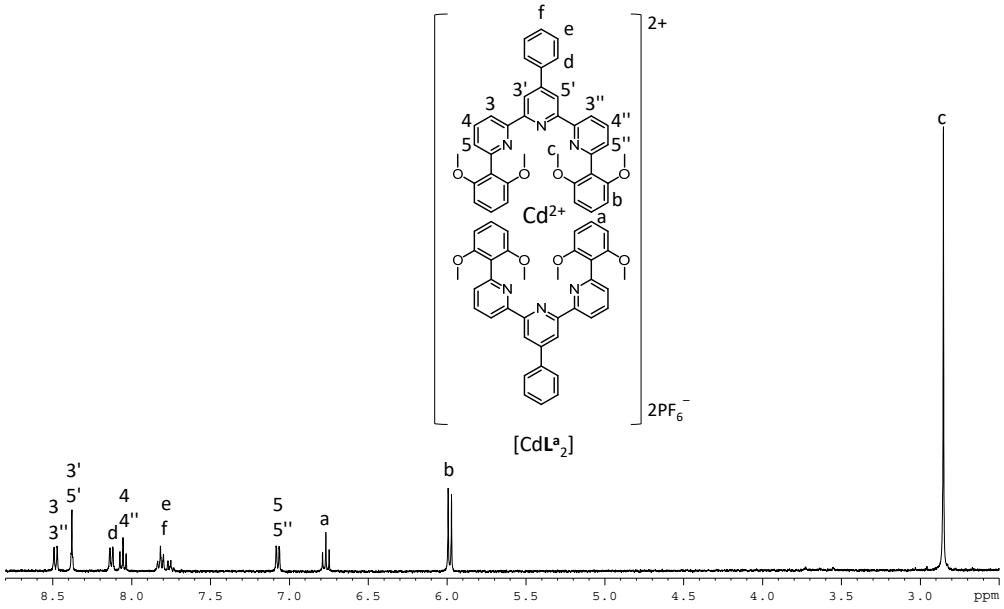


Figure S1. ^{1}H NMR spectrum of [CdL^a_2].

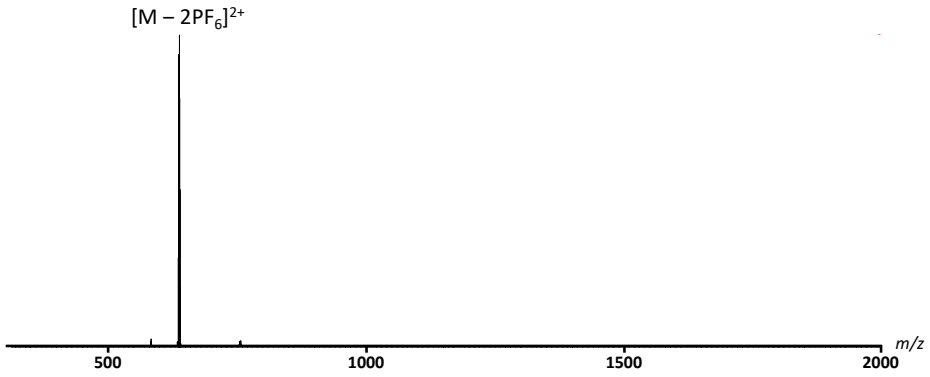


Figure S2. ESI-MS spectrum of [CdL^a_2].

Ligand exchange behavior of [CdL^a_2].

An equimolar mixture of [Cd$\mathbf{L}^a_2$] and $\mathbf{L}^a$ in $CDCl_3/CD_3CN$ (1/1, v/v) was prepared for EXSY experiments (Fig. S3). 2D/1D exchange spectroscopy (EXSY) NMR (500 MHz) experiments were conducted at 25 °C to estimate the ligand exchange rate constants. A peak at δ 3.72 ppm, corresponding to H^c in the free ligand $\mathbf{L}^a$, was identified as the diagonal signal. It was anticipated that a cross peak at δ 2.84 ppm, corresponding to H^c in [Cd$\mathbf{L}^a_2$], would appear at different mixing times. However, no signals were detected at δ 2.84 ppm in the selective excitation 1D EXSY NMR (Fig. S3b). The 2D EXSY NMR spectrum (Fig. S3a) also showed the absence of cross signals, indicating that no ligand exchange occurred between [Cd$\mathbf{L}^a_2$] and $\mathbf{L}^a$ at 25°C.

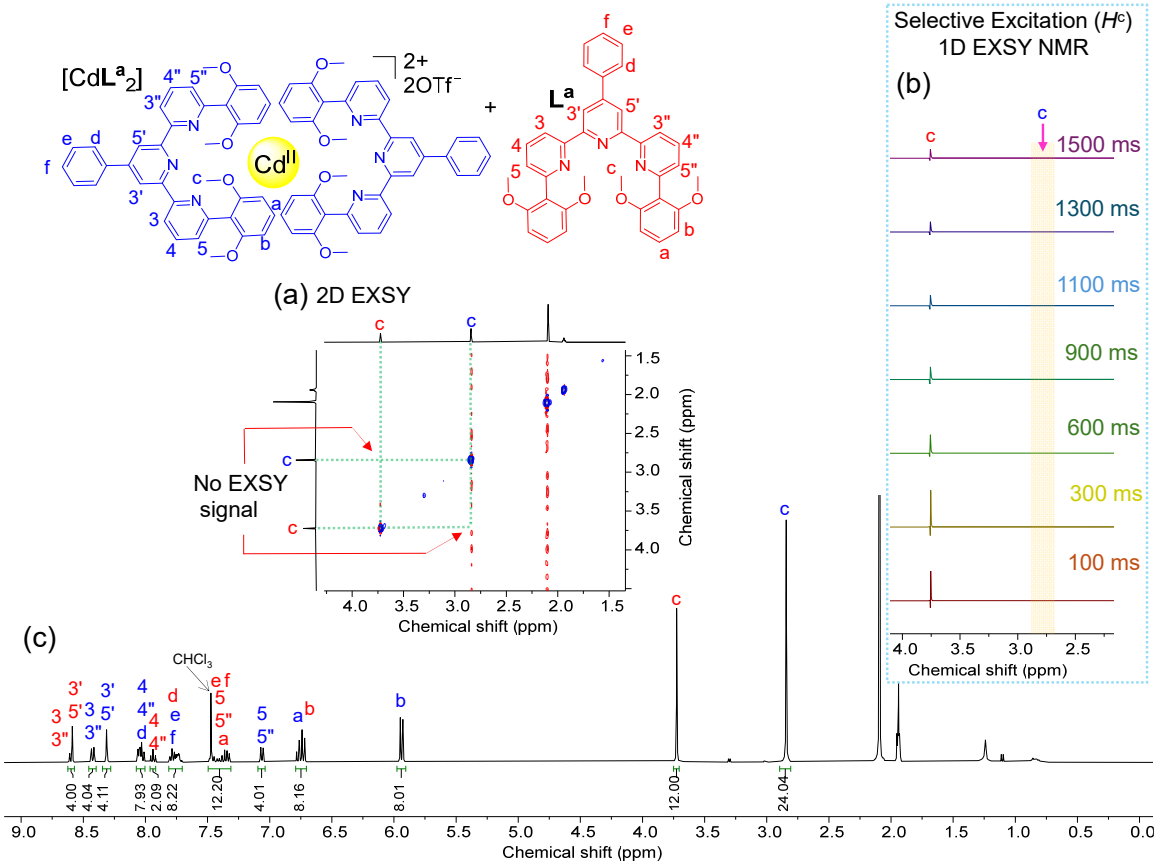
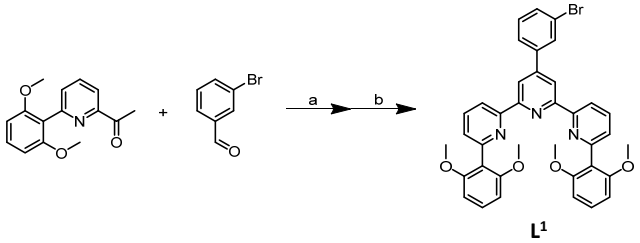


Figure S3. (a) ^{1}H–^{1}H 2D EXSY, (b) selective excitation (H^c) 1D EXSY, and (c) ^{1}H NMR spectra of an equimolar mixture of [Cd$\mathbf{L}^a_2$] and $\mathbf{L}^a$.

Synthesis of L^1 and compounds 1-2.

2-Acetyl-6-(2,6-dimethoxyphenyl)pyridine and 4'-(4-pinacolborylphenyl)-6,6"-di(2,6-dimethoxyphenyl)-2,2':6',2"-terpyridine were synthesized according to the literature procedures.[8]



Scheme S1. Synthesis of $\mathbf{L^1}$. *Reagents and conditions*: (a) NaOH, MeOH, 25 °C; (b) $NH_4OH_{(aq)}$, reflux.

Ligand L^1. To a solution of 2-acetyl-6-(2,6-dimethoxyphenyl)pyridine (2.5 g, 9.7 mmol) and 3-bromobenzaldehyde (0.8 g, 4.4 mmol) in EtOH (70 mL), NaOH (0.4 g, 10.0 mmol) was added. The mixture was stirred at room temperature for 24 h, and then $NH_4OH_{(aq)}$ (28 wt%, 4 mL) was added into the reaction mixture. After refluxing for 24 h, the solution was cooled to room temperature and the mixture was filtered, washed with EtOH, and dried under reduced pressure to give $\mathbf{L^1}$ as a light grey solid (1.5 g, 2.2 mmol) in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.62 (s, 2H), 8.58 (d, J = 8.2 Hz, 2H), 7.92 (t, J = 1.5 Hz, 1H), 7.89 (t, J = 7.6 Hz, 2H), 7.70 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 8.1 Hz, 1H), 7.37–7.32 (m, 4H), 7.28 (t, J = 8.1 Hz, 1H), 6.69 (d, J = 8.6 Hz, 4H), and 3.76 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.35, 156.57, 155.94, 153.88, 148.18, 141.25, 136.41, 131.45, 130.36, 130.22, 129.63, 126.32, 126.07, 122.82, 119.74, 119.51, 119.20, 104.62, and 56.16. MALDI-TOF-MS: calcd for $C_{37}H_{31}BrN_3O_4$ $[M + H]^+$: m/z = 660.1498; found: 660.1503.

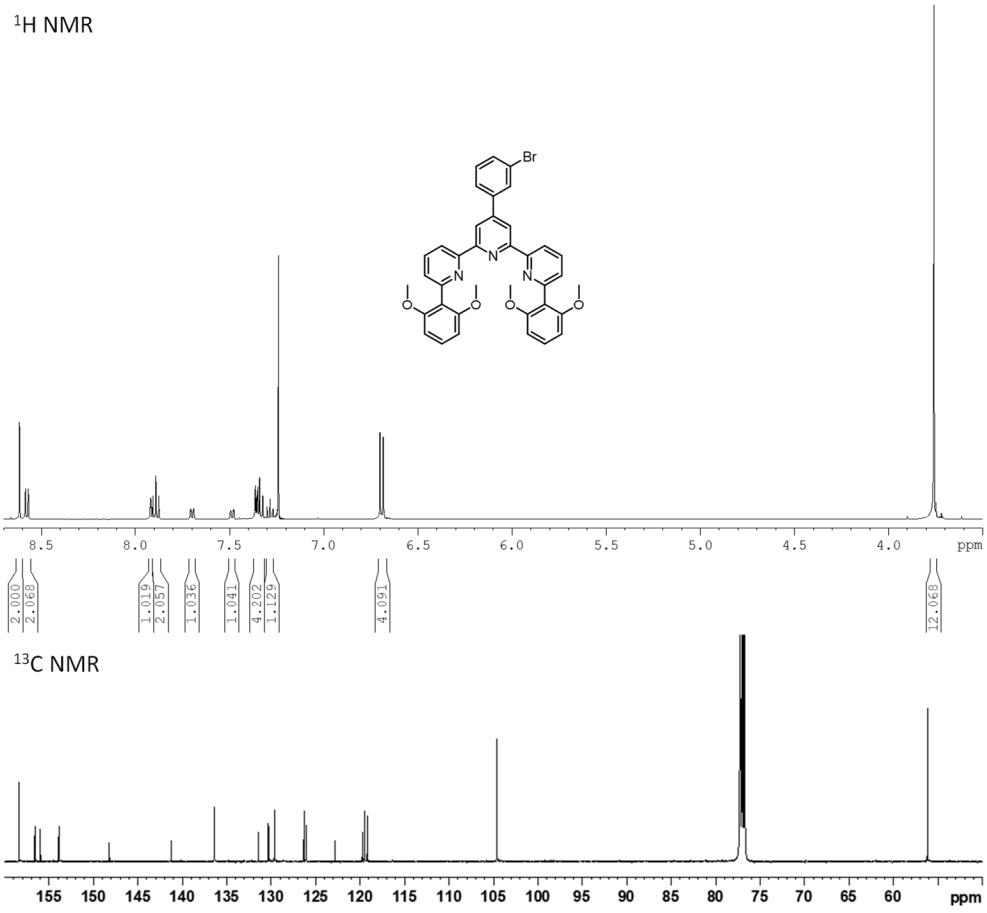


Figure S4. ^{1}H and ^{13}C NMR spectra of **L^{1}**.

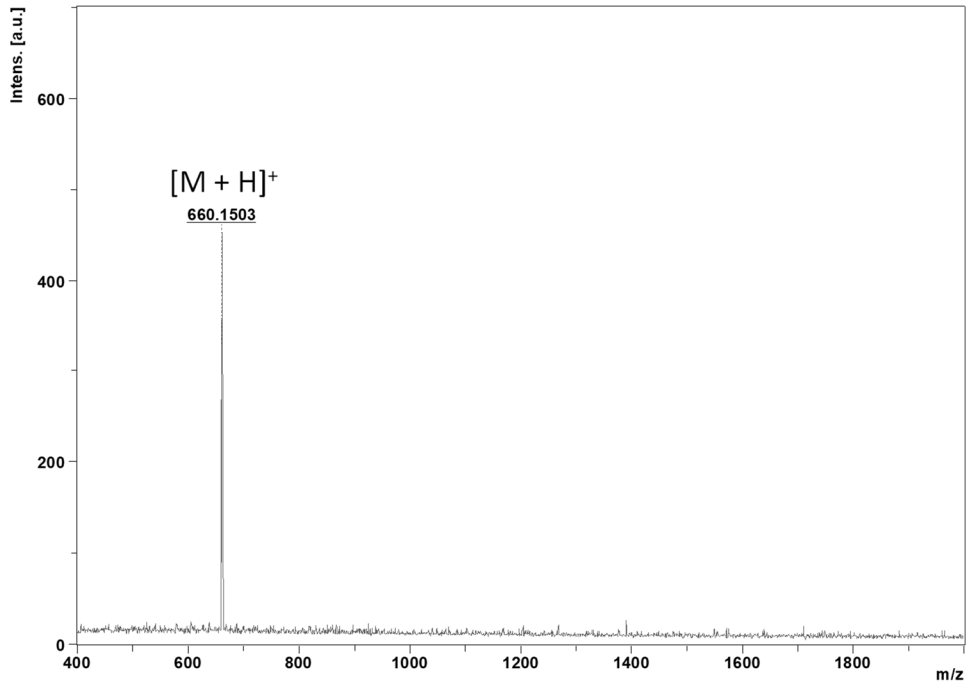
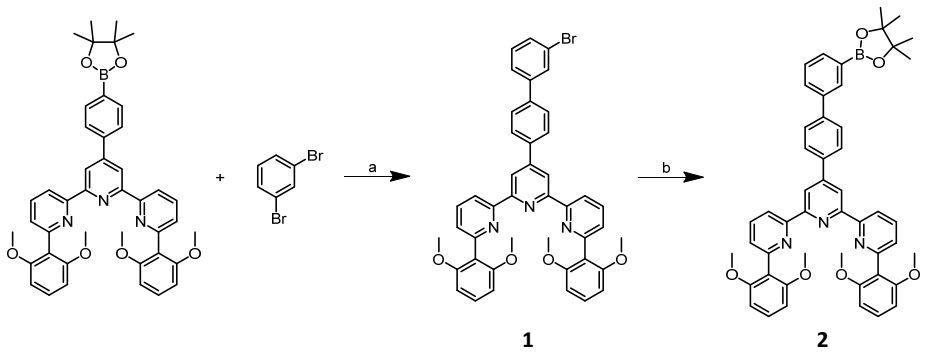


Figure S5. MALDI-TOF-MS spectrum of **L^{1}**.



Scheme S2. Synthesis of **1** and **2**. *Reagents and conditions*: (a) $Pd(PPh_3)_4$, K_2CO_3, toluene/H_2O/*t*-BuOH (3/3/1, v/v/v), reflux; (b) bis(pinacolato)diboron, $Pd(dppf)Cl_2$, KOAc, 1,4-dioxane, 80 °C.

Compound 1. To a degassed two-necked flask containing 4'-(4-pinacolborylphenyl)-6,6"-di(2,6-dimethoxyphenyl)-2,2':6',2"-terpyridine (1.0 g, 1.4 mmol), 1,3-dibromobenzene (1.0 g, 4.2 mmol), and K_2CO_3 (390.0 mg, 2.8 mmol), a mixed solvent (40 mL) of toluene/H_2O/*t*-BuOH (3/3/1, v/v/v) was added. After being purged with N_2 for 30 min, $Pd(PPh_3)_4$ (99.2 mg, 70.6 μmol) was added into the mixture, which was then refluxed for 1 day under N_2. After cooling to room temperature, the mixture was extracted with CH_2Cl_2, and the combined organic extract was dried over $MgSO_4$ and then evaporated to dryness under reduced pressure. The residue was recrystallized from a mixture of CH_2Cl_2/MeOH to give **1** as a yellow solid (676.7 mg, 0.9 mmol) in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.74 (s, 2H), 8.64 (d, J = 8.0 Hz, 2H), 7.96–7.91 (m, 4H), 7.79 (t, J = 1.7 Hz, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.41–7.31 (m, 6H), 6.74 (d, J = 8.3 Hz, 4H), and 3.80 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$ with trace amount of trifluoroacetic acid): δ (ppm) 158.06, 151.64, 150.57, 150.22, 149.85, 143.19, 141.99, 141.33, 135.57, 133.26, 130.73, 130.41, 130.01, 129.79, 128.05, 127.92, 125.76, 122.93, 122.77, 122.42, 110.61, 104.17, and 56.05. MALDI-TOF-MS: calcd for $C_{43}H_{34}BrN_3O_4$ $[M + H]^+$: m/z = 736.1811; found: 736.1825.

Compound 2. To a degassed flask containing **1** (0.5 g, 0.8 mmol), bis(pinacolato)diboron (0.4 g, 1.7 mmol), KOAc (0.4 g, 4.1 mmol), and $Pd(dppf)Cl_2$ (24.8 mg, 33.9 μmol), anhydrous 1,4-dioxane (5 mL) was added. The mixture was stirred at 80 °C for 12 h under N_2. After cooling to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2. The combined organic extract was dried over anhydrous $MgSO_4$, and then evaporated to dryness under reduced pressure. The crude product was recrystallized from a mixture of CH_2Cl_2/MeOH to give **2** as a dark brown solid (462.8 mg,

0.6 mmol) in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.75 (s, 2H), 8.63 (d, J = 7.8 Hz, 2H), 8.10 (s, 1H), 7.96–7.89 (m, 4H), 7.82 (d, J = 7.1 Hz, 1H), 7.76–7.71 (m, 3H), 7.48 (d, J = 7.1 Hz, 2H), 7.41–7.35 (m, 4H), 6.74 (d, J = 7.8 Hz, 2H), 3.80 (s, 12H), and 1.39 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 158.35, 155.44, 153.35, 149.62, 146.27, 141.51, 139.79, 137.35, 136.77, 133.88, 133.42, 130.03, 129.91, 128.21, 128.06, 127.81, 127.58, 126.67, 126.36, 119.99, 119.78, 104.64, 83.88, 56.22, and 24.87. MALDI-TOF-MS: calcd for $C_{49}H_{46}BN_3O_6$ $[M + H]^+$: m/z = 784.3558; found: 784.3551.

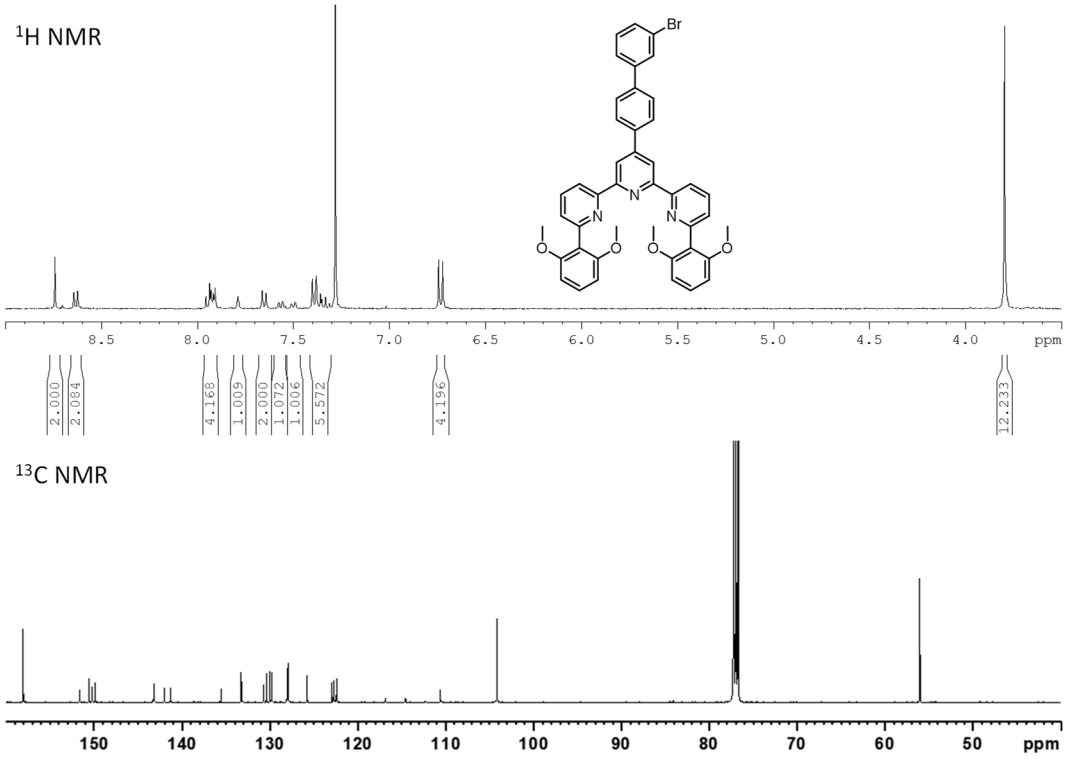


Figure S6. ^{1}H and ^{13}C NMR spectra of **1**.

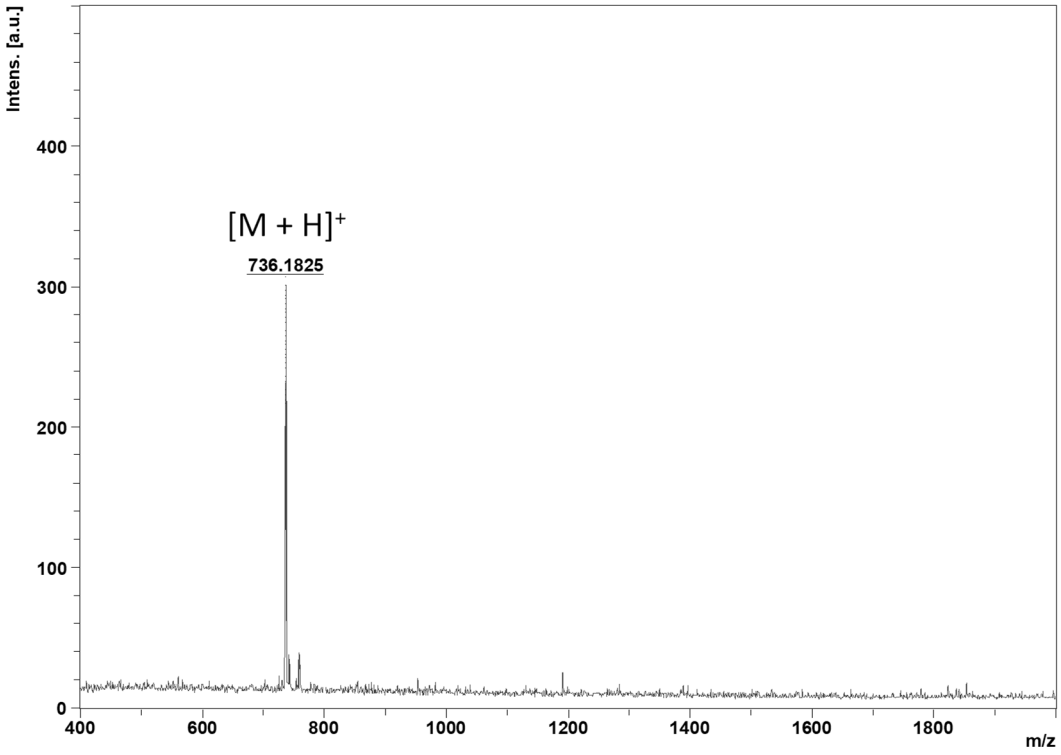


Figure S7. MALDI-TOF-MS spectrum of **1**.

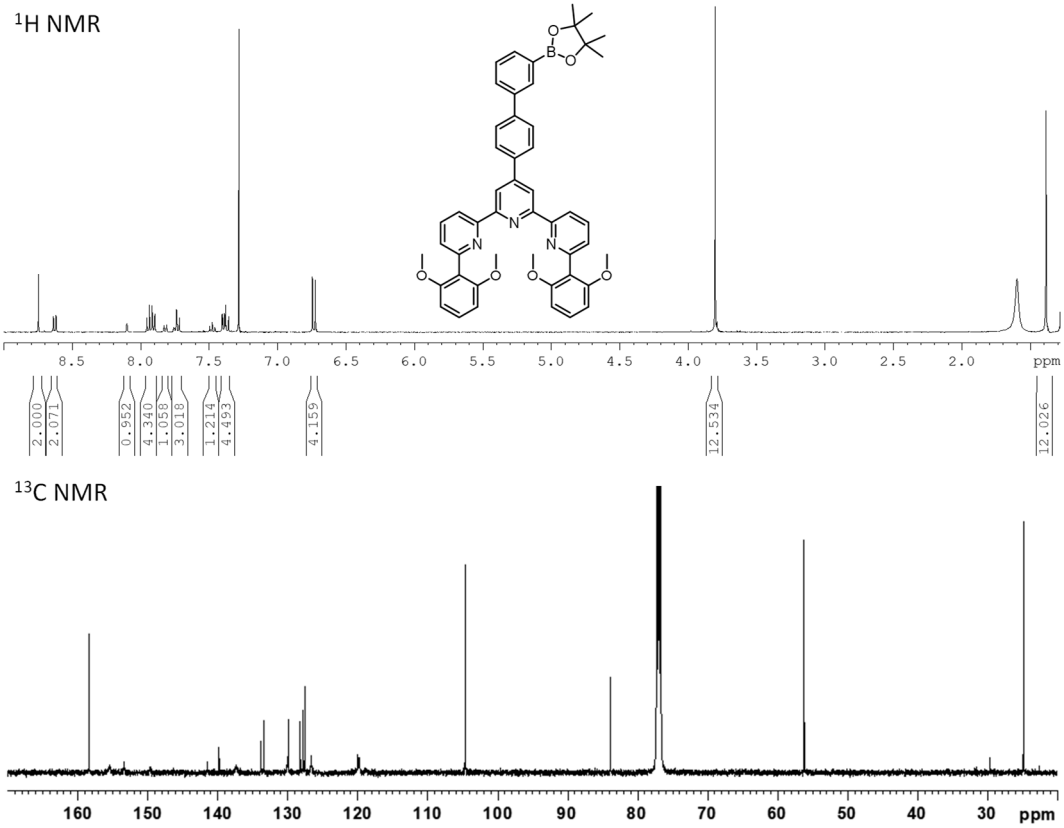


Figure S8. ^{1}H and ^{13}C NMR spectra of **2**.

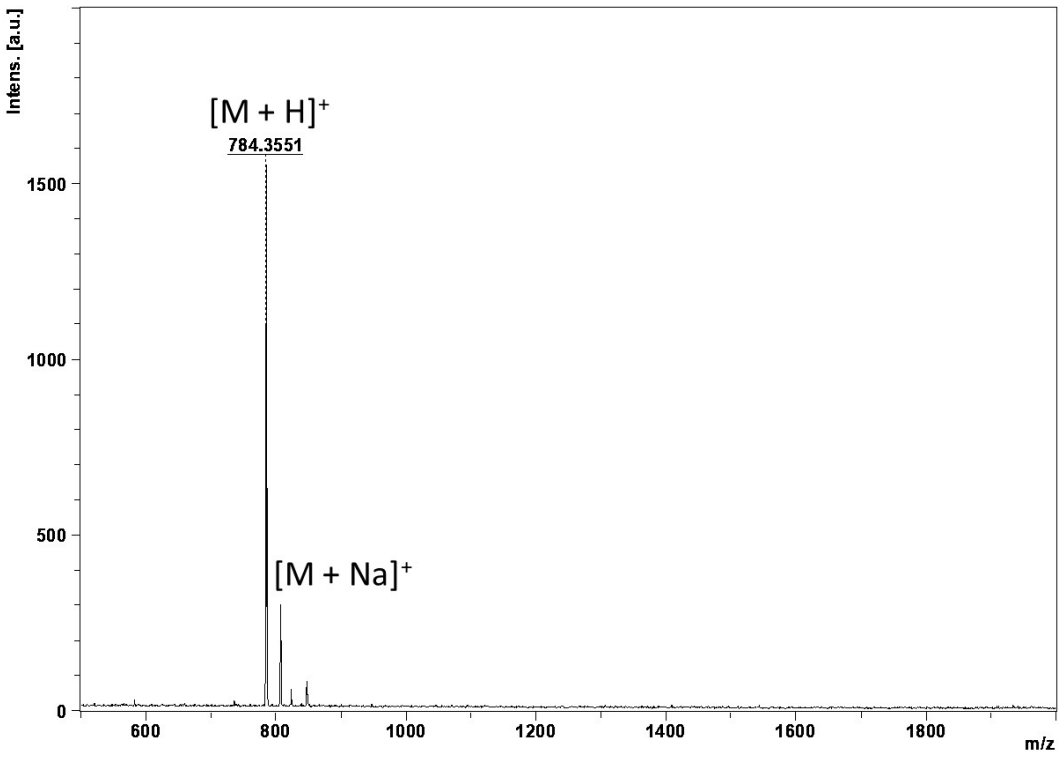
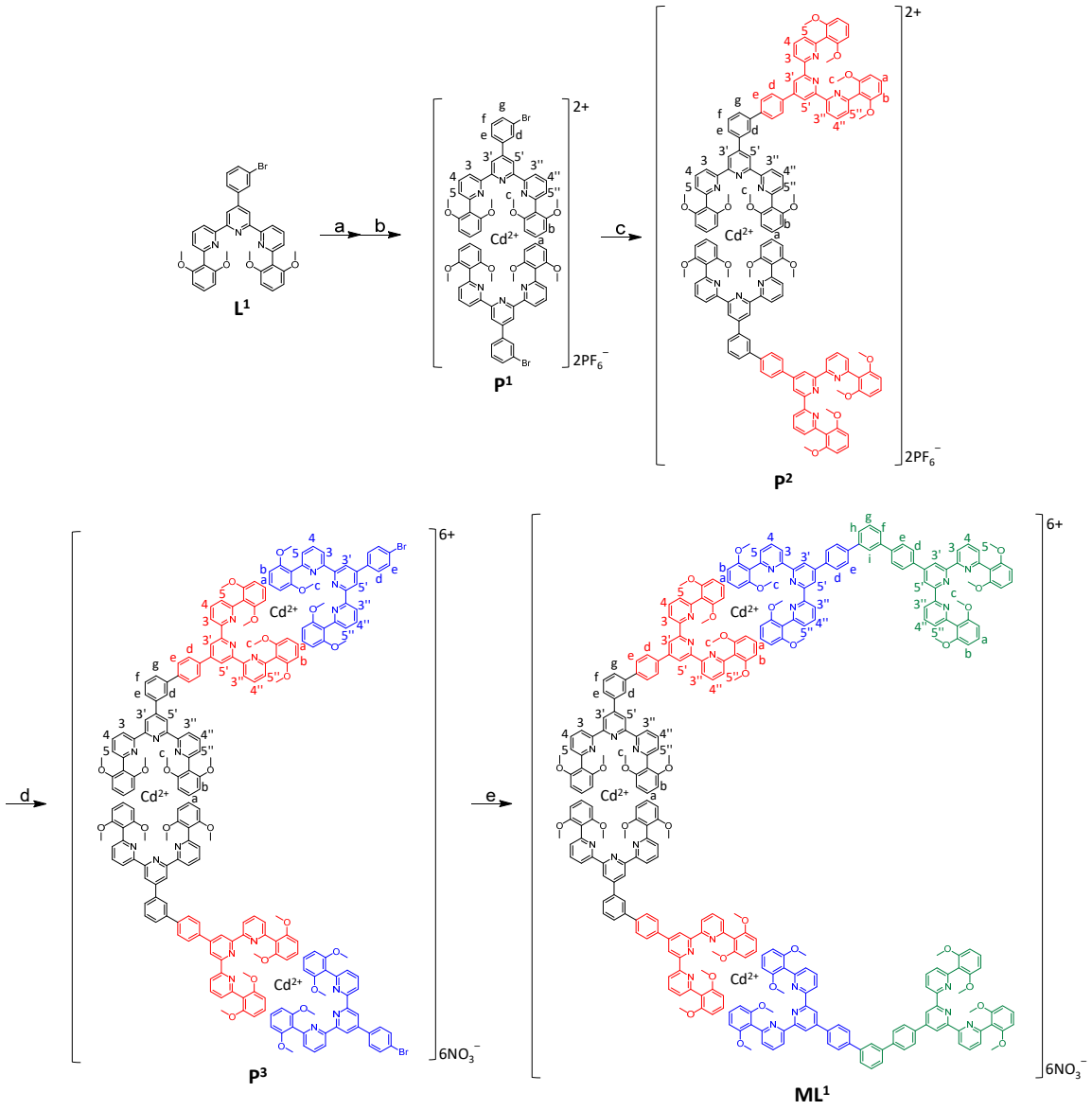


Figure S9. MALDI-TOF-MS spectrum of **2**.

Synthesis of P^1, P^2, P^3, and ML^1.

4'-(4-Pinacolborylphenyl)-6,6"-di(2,6-dimethoxyphenyl)-2,2':6',2"-terpyridine and 4'-(4-boromophenyl)-6,6"-di(2,6-dimethoxyphenyl)-2,2':6',2"-terpyridine were synthesized according to the literature procedures.[8]



Scheme S3. Synthesis of P^1, P^2, P^3, and ML^1. *Reagents and conditions*: (a) $Cd(NO_3)_2 \cdot 4H_2O$, $CHCl_3$/MeOH (1/1, v/v), reflux; (b) NH_4PF_6, r.t.; (c) $Pd(PPh_3)_4$, K_2CO_3, 4'-(4-pinacolborylphenyl)-6,6"-di(2,6-dimethoxyphenyl)-2,2':6',2"-terpyridine, 1,4-dioxane/MeCN/MeOH (10/10/1, v/v/v), 80 °C; (d) $Cd(NO_3)_2 \cdot 4H_2O$, 4'-(4-boromophenyl)-6,6"-di(2,6-dimethoxyphenyl)-2,2':6',2"-terpyridine, $CHCl_3$/MeCN/MeOH (5/5/1, v/v/v), reflux; (e) $Pd(PPh_3)_4$, K_2CO_3, **3**, 1,4-dioxane/MeCN/MeOH (10/10/1, v/v/v), 80 °C.

Precursor P[1]. Ligand **L[1]** (500.0 mg, 0.8 mmol) in $CHCl_3$ (5 mL) was mixed with $Cd(NO_3)_2 \cdot 4H_2O$ (119.1 mg, 0.4 mmol) in MeOH (5 mL). After refluxing for 8 h, NH_4PF_6 (1.2 g, 7.6 mmol) was added and the mixture was stirred for additional 1 h at room temperature. The mixture was precipitated by Et_2O, filtered, washed with Et_2O, and dried under reduced pressure to give **P[1]** as a white solid (619.7 mg, 0.4 mmol) in 95% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.49 (d, J = 7.9 Hz, 4H), 8.38−8.36 (m, 6H), 8.11 (d, J =7.6 Hz, 2H), 8.06 (t, J = 7.9 Hz, 4H), 7.92 (d, J = 7.6 Hz, 2H), 7.73 (t, J = 7.9 Hz, 2H), 7.08 (d, J = 7.6 Hz, 4H), 6.74 (t, J = 8.3 Hz, 4H), 5.98 (d, J = 8.3 Hz, 8H), and 2.85 (s, 24H). ESI-MS (*m/z*): 717.0964 $[M - 2PF_6]^{2+}$ (calcd *m/z* = 717.0952).

Precursor P[2]. To a degassed two-necked flask containing **P[1]** (200.0 mg, 0.1 mmol), 4'-(4-pinacolborylphenyl)-6,6"-di(2,6-dimethoxyphenyl)-2,2':6',2"-terpyridine (246.4 mg, 0.3 mmol), K_2CO_3 (64.1 mg, 0.5 mmol), and $Pd(PPh_3)_4$ (13.4 mg, 11.6 μmol), a mixed solvent (3 mL) of 1,4-dioxane/MeCN/MeOH (10/10/1, v/v/v) was added. After being purged with N_2 for 30 min, the reaction mixture was stirred at 80 °C for 8 h under N_2. After cooling to room temperature, the mixture was poured into water, and the precipitate was collected by filtration. The residue was recrystallized from a mixture of $CHCl_3$/MeCN/MeOH to give **P[2]** as a white solid (189.7 mg, 69.6 μmol) in 60% yield. ^{1}H NMR (400 MHz, $CD_3CN/CDCl_3$ = 9/1, v/v): δ (ppm) 8.76 (s, 4H), 8.70 (d, J = 7.8 Hz, 4H), 8.50 (d, J = 7.8 Hz, 4H), 8.43 (s, 4H), 8.34 (s, 2H), 8.12−8.00 (m, 20H), 7.91 (t, J = 7.8 Hz, 2H), 7.42−7.38 (m, 8H), 7.08 (d, J = 7.4 Hz, 4H), 6.80−6.77 (m, 12H), 5.99 (d, J = 8.3 Hz, 8H), 3.75 (s, 24H), and 2.86 (s, 24H). ESI-MS (*m/z*): 1217.4141 $[M - 2PF_6]^{2+}$ (calcd *m/z* = 1217.4005), and 811.8734 $[M - 2PF_6 + H]^{3+}$ (calcd *m/z* = 811.9352).

Precursor P[3]. Precursor **P[2]** (200.0 mg, 73.4 μmol), 4'-(4-boromophenyl)-6,6"-di(2,6-dimethoxyphenyl)-2,2':6',2"-terpyridine (145.4 mg ,0.2 mmol), and $Cd(NO_3)_2 \cdot 4H_2O$ (69.2 mg, 0.2 mmol) were dissolved and mixed in $CHCl_3$/MeCN/MeOH (5/5/1, v/v/v, 25 mL). After the mixture was refluxed for 12 h, the solvent was removed under reduced pressure, and the residue dissolved in MeCN was subjected to column chromatography (SiO_2, sat. $KNO_{3(aq)}/H_2O$/MeCN = 1/1/30, v/v/v). The combined fractions were evaporated under reduced pressure to afford the residue, which was washed with H_2O and Et_2O to give **P[3]** as a pale-yellow solid (35.0 mg, 8.0 μmol) in 11% yield. Due to the irreversible complexation, which lacks selectivity, oligomers from **P[2]** and the homoleptic complex of monotopic tpy ligands, along with **P[3]**, were produced, resulting in a low isolated yield of **P[3]**. ^{1}H NMR (400 MHz, $CD_3CN/CDCl_3$ = 9/1, v/v): δ (ppm) 8.70 (d, J = 8.3 Hz, 4H), 8.63−8.66 (m, 6H), 8.63 (d, J = 8.3 Hz, 4H), 8.56 (s, 4H), 8.51 (d, J = 8.3 Hz, 4H), 8.49−8.43 (m, 10H),

8.39 (s, 4H), 8.30 (d, J = 6.9 Hz, 2H), 8.26 (d, J = 6.9 Hz, 2H), 8.30−8.03 (m, 18H), 8.00 (d, J = 8.9 Hz, 4H), 7.15 (d, J = 7.6 Hz, 4H), 7.12−7.09 (m, 8H), 6.90−6.83 (m, 8H), 6.77 (t, J = 8.9 Hz, 4H), 6.12 (d, J = 8.3 Hz, 8H), 6.07 (d, J = 8.3 Hz, 8H), 5.99 (d, J = 8.3 Hz, 8H), 2.94 (s, 24H), 2.90 (s, 24H), and 2.87 (s, 24H). ESI-MS (*m/z*): 663.6084 $[M - 6NO_3]^{6+}$ (calcd *m/z* = 663.6180), 808.5351 $[M - 5NO_3]^{5+}$ (calcd *m/z* = 808.5353), and 1026.2264 $[M - 4NO_3]^{4+}$ (calcd *m/z* = 1026.2160).

Metalloligand ML^1. To a degassed two-necked flask containing **P^3** (100.0 mg, 23.0 μmol), **2** (54.0 mg, 68.9 μmol), K_2CO_3 (12.7 mg, 91.9 mmol), and $Pd(PPh_3)_4$ (4.6 mg, 4.6 μmol), a mixed solvent (3 mL) of 1,4-dioxane/MeCN/MeOH (10/10/1, v/v/v) was added. After being purged with N_2 for 30 min, the mixture was stirred at 80 °C for 8 h under N_2. After cooling to room temperature, the mixture was poured into water, and the precipitate was collected by filtration. The residue was subjected to column chromatography (SiO_2, sat. $KNO_{3(aq,)}$/H_2O/MeCN = 1/1/28, v/v/v) to give **ML^1** as a white solid (38.0 mg, 6.9 μmol) in 30% yield. ^{1}H NMR (400 MHz, CD_3CN/$CDCl_3$ = 9/1, v/v): δ (ppm) 8.76−8.67 (m, 12H), 8.66−8.61 (m, 8H), 8.58−8.52 (m, 8H), 8.50−8.43 (m, 10H), 8.30−8.24 (m, 12H), 8.20−8.02 (m, 24H), 8.00−7.97 (m, 8H), 7.91 (d, J = 7.7 Hz, 2H), 7.83 (d, J = 7.8 Hz, 2H), 7.72 (t, J = 7.2 Hz, 2H), 7.41−7.38 (m, 8H), 7.17−7.08 (m, 12H), 6.92−6.78 (m, 20H), 6.11 (d, J = 8.6 Hz, 8H), 6.07 (d, J = 8.6 Hz, 8H), 6.03 (d, J = 8.6 Hz, 8H), 3.76 (s, 24H), 2.95 (s, 24H), 2.91 (s, 24H), and 2.89 (s, 24H). ESI-MS (*m/z*): 1039.3177 $[M - 5NO_3]^{5+}$ (calcd *m/z* = 1039.3119), 1773.5160 $[M - 4NO_3]^{4+}$ (calcd *m/z* = 1773.5145), and 1314.6447 $[M - 3NO_3]^{3+}$ (calcd *m/z* = 1314.6468).

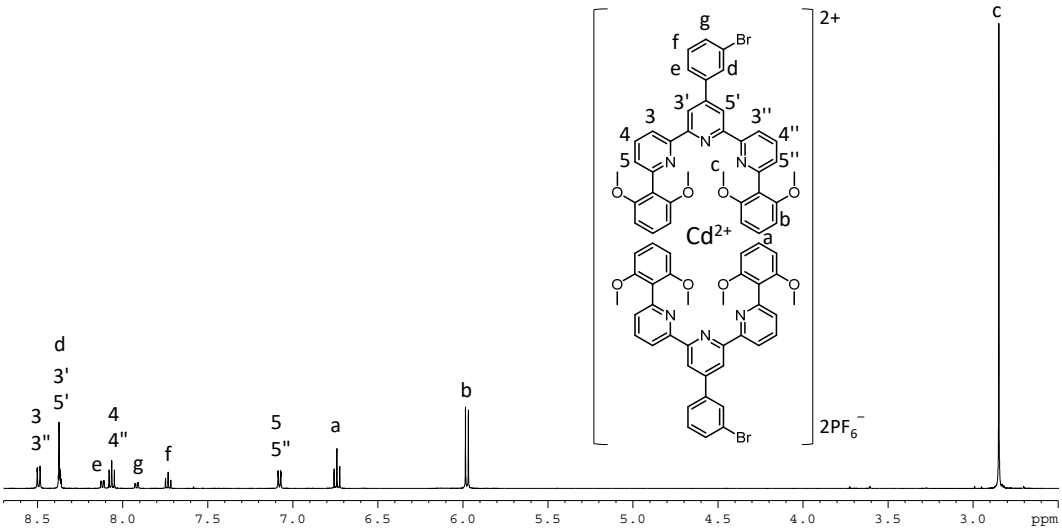


Figure S10. ^{1}H NMR spectrum of **P^1**.

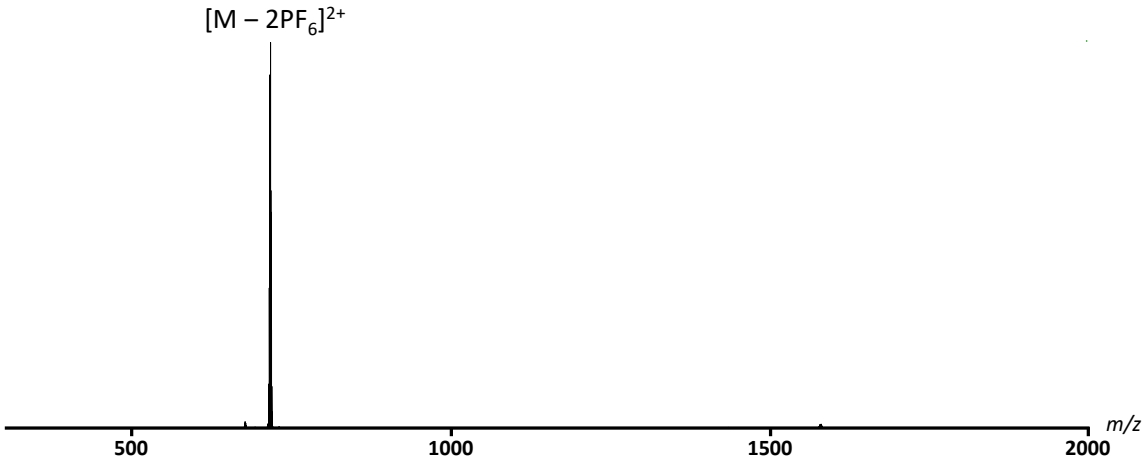


Figure S11. ESI-MS spectrum of **P[1]**.

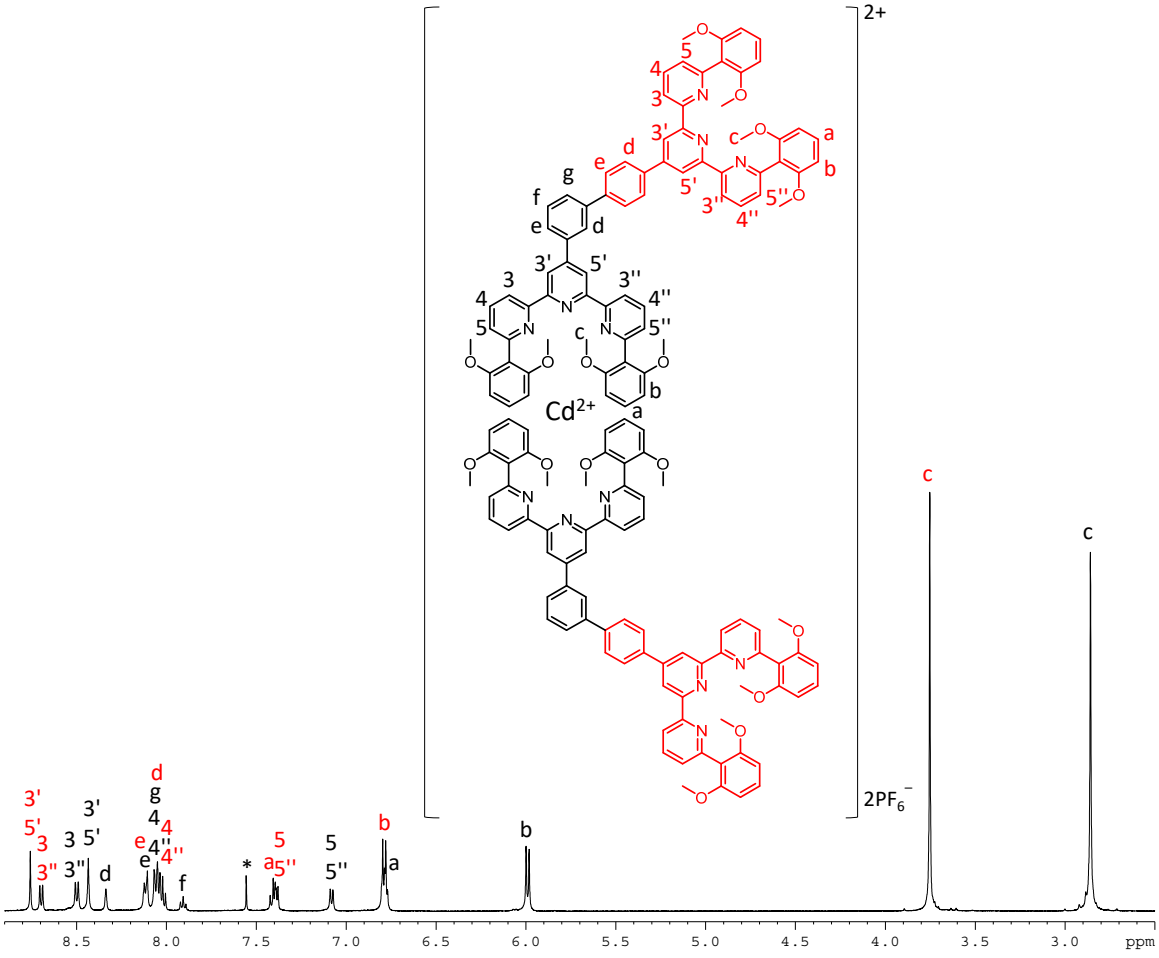


Figure S12. ^{1}H NMR spectrum of **P[2]**.

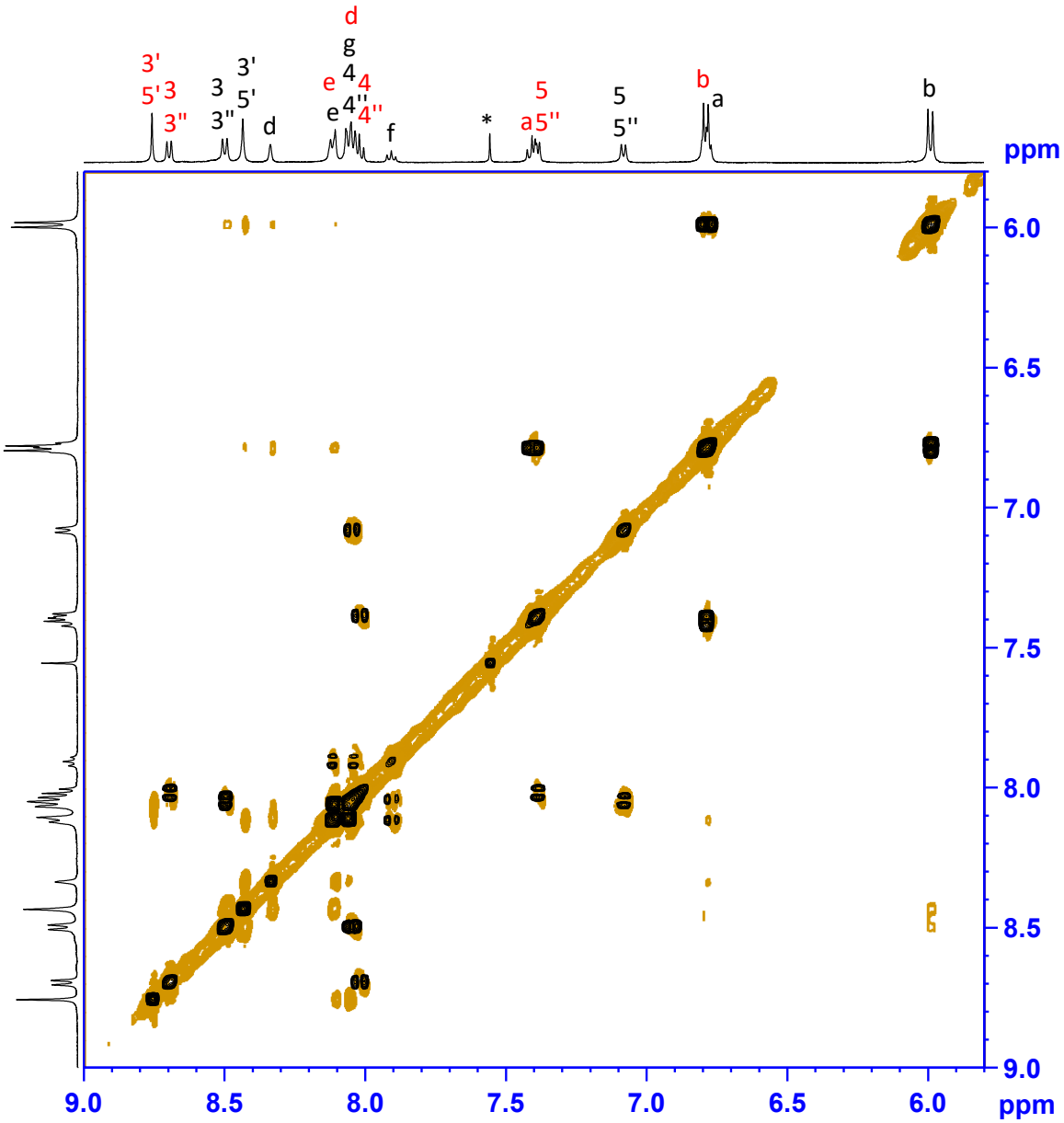


Figure S13. Partial ROESY NMR spectrum of $\mathbf{P^2}$ (yellow: ROESY signals, black: COSY signals).

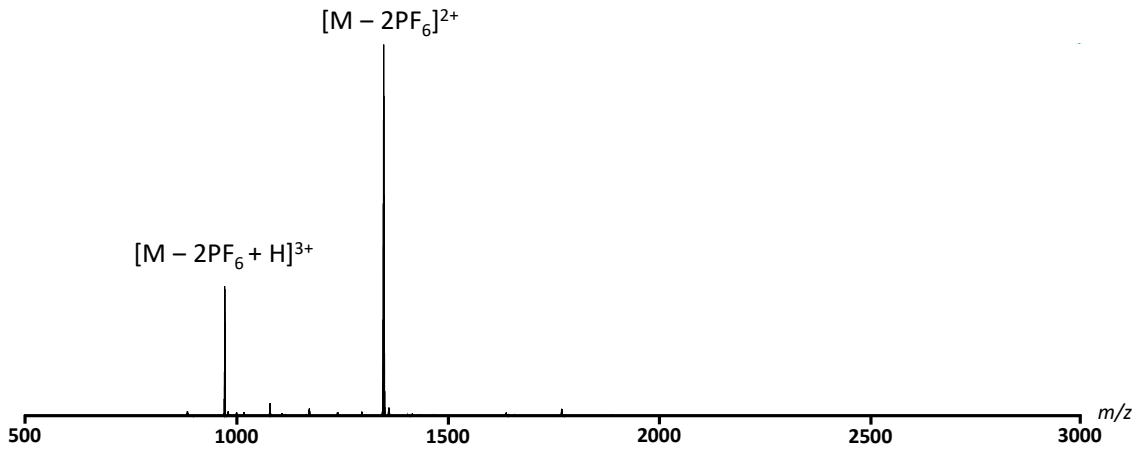


Figure S14. ESI-MS spectrum of **P²**.

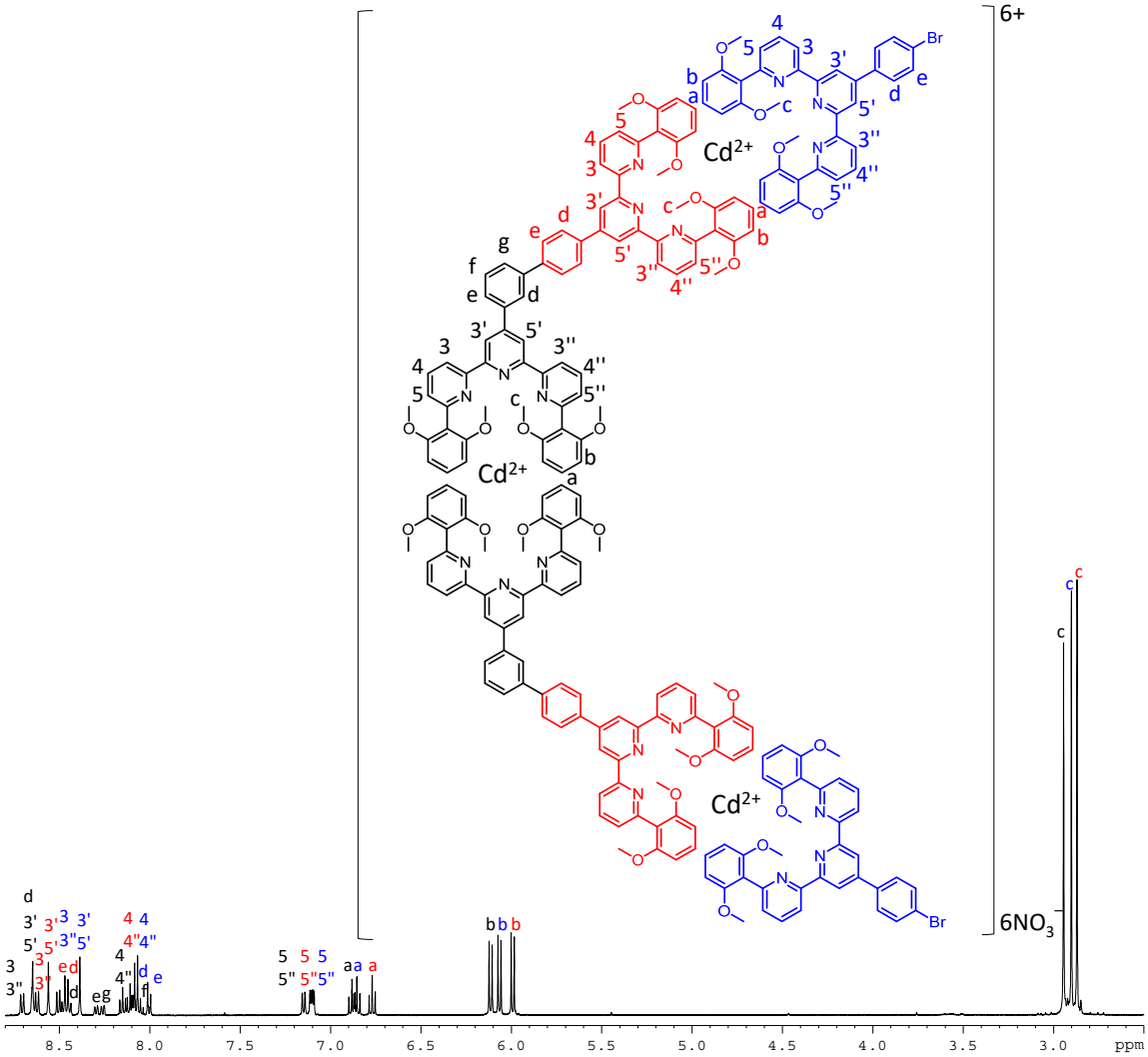


Figure S15. ^{1}H NMR spectrum of **P³**.

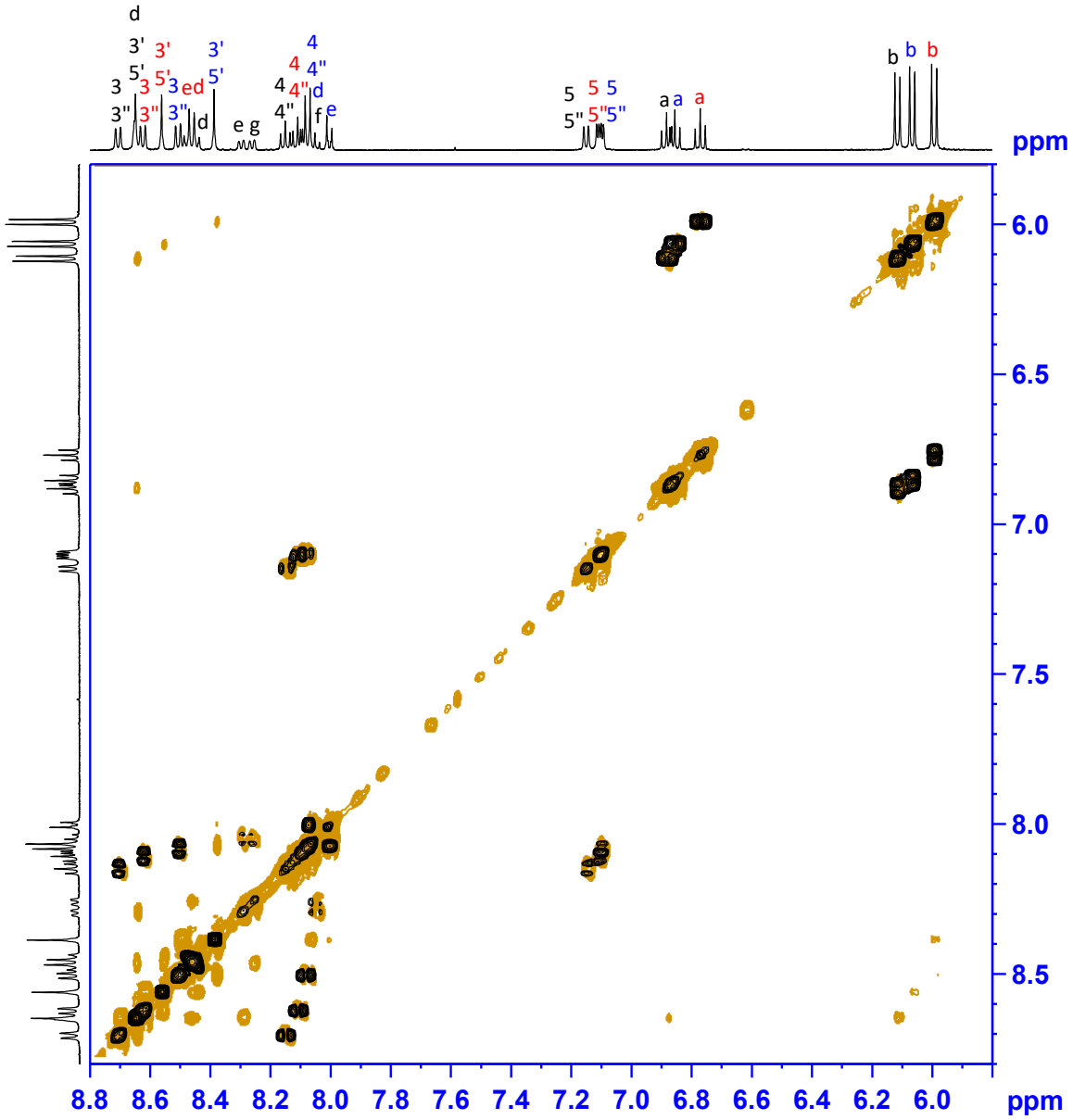


Figure S16. Partial ROESY NMR spectrum of **P^3** (yellow: ROESY signals, black: COSY signals).

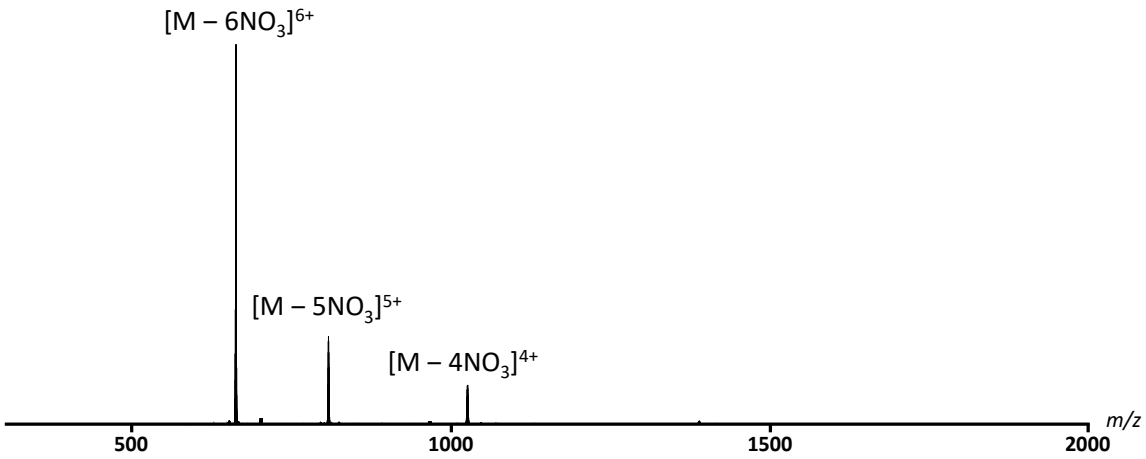


Figure S17. ESI-MS spectrum of **P**[3].

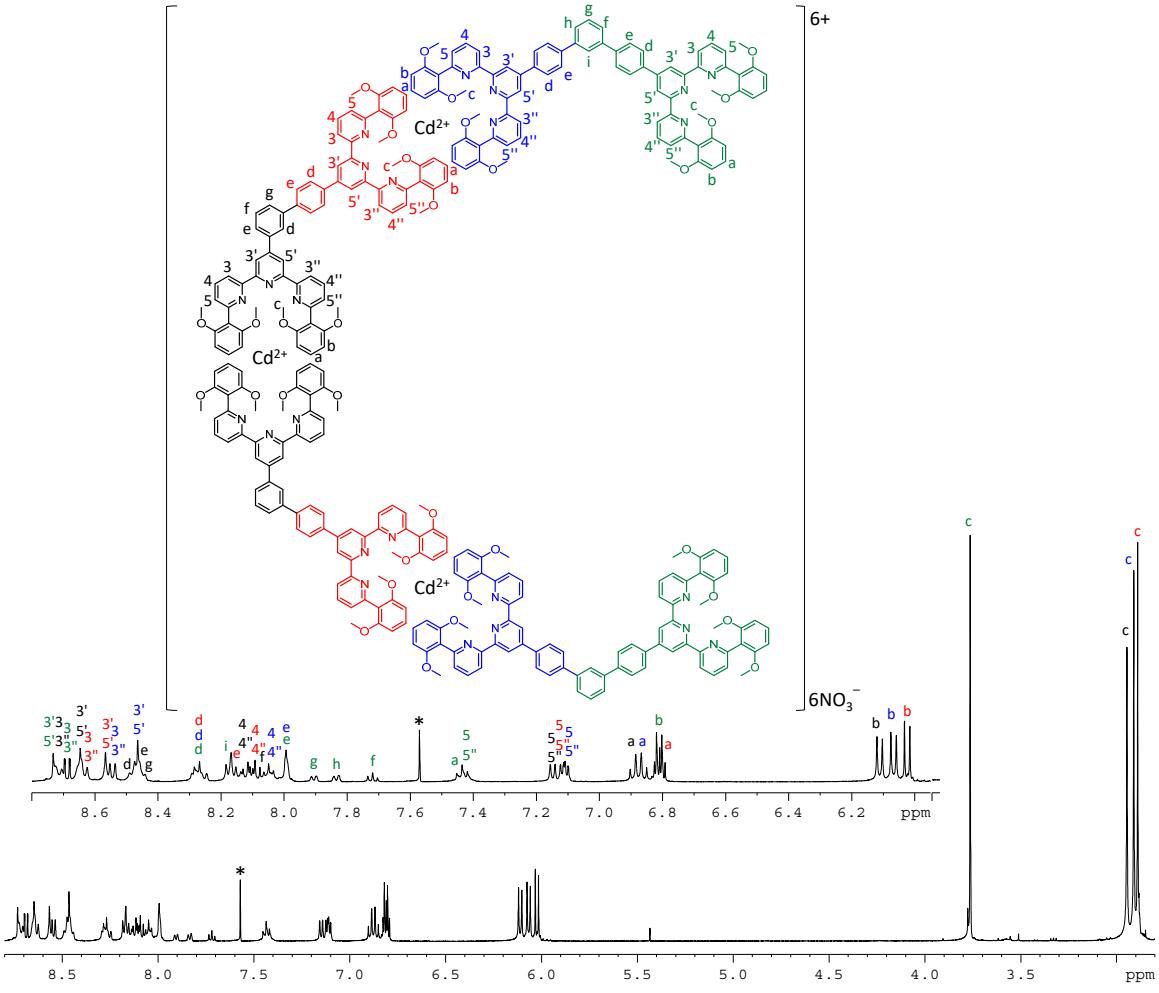


Figure S18. [1]H NMR spectrum of **ML**[1].

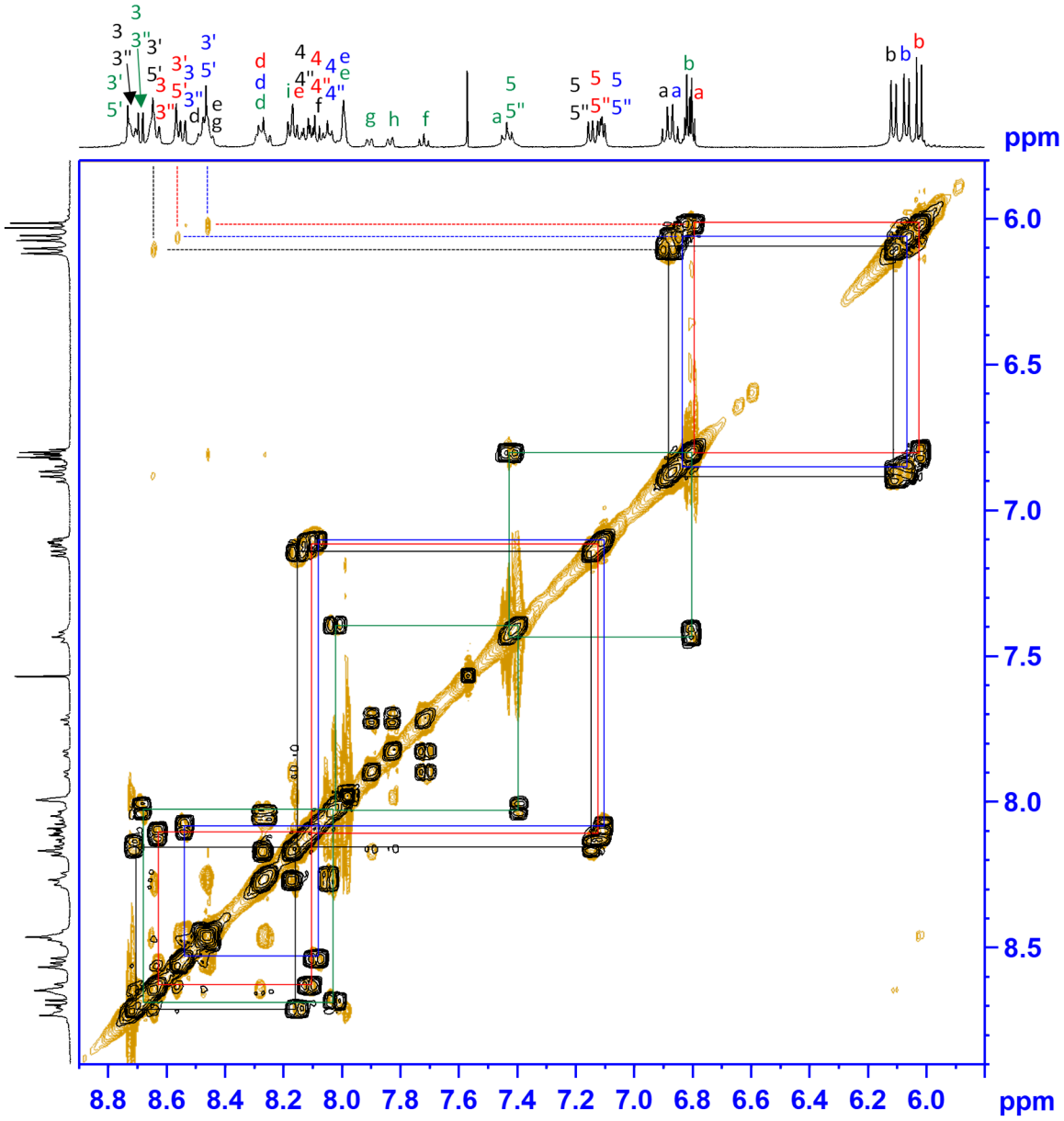


Figure S19. Partial ROESY NMR spectrum of **ML**[1]. (yellow: ROESY signals, black: COSY signals).

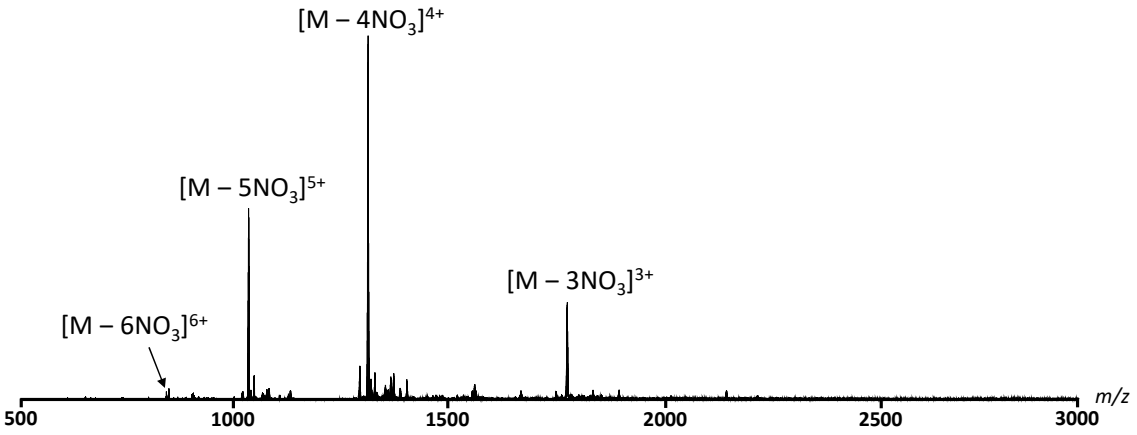
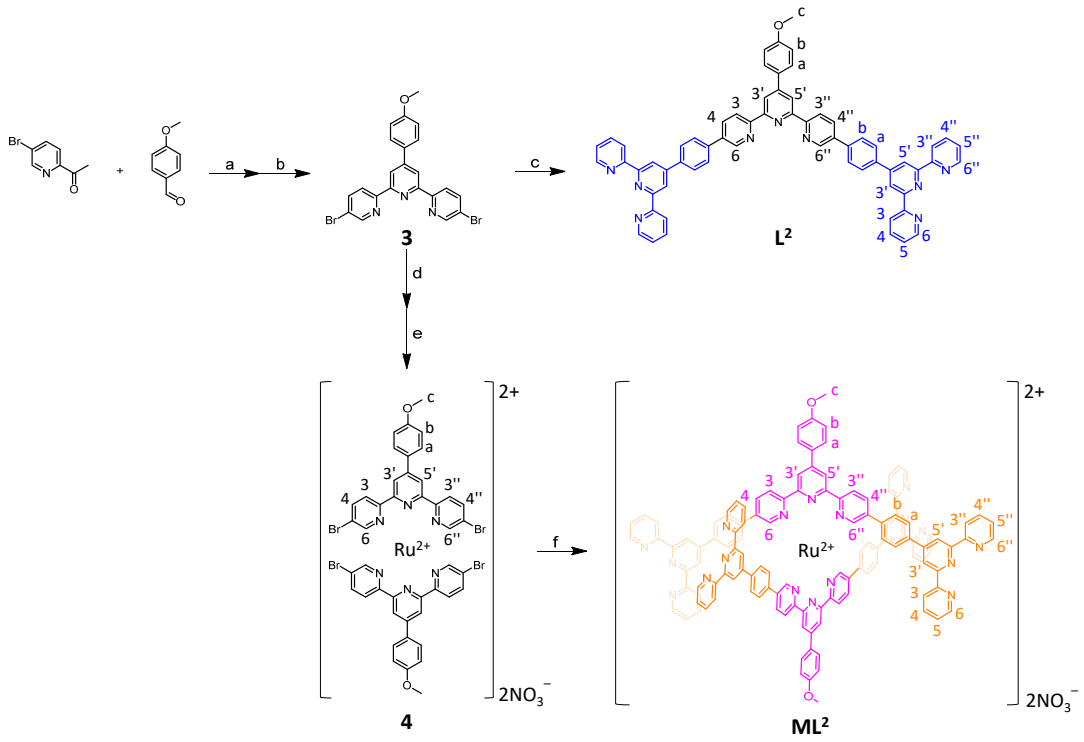


Figure S20. ESI-MS spectrum of **ML**[1].

Synthesis of compounds 3-4, L^2, and ML^2.

2-Acetyl-5-bromopyridine,[9] 4-methoxybenzaldyhyde,[10] and 4'-(4-boronophenyl)-2,2':6',2''-terpyridine[11] were synthesized according to the literature procedures.



Scheme S4. Synthesis of **3**, **4**, L^2, and ML^2. *Reagents and conditions*: (a) NaOH, MeOH, 25 °C; (b) $NH_4OH_{(aq)}$, reflux; (c) $Pd(PPh_3)_4$, K_2CO_3, 4'-(4-boronophenyl)-2,2':6',2''-terpyridine, toluene/H_2O/*t*-BuOH (3/3/1, v/v/v), reflux; (d) $RuCl_3 \cdot 3H_2O$, EtOH, reflux; (e) **7**, 4-ethylmorpholine, EtOH/$CHCl_3$ (1/1, v/v), reflux; (f) $Pd(PPh_3)_4$, K_2CO_3, 4'-(4-boronophenyl)-2,2':6',2''-terpyridine, 1,4-dioxane/MeCN (1/1, v/v), reflux.

Compound 3. To a solution of 2-acetyl-5-bromopyridine (2.0 g, 10.0 mmol) and 4-methoxybenzaldehyde (0.6 g, 4.5 mmol) in EtOH (80 mL), NaOH (0.4 g, 10.0 mmol) was added. The mixture was stirred at room temperature for 24 h, and then $NH_4OH_{(aq)}$ (28 wt%, 4 mL) was added into the reaction mixture. After refluxing for 24 h, the solution was cooled to room temperature and the mixture was filtered and washed with EtOH under reduced pressure to give **3** as a light grey solid (1.6 g, 3.2 mmol) in 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.74 (d, J = 2.7 Hz, 2H), 8.65 (s, 2H), 8.50 (d, J = 8.7 Hz, 2H), 7.96 (dd, J = 8.7 and 2.7 Hz, 2H), 7.83 (d, J = 8.7 Hz, 2H), 7.02 (d, J = 8.7 Hz, 2H), and 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.67, 154.97, 154.65, 150.13, 150.00, 139.44, 130.39, 128.48, 122.56, 121.22, 118.42, 114.42, and 55.41. MALDI-TOF-MS: calcd for $C_{22}H_{16}Br_2N_3O$ $[M + H]^+$: m/z = 495.9660; found: 495.9658.

Ligand L^2. To a degassed two-necked flask containing **3** (1.0 g, 2.0 mmol), 4'-(4-boronophenyl)-2,2':6',2''-terpyridine (1.7 g, 4.8 mmol), and K_2CO_3 (1.1 g, 8.0 mmol), a mixed solvent (50 mL) of toluene/H_2O/*t*-BuOH (3/3/1, v/v/v) was added. After being purged with N_2 for 30 min, $Pd(PPh_3)_4$ (232.4 mg, 201.1 μmol) was added into the mixture, which was then refluxed for 1 day under N_2. After cooling to room temperature, the mixture was extracted with $CHCl_3$, and the combined organic extract was dried over $MgSO_4$ and then evaporated to dryness under reduced pressure. The residue was subjected to flash column chromatography (Al_2O_3, $CHCl_3$). The crude was recrystallized from a mixture of CH_2Cl_2/MeOH to give $\mathbf{L^2}$ as a grey solid (1.1 g, 1.1 mmol) in 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.05 (d, J = 2.4 Hz, 2H), 8.81 (s, 4H), 8.79–8.76 (m, 4H), 8.74 (dd, J = 5.12, and 1.79 Hz, 4H), 8.68 (d, J = 8.2 Hz, 4H), 8.16 (dd, J = 8.2, and 2.6 Hz, 2H), 8.07 (d, J = 8.4 Hz, 4H), 7.94–7.81 (m, 8H), 7.36 (ddd, J = 7.4, 4.6, and 1.0 Hz, 4H), 7.06 (d, J = 8.9 Hz, 2H), and 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 160.56, 156.19, 156.08, 155.61, 155.49, 149.81, 149.47, 149.17, 147.55, 138.33, 138.29, 136.92, 135.78, 135.14, 130.77, 128.57, 128.10, 127.58, 123.90, 121.40, 120.90, 118.73, 118.39, 114.38, and 55.41. MALDI-TOF-MS: calcd for $C_{64}H_{44}N_9O$ $[M + H]^+$: m/z = 954.3669; found: 954.3672.

Compound 4. A mixture of **3** (1.0 g, 2.0 mmol) and $RuCl_3 \cdot 3H_2O$ (788.8 mg, 3.0 mmol) in EtOH (20 mL) was refluxed for 2 days. After cooling to room temperature, the crude was filtered and the residue was washed with EtOH and acetone. The dark residue, **3** (1.0 g, 2.0 mmol), and three drops of 4-ethylmorpholine were mixed in EtOH/$CHCl_3$ (30 mL, 1/1, v/v). After the mixture was refluxed overnight, the solvent was removed under reduced pressure, and the residue dissolved in MeCN was subjected to column chromatography (SiO_2, sat. $KNO_{3(aq,)}$/H_2O/MeCN = 1/1/20, v/v/v). The combined fraction was evaporated and then washed with H_2O and Et_2O to give **4** as a red solid (1.8 g, 1.5 mmol) in 73% yield. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.97 (s, 4H), 8.54 (d, J = 8.3 Hz, 4H), 8.20 (d, J = 8.9 Hz, 4H), 8.14 (dd, J = 8.8, and 2.1 Hz, 4H), 7.42 (d, J = 1.8 Hz, 4H), 7.30 (d, J = 8.9 Hz, 4H), and 3.97 (s, 6H). ESI-MS (m/z): 547.9107 $[M - 2NO_3]^{4+}$ (calcd m/z = 547.9120).

Metalloligand ML^2. To a degassed two-necked flask containing **4** (150.0 mg, 123.0 μmol), 4'-(4-boronophenyl)-2,2':6',2''-terpyridine (260.7 mg, 738.0 μmol), K_2CO_3 (135.8 mg, 984.0 μmol), and $Pd(PPh_3)_4$ (56.9 mg, 49.2 μmol), a mixed solvent (15 mL) of 1,4-dioxane/MeCN (1/1, v/v) was added. After being purged with N_2 for 30 min, the mixture was refluxed for 12 h under N_2. After cooling to room temperature, the mixture was poured into water, and the precipitate was filtered and then subjected to column chromatography

(Al_2O_3, $CHCl_3$) to give **ML²** as a dark red solid (170.6 mg, 80.0 μmol) in 65% yield. ^{1}H NMR (400 MHz, $CD_3CN/CDCl_3$ = 9/1, v/v): δ (ppm) 9.41 (s, 4H), 9.31 (d, J = 8.4 Hz, 4H), 8.68−8.75 (m, 16H), 8.66 (d, J = 8.4 Hz, 8H), 8.54 (d, J = 8.4 Hz, 4H), 8.30 (d, J = 6.7 Hz, 4H), 7.97 (d, J = 7.5 Hz, 8H), 7.89 (t, J = 7.5 Hz, 8H), 7.68 (s, 4H), 7.50 (d, J = 7.5 Hz, 8H), 7.37 (t, J = 6.7 Hz, 8H), and 3.95 (s, 6H). ESI-MS (m/z): 502.6619 $[M - 2NO_3 + H]^{4+}$ (calcd m/z = 502.6603), 669.8823 $[M - 2NO_3 + H]^{3+}$ (calcd m/z = 669.8805), and 1004.3228 $[M - 2NO_3]^{2+}$ (calcd m/z = 1004.3129).

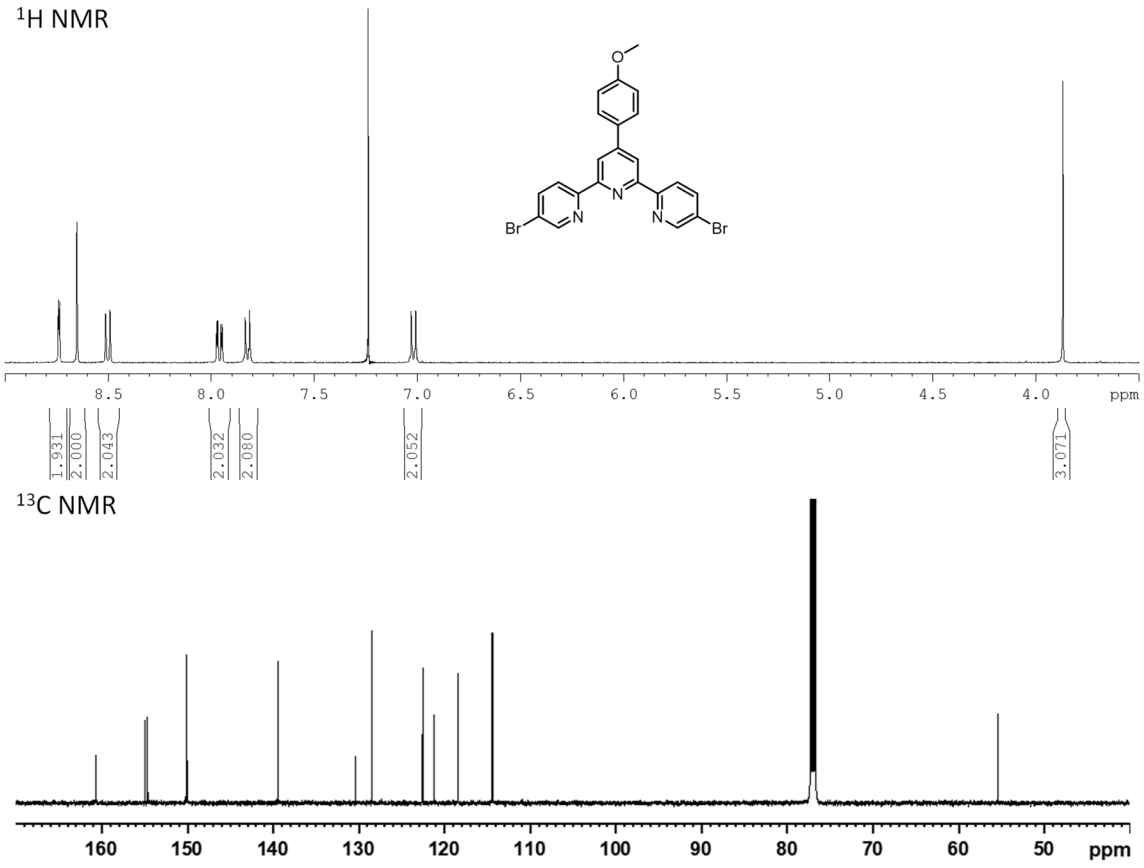


Figure S21. ^{1}H and ^{13}C NMR spectra of **3**.

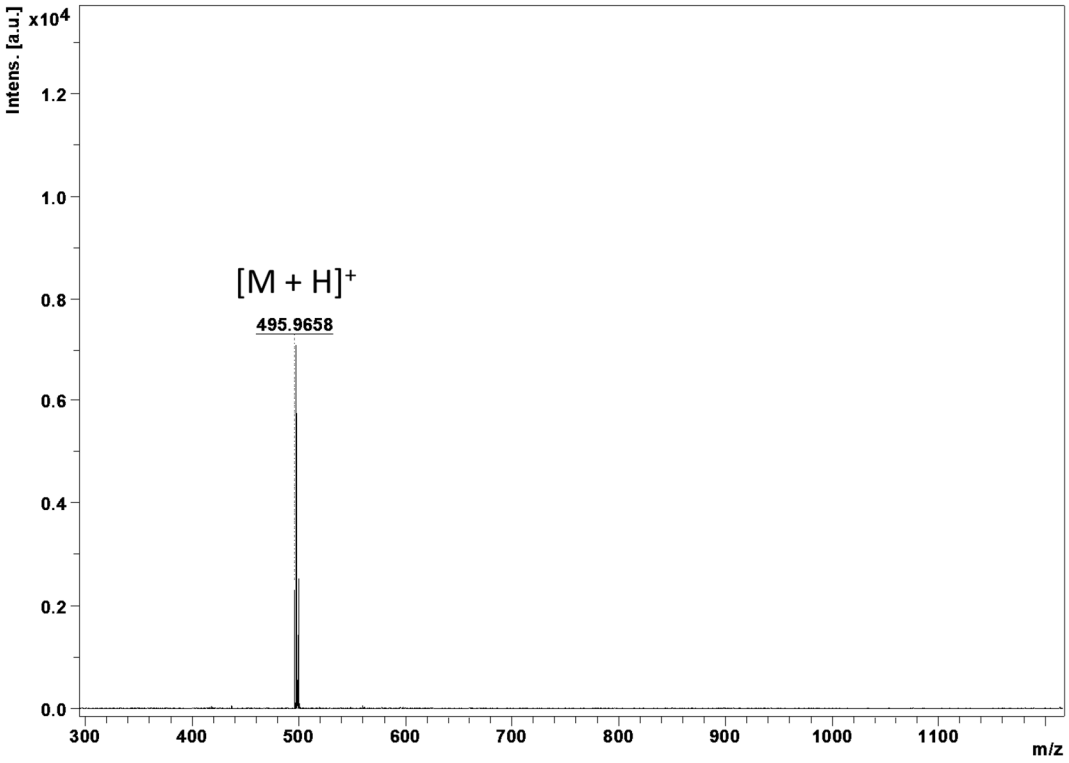


Figure S22. MALDI-TOF spectrum of **3**.

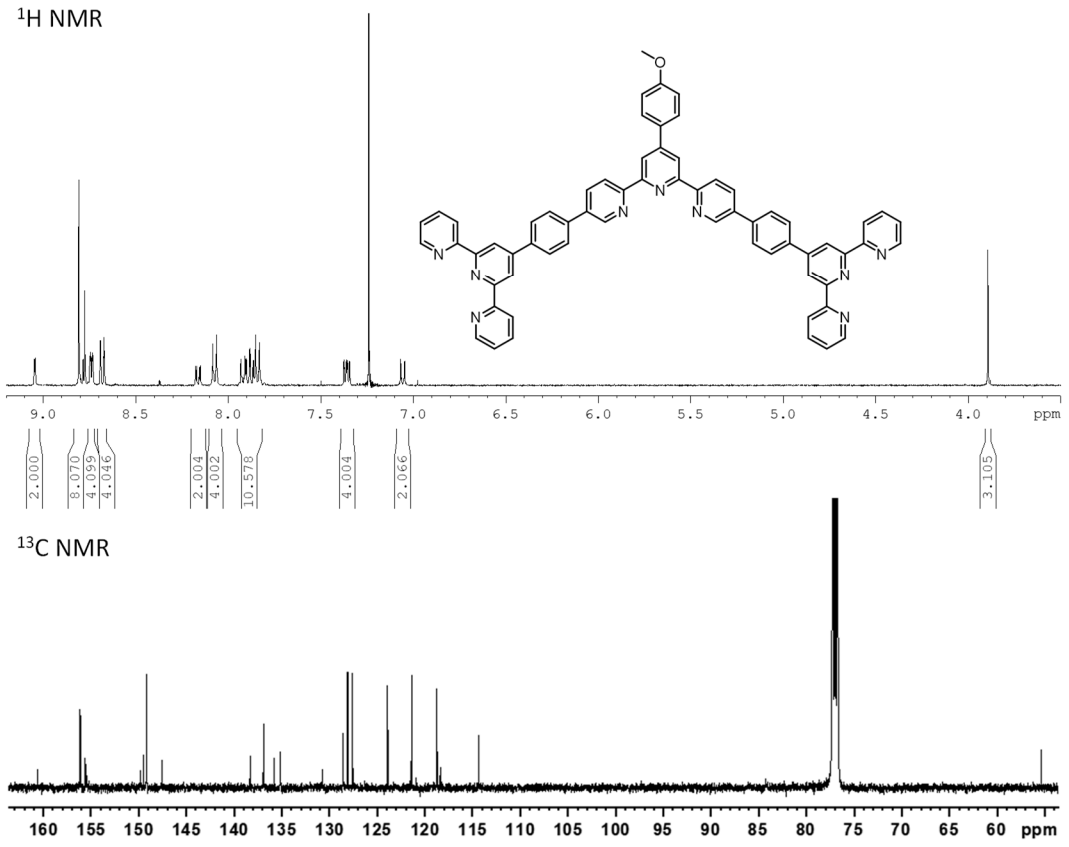


Figure S23. ^{1}H and ^{13}C NMR spectra of $\mathbf{L^2}$.

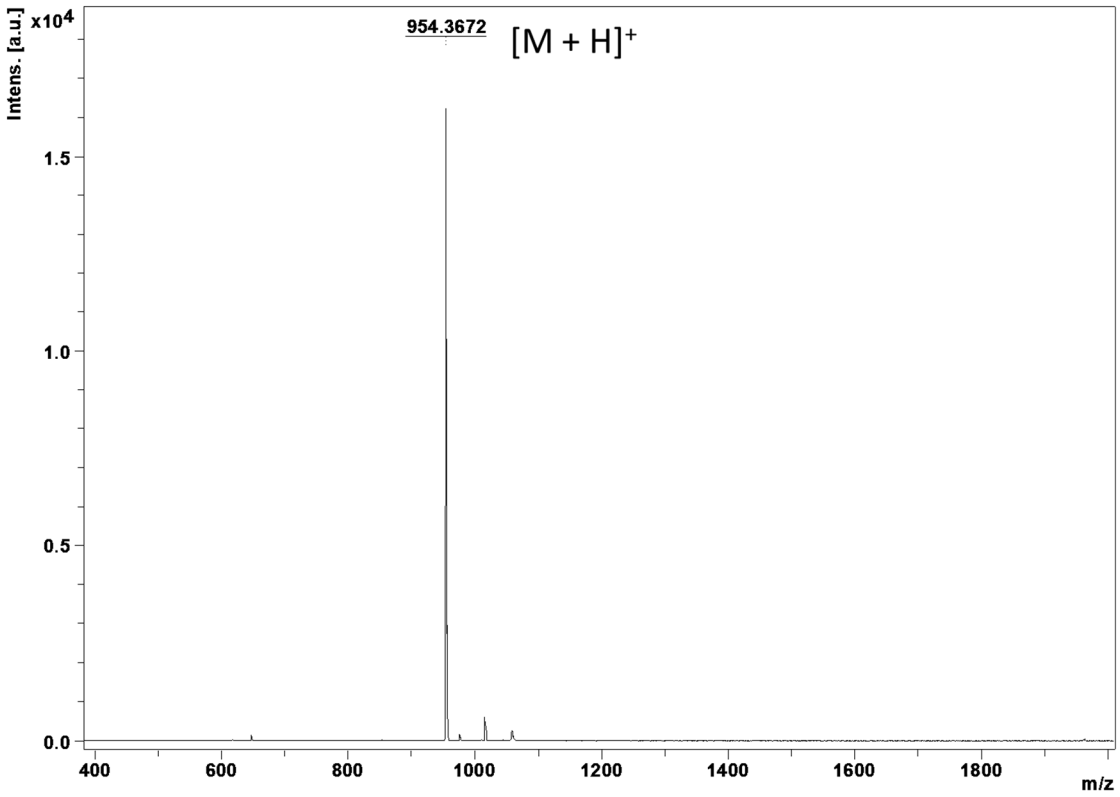


Figure S24. MALDI-TOF spectrum of $\mathbf{L^2}$.

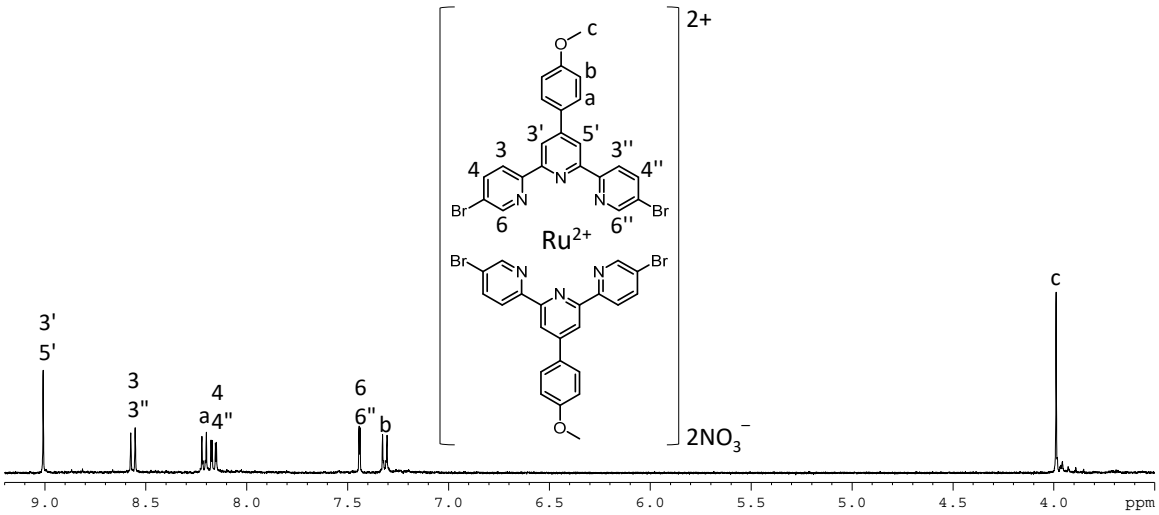


Figure S25. ^{1}H NMR spectrum of **4**.

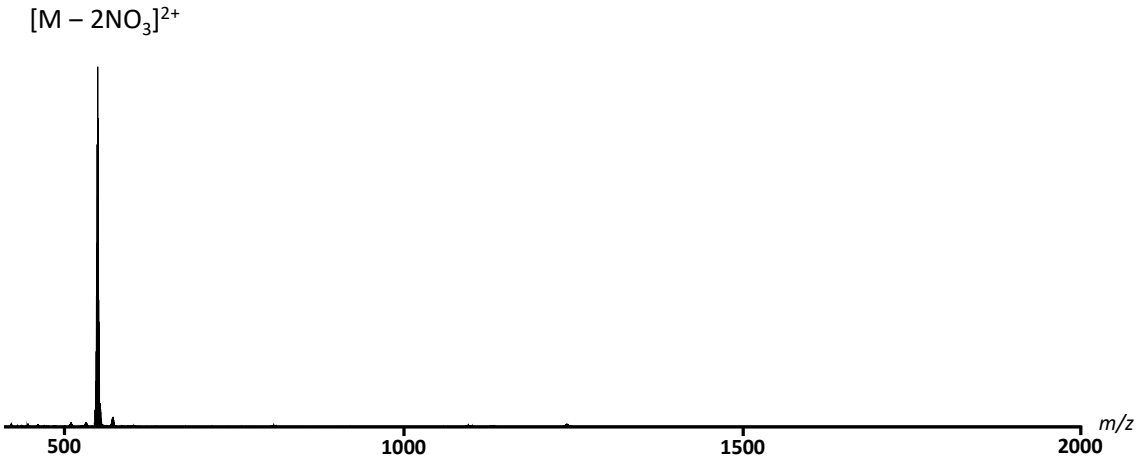


Figure S26. ESI-MS spectrum of **4**.

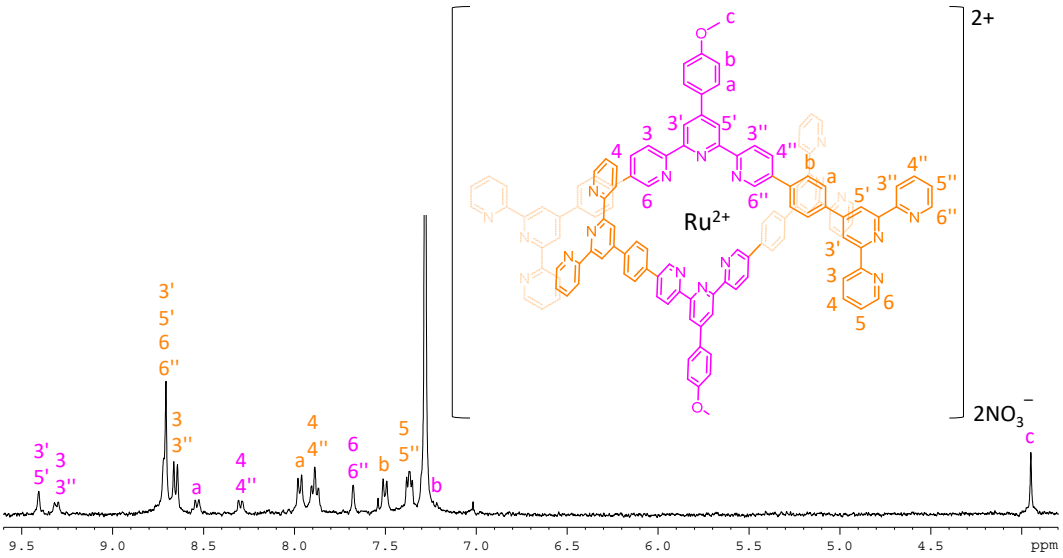


Figure S27. ^{1}H NMR spectrum of **ML^{2}**.

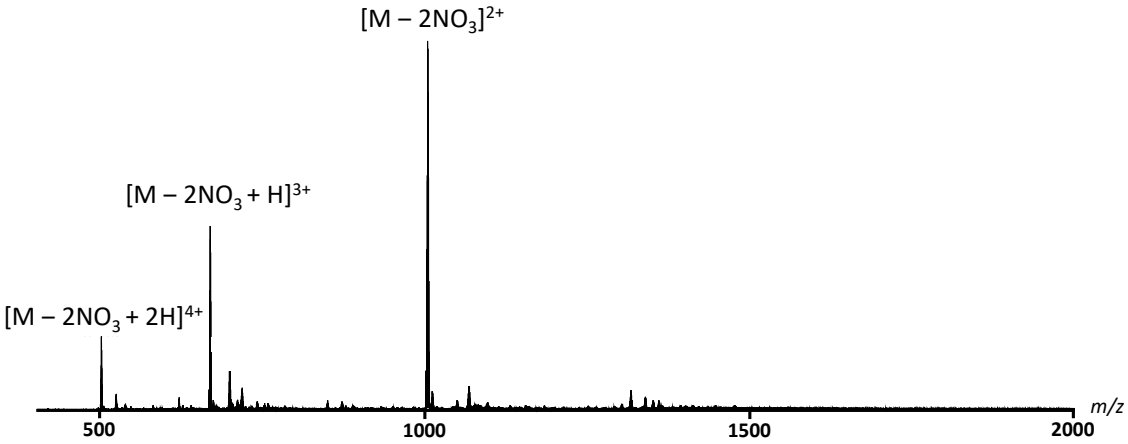
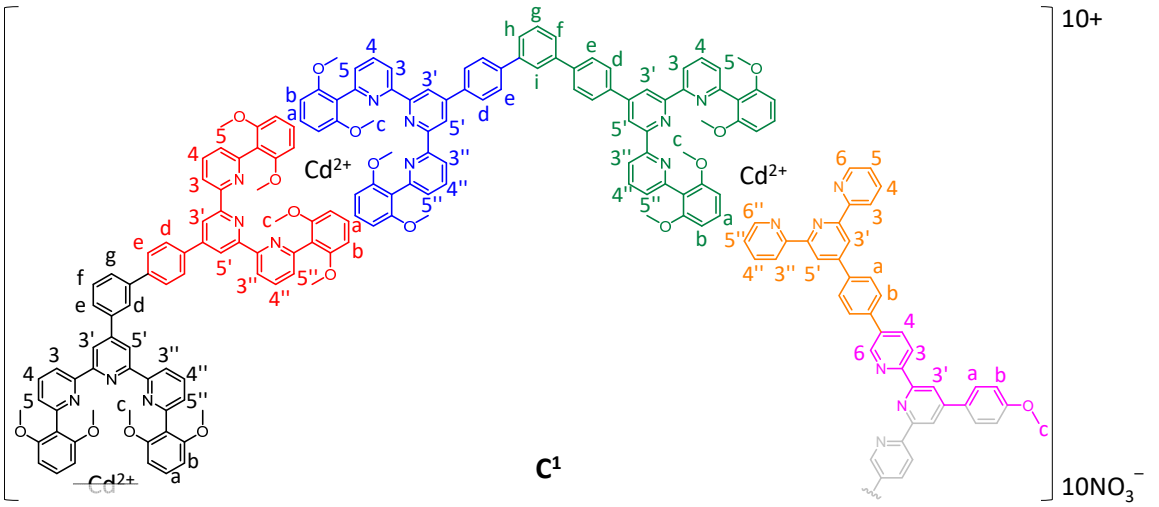
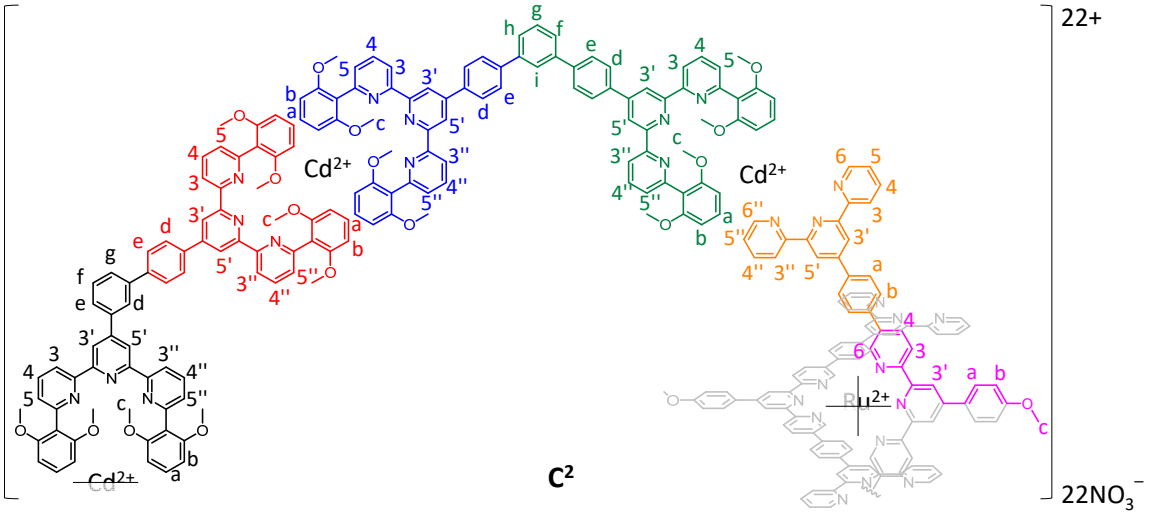


Figure S28. ESI-MS spectrum of **ML^{2}**.

Synthesis of complexes C^1 and C^2.



Complex C^1. To a solution (3.5 mL) of **ML^1** (10.0 mg, 1.8 μmol) and **L^2** (1.7 mg, 1.8 μmol) in $CHCl_3$/MeOH (6/1, v/v), $Cd(NO_3)_2{\cdot}4H_2O$ (1.1 mg, 3.7 μmol) in MeOH (0.5 mL) was added. The mixture was heated at 60 °C for 8 h. After removal of solvent, the residue was washed with H_2O and MeOH to afford **C^1** in 96% yield (12.2 mg, 1.7 μmol). ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ = 9/1, v/v): δ (ppm) 9.33 (s, 2H), 9.24 (s, 4H), 9.20 (d, J = 6.2 Hz, 2H), 8.99 (d, J = 8.0 Hz, 4H), 8.93−8.80 (m, 12H), 8.79−8.72 (m, 12H), 8.71−8.58 (m, 18H), 8.47−8.38 (m, 18H), 8.35−8.30 (m, 8H), 8.29−8.10 (m, 30H), 8.07−7.99 (m, 6H), 7.96−7.91 (m, 4H), 7.85 (d, J = 7.2 Hz, 2H), 7.78 (t, J = 7.7 Hz, 2H), 7.60 (t, J = 5.7 Hz, 4H), 7.25 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 7.7 Hz, 4H), 7.19−7.07 (m, 12H), 6.99−6.83 (m, 16H), 6.15 (d, J = 8.6 Hz, 8H), 6.10 (d, J = 8.6 Hz, 8H), 6.07 (d, J = 8.6 Hz, 8H), 5.93 (d, J = 8.6 Hz, 8H), 3.97 (s, 3H), 2.99 (s, 24H), 2.98 (s, 24H), 2.95 (s, 24H), and 2.94 (s, 24H). The counter anion was changed from NO_3^- to PF_6^- in order to reduce fragmentation during MS analysis. ESI-MS (*m/z*): 1407.7178 $[M - 5PF_6]^{5+}$ (calcd *m/z* = 1407.7136), 1148.9335 $[M - 6PF_6]^{6+}$ (calcd *m/z* = 1148.9301), 964.0896 $[M - 7PF_6]^{7+}$ (calcd *m/z* = 964.0903), 825.4606 $[M - 8PF_6]^{8+}$ (calcd *m/z* = 825.4584), 717.6337 $[M - 9PF_6]^{9+}$ (calcd *m/z* = 717.6320), and 631.3731 $[M - 10PF_6]^{10+}$ (calcd *m/z* = 631.3708).



Complex C^2. To a solution (3.5 mL) of **ML^1** (10.0 mg, 1.8 μmol) and **ML^2** (1.9 mg, 0.9 μmol) $CHCl_3$/MeOH (6/1, v/v), $Cd(NO_3)_2{\cdot}4H_2O$ (1.1 mg, 3.7 μmol) in MeOH (0.5 mL) was added. The mixture was heated at 60 °C for 8 h. After removal of solvent, the residue was washed with H_2O and MeOH to afford **C^2** in 95% yield (11.9 mg, 0.9 μmol). ^{1}H NMR (400 MHz, $CD_3OD/CDCl_3$ = 9/1, v/v): δ (ppm) 9.49 (s, 4H), 9.27−9.19 (m, 12H), 8.91−8.81 (m, 16H), 8.80−8.68 (m, 40H), 8.67−8.54 (m, 20H), 8.53−8.41 (m, 28H), 8.37−8.31 (m, 12H), 8.30−8.13 (m, 68H), 8.09−8.02 (m, 12H), 8.00 (d, J = 1.9 Hz, 4H), 7.98−7.92 (m, 8H), 7.88 (d, J = 7.6 Hz, 8H), 7.80−7.74 (m, 4H), 7.58 (d, J = 6.2 Hz, 8H), 7.26−7.11 (m, 28H), 6.99−6.87 (m, 24H), 6.74 (d, J = 8.3 Hz, 8H), 6.19−6.04 (m, 48H), 5.86 (d, J = 8.9 Hz, 16H), 3.79 (s, 6H), 3.00 (s, 48H), 2.97 (s, 48H), 2.96 (s, 48H), and 2.92 (s, 48H). The counter anion was changed from NO_3^- to PF_6^- in order to reduce fragmentation during MS analysis. ESI-MS (*m/z*): 2129.3550 $[M - 7PF_6]^{7+}$ (calcd *m/z* = 2129.2659), 1845.0475 $[M - 8PF_6]^{8+}$ (calcd *m/z* = 1844.9871), 1624.0475 $[M - 9PF_6]^{9+}$ (calcd *m/z* = 1623.9832), 1447.1410 $[M - 10PF_6]^{10+}$ (calcd *m/z* = 1447.1169), 1302.3020 $[M - 11PF_6]^{11+}$ (calcd *m/z* = 1302.2910), 1181.6885 $[M - 12PF_6]^{12+}$ (calcd *m/z* = 1181.6834), 1079.6339 $[M - 13PF_6]^{13+}$ (calcd *m/z* = 1079.6243), 992.1533 $[M - 14PF_6]^{14+}$ (calcd *m/z* = 992.1508), 916.3499 $[M - 15PF_6]^{15+}$ (calcd *m/z* = 916.3458), 850.0132 $[M - 16PF_6]^{16+}$ (calcd *m/z* = 850.0115), 791.4770 $[M - 17PF_6]^{17+}$ (calcd *m/z* = 791.4781), and 739.4597 $[M - 18PF_6]^{18+}$ (calcd *m/z* = 739.4595).

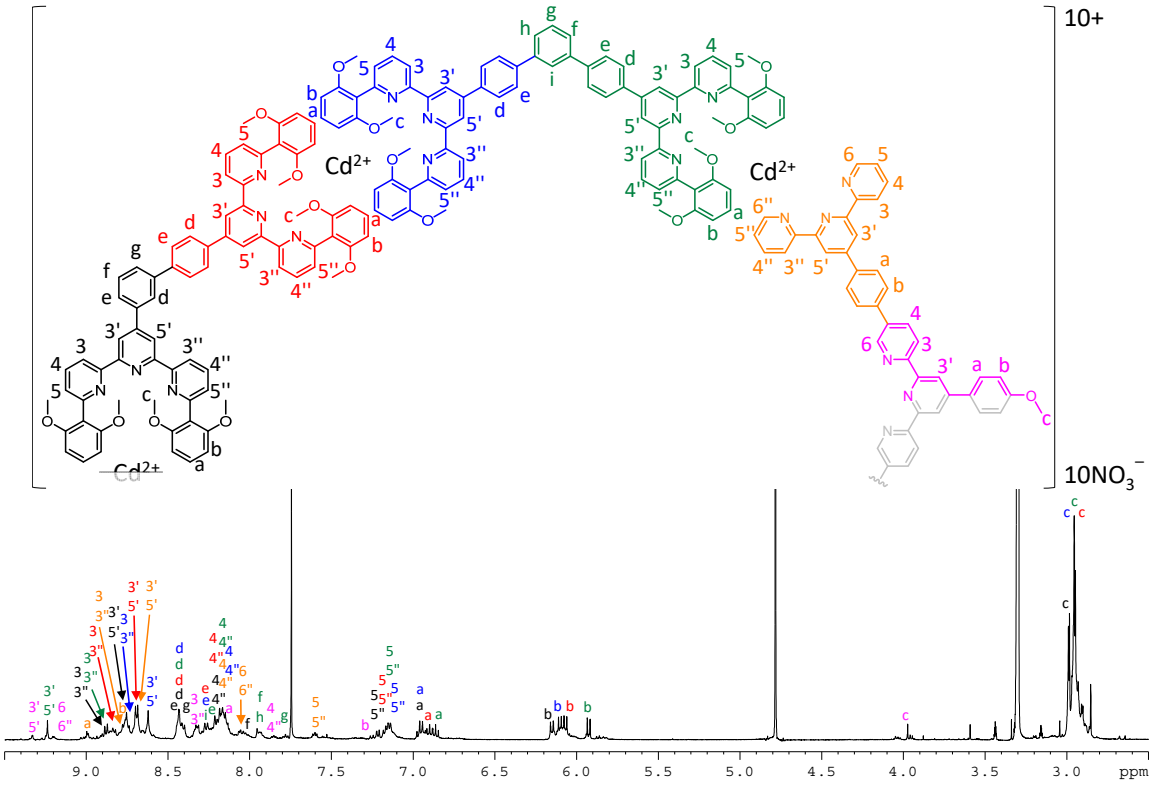


Figure S29. ^{1}H NMR spectrum of **C^{1}**.

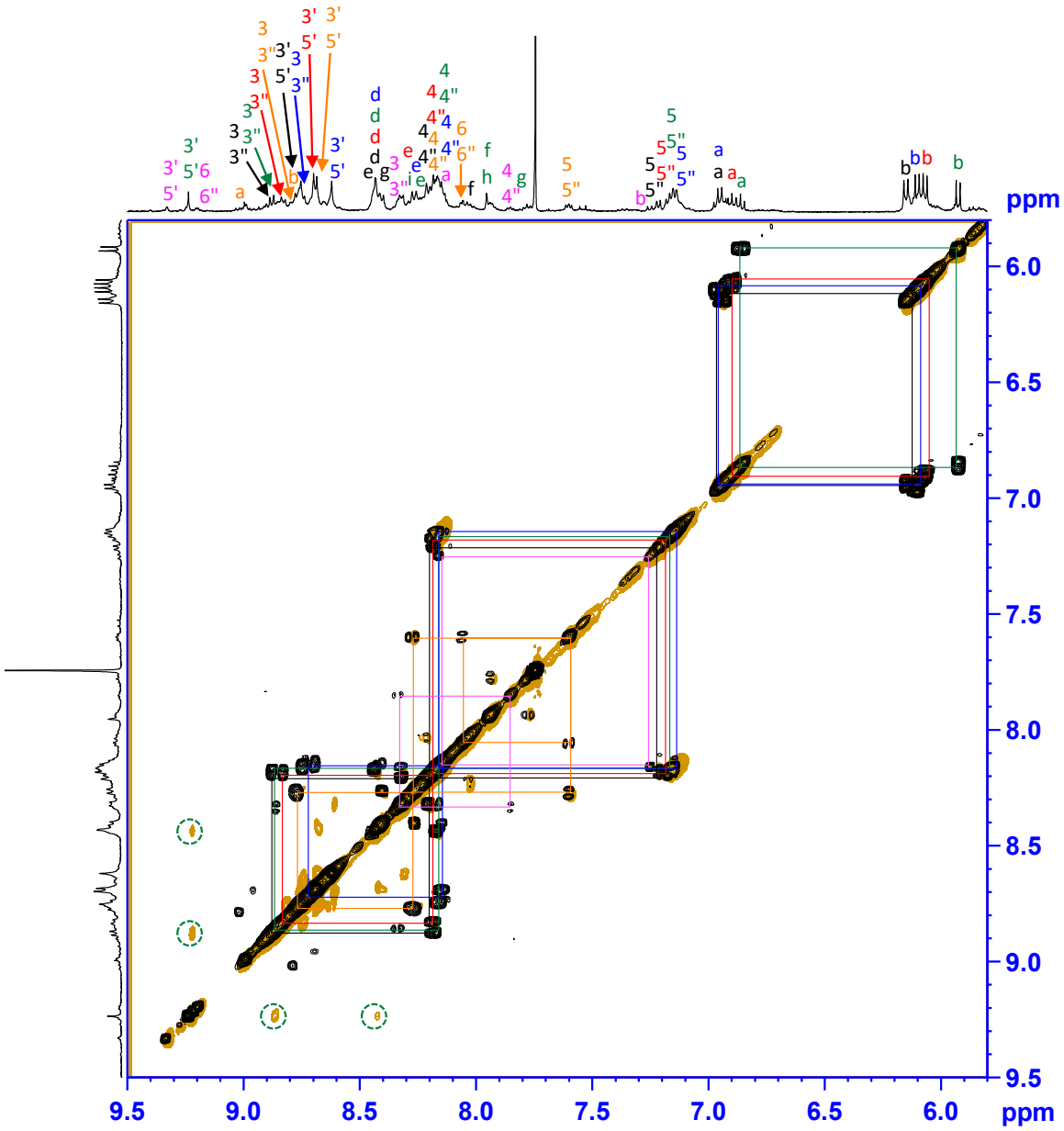


Figure S30. Partial ROESY NMR spectrum of **C**[1] (yellow: ROESY signals, black: COSY signals).

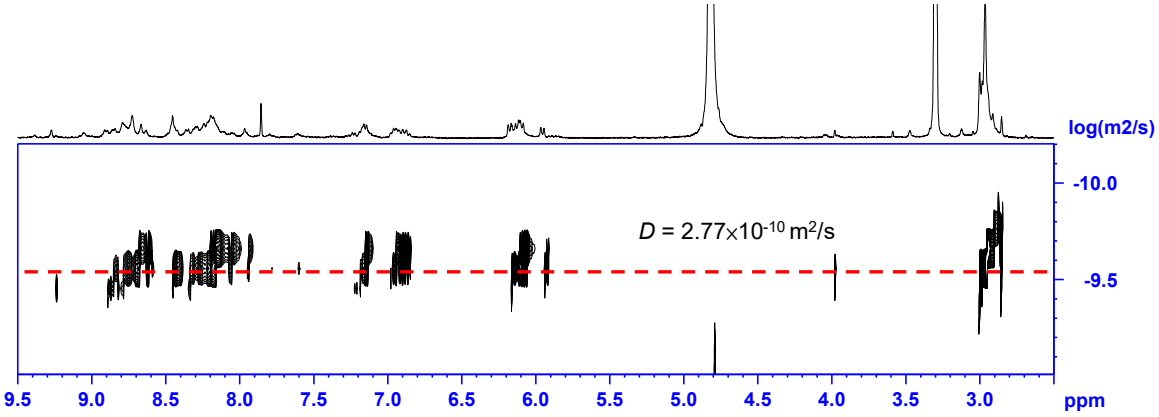


Figure S31. DOSY NMR spectrum of **C**[1].

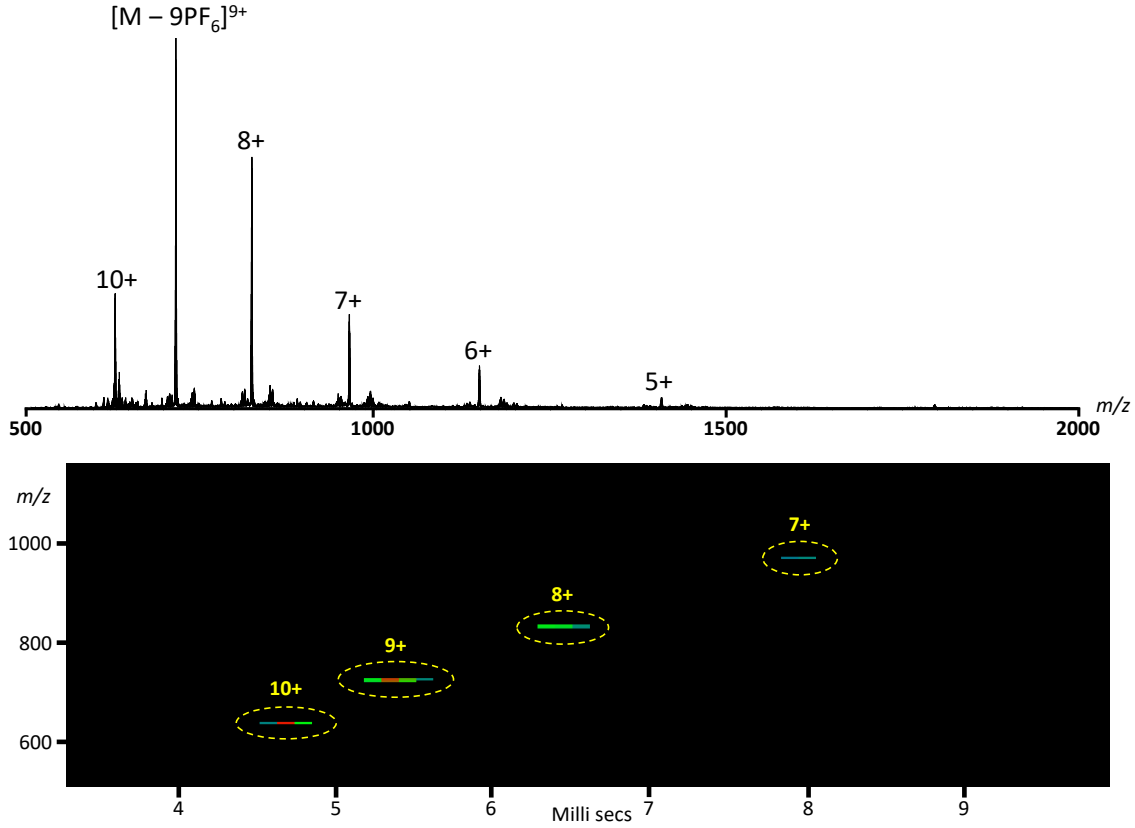


Figure S32. ESI-MS spectrum and TWIM-MS plot of **C**[1].

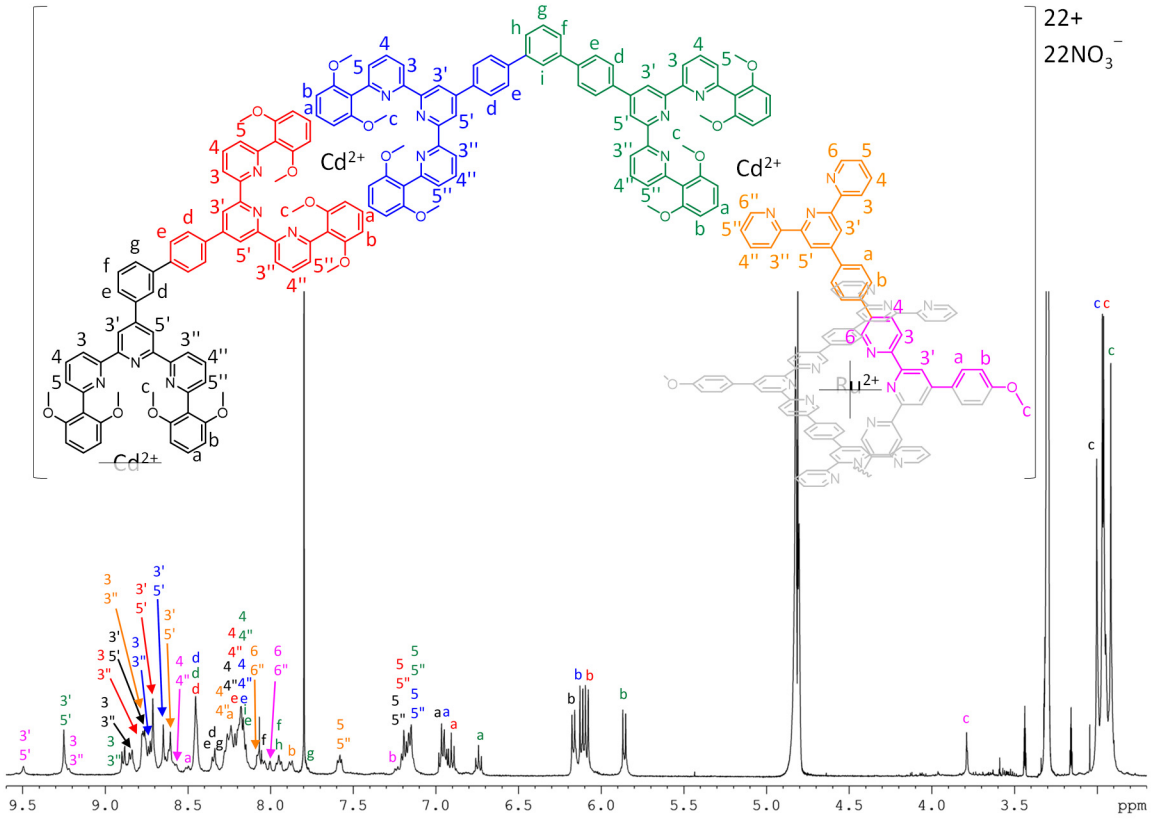


Figure S33. ^{1}H NMR spectrum of **C²**.

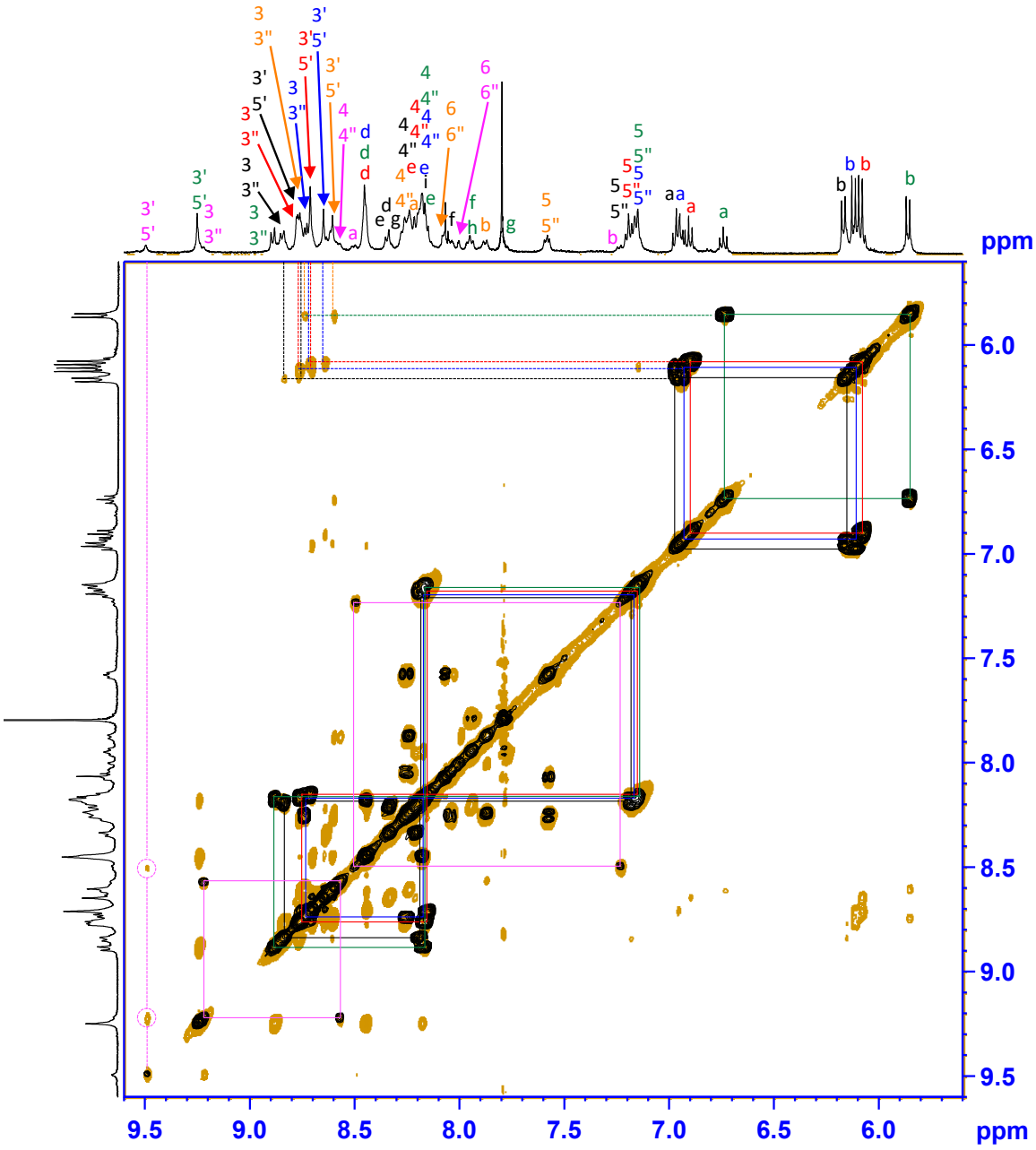


Figure S34. Partial ROESY NMR spectrum of **C²** (yellow: ROESY signals, black: COSY signals).

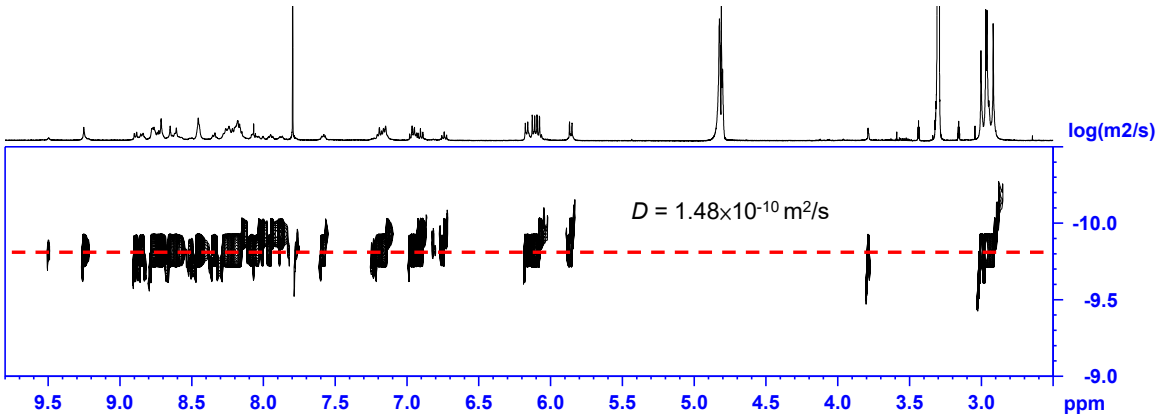


Figure S35. DOSY NMR spectrum of **C²**.

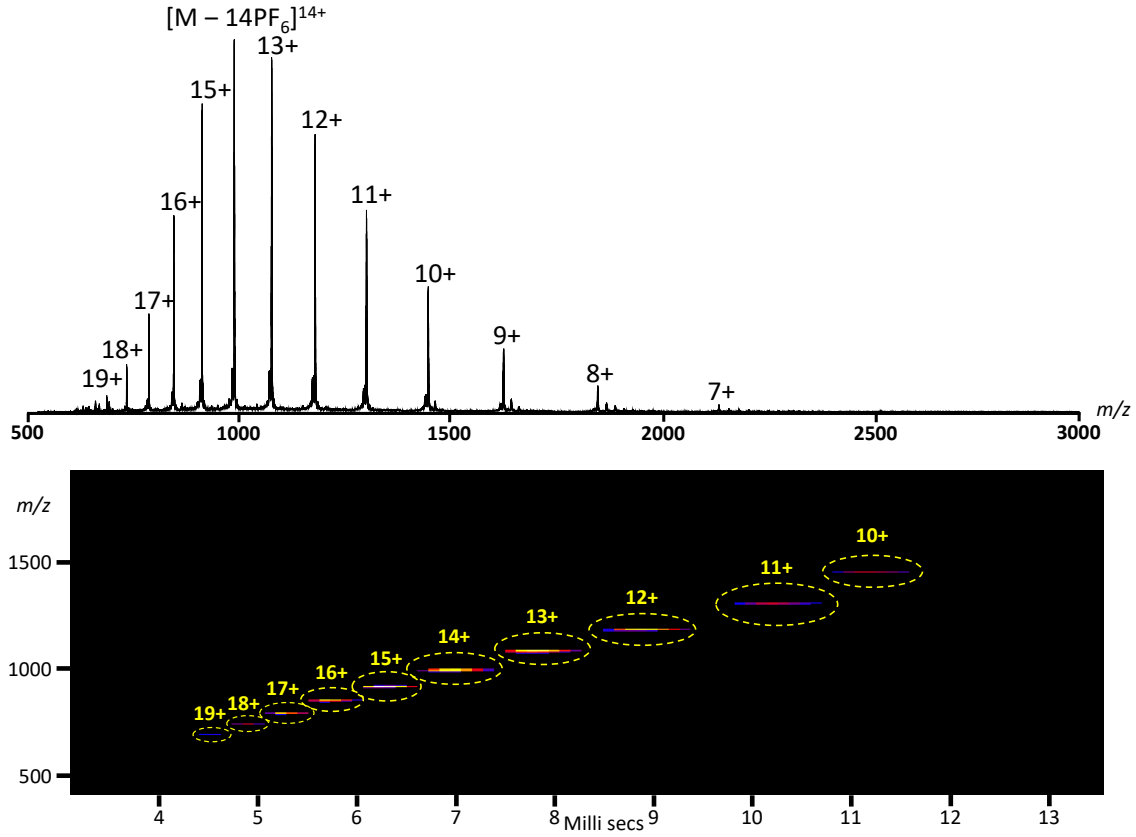


Figure S36. ESI-MS spectrum and TWIM-MS spectrum of **C²**.

Table S1. Experimental and theoretical values of collision cross-sections for **C¹** and **C²**.

	Exp. CCS	PA	TM
C¹	1031.7±26.5	953.4±3.8	1096.9±5.2
C²	1920.8±45.6	1658.3±45.1	1934.4±48.5

AFM images

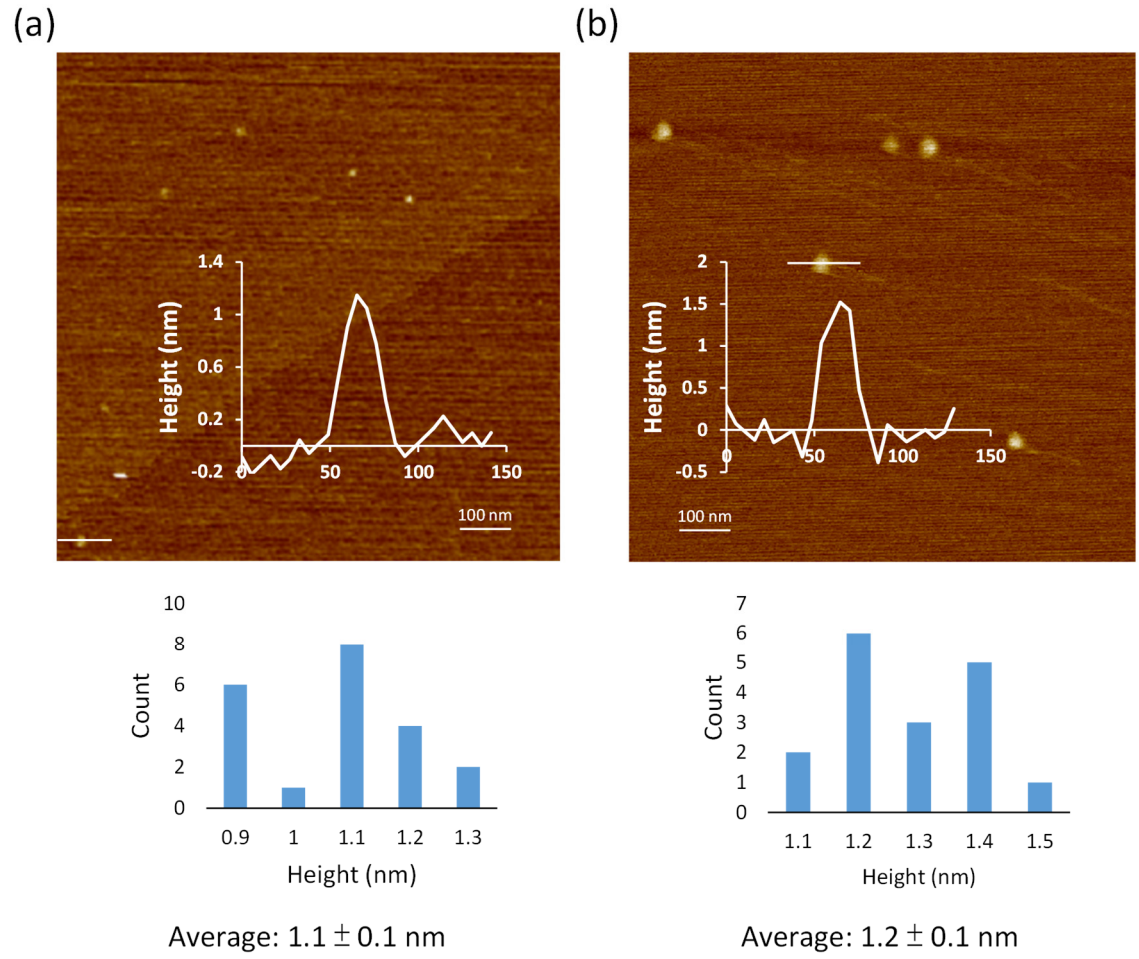


Figure S37. AFM images of (a) $\mathbf{C^1}$ and (b) $\mathbf{C^2}$, and the statistical analysis for the heights.

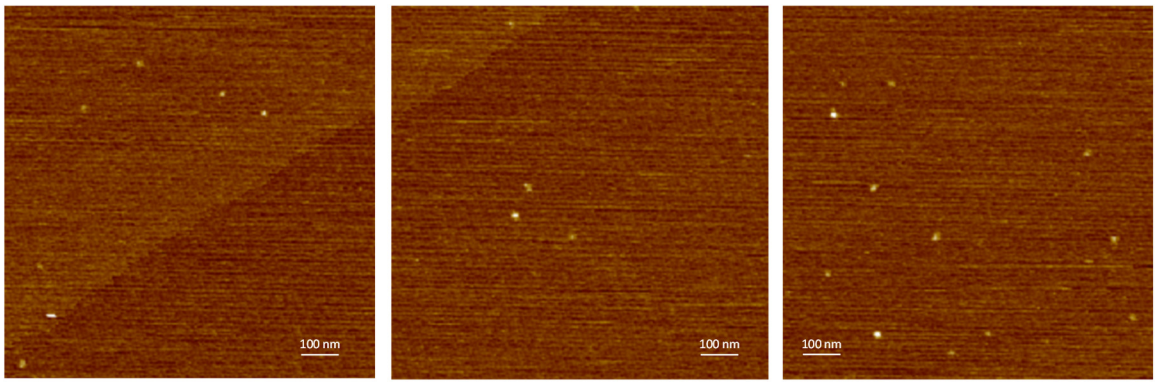


Figure S38. AFM images of $\mathbf{C^1}$.

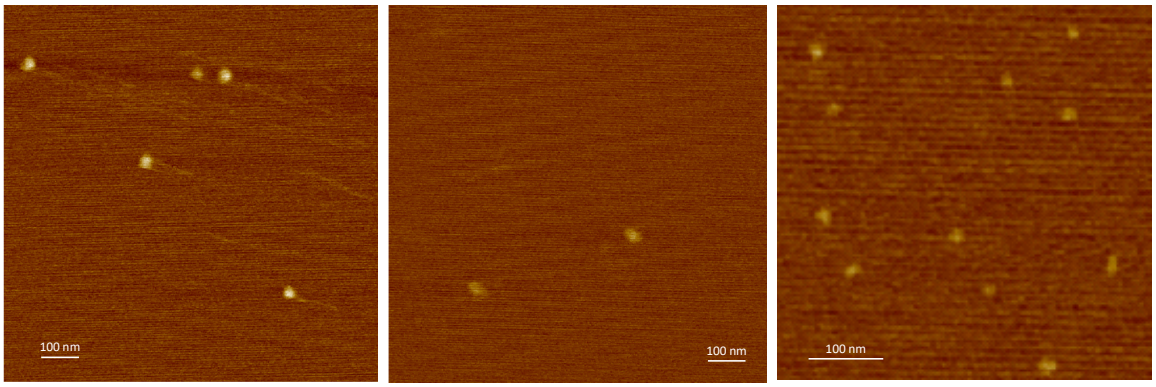


Figure S39. AFM images of **C²**.

TEM images

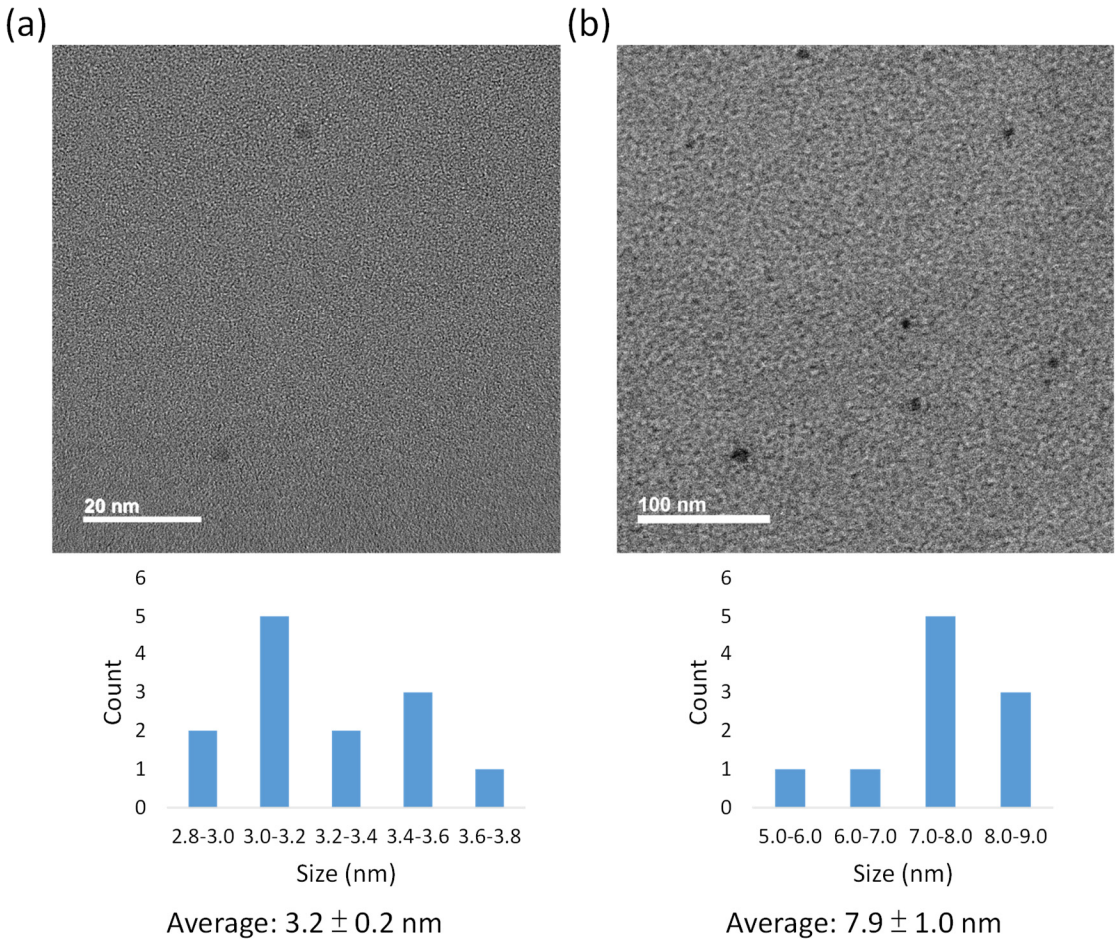


Figure S40. TEM images of (a) **C¹** and (b) **C²**, and the statistical analysis for the diameters.

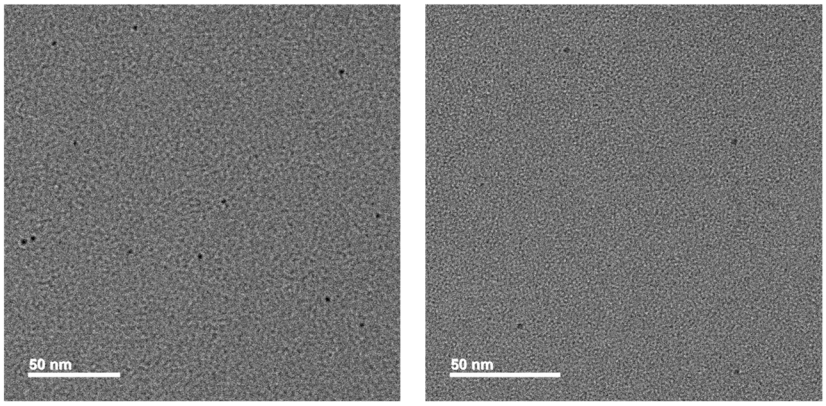


Figure S41. TEM images of $\mathbf{C^1}$.

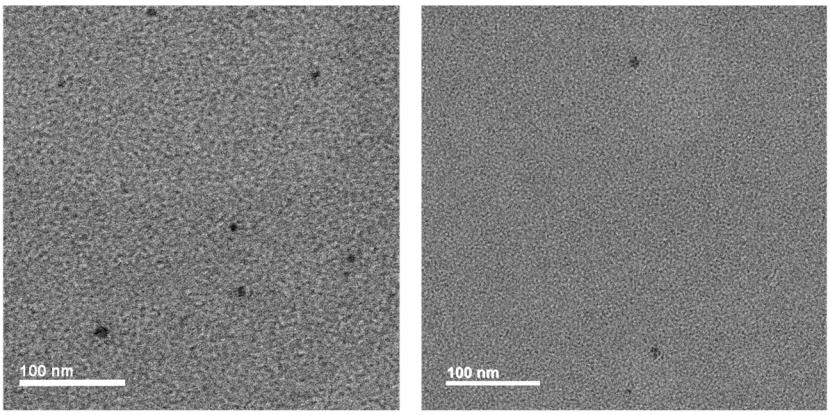


Figure S42. TEM images of $\mathbf{C^2}$.

Molecular Modeling

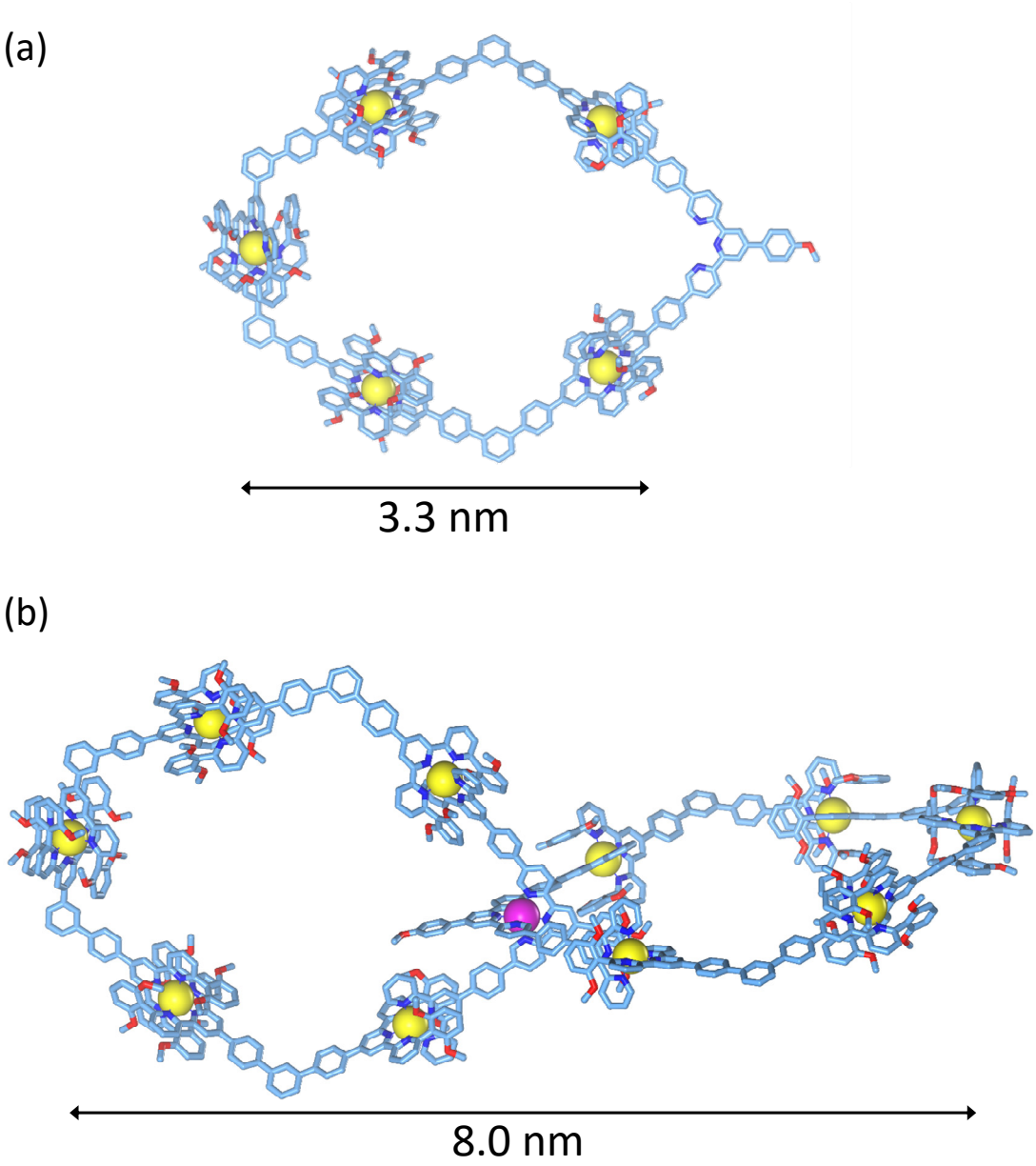


Figure S43. Energy-minimized structures of (a) $\mathbf{C^1}$ and (b) $\mathbf{C^2}$.

Table S2. Crystal data and structure refinement for [Cd**L**$^{a}_{2}$].

Identification code	ic18379	
Empirical formula	C79 H69.50 Cd F12 N8.50 O8 P2	
Formula weight	1668.27	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.4369(2) Å	a= 90°.
	b = 24.8732(5) Å	b= 101.228(2)°.
	c = 25.4913(5) Å	g = 90°.
Volume	7734.7(3) Å^3	
Z	4	
Density (calculated)	1.433 Mg/m^3	
Absorption coefficient	0.414 mm^{-1}	
F(000)	3412	
Crystal size	0.25 x 0.20 x 0.10 mm^3	
Theta range for data collection	2.94 to 27.50°.	
Index ranges	-15<=h<=16, -30<=k<=32, -31<=l<=33	
Reflections collected	57324	
Independent reflections	17384 [R(int) = 0.0521]	
Completeness to theta = 27.50°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.99507	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	17384 / 31 / 1106	
Goodness-of-fit on F^2	1.125	
Final R indices [I>2sigma(I)]	R1 = 0.0747, wR2 = 0.1944	
R indices (all data)	R1 = 0.1074, wR2 = 0.2114	
Largest diff. peak and hole	1.399 and -0.707 e.Å^{-3}	

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