Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Conformations of Large Macrocycles and Ring-in-Ring Complexes

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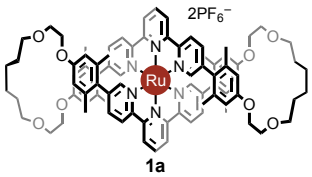
Contents

1. Materials and Methods:

^{1}H- and ^{13}C-NMR spectra were recorded on Bruker 300, 400, 500, and 600 MHz spectrometers and were referenced to residual solvent: $CDCl_3$ (^{1}H-NMR: 7.26 ppm; and ^{13}C-NMR 77.00 ppm); CD_3CN (^{1}H-NMR: 1.94 ppm and ^{13}C-NMR: 1.39 ppm); $(CD_3)_2CO$ (^{1}H-NMR: 2.05 ppm and ^{13}C-NMR: 29.84 ppm); DMSO-d_6 (^{1}H-NMR: 2.50 ppm and ^{13}C-NMR: 39.52 ppm); or CD_2Cl_2 (^{1}H-NMR: 5.31 ppm and ^{13}C-NMR: 54.00 ppm). Routine ESI-MS were recorded on a ThermoFinnigan Surveyor MSQ detector and hi-resolution MS measurements were performed by the Universität Zürich Mass Spectrum Facility. All experiments were carried out under normal atmosphere in reagent grade solvents unless otherwise noted. Commercial chemicals were used as supplied from Aldrich or Acros Chemical Co. Column chromatography was performed on neutral aluminum oxide (Brockmann III) and silica gel (230-425 mesh). Melting points are uncorrected and recorded on a Mel-Temp Laboratory Device. Dichlorotetrakis (dimethyl sulphoxide) ruthenium(II),[1] dichloro (1,5-cyclooctadien) platinum(II),[2] (2-trimethylsilyl- ethynyl) tributylstannane,[3] 5,5''-bromo- 2,2':6':2''-terpyridine,[4] 5,5''-bis-(4-methoxy-2,6-dimethyl-phenyl)- 2,2':6',2''-terpyridine, 5,5''-bis-(4-hydroxy-2,6-dimethyl-phenyl)-2,2':6',2''- terpyridine, 5,5''-bis-(4-methoxy-2,6-dimethyl-phenyl)- 2,2':6',2''-terpyridine, 5,5'-bis-(4-methoxy- 2,6-dimethyl-phenyl)-2,2'-bipyridine,[5] 4,4''-bis- (4-hydroxy- 2,6-dimethyl-phenyl)- 2,2':6',2''-terpyridine macrocycle **1** and Ru[4,4''-bis-(4-hydroxy-2,6-dimethyl-phenyl)-2,2':6',2''-terpyridine]Cl_3,[6] were prepared according to literature procedures.

Single crystal diffraction measurements for **1a**, **1b'**, and **2** were made on a *Nonius KappaCCD* area-detector diffractometer[7] using graphite-monochromated Mo *K*α radiation (*λ* = 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. Diffraction data for **2-terpy** were recorded on a protein beamline at the Swiss Light Source where only a single phi scan was possible. Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1437407– 1437409 and 1432774 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures. All images were generated with PyMOL.[8]

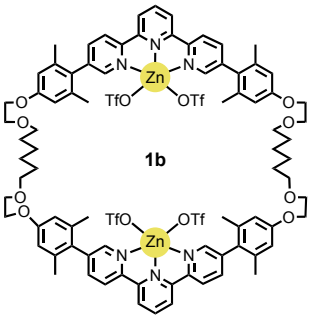
2. Synthetic Procedures:



1a

Ru (5’5’’- bis-(4-(2-(propoxy-ethoxy)- 2,6-dimethyl-phenyl)- 2,2’:6’,2’’-terpyridine) macrocycle)] $[PF_6]_2$ (1a)

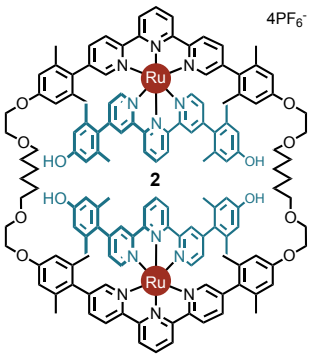
A 10:4:1 solution of ethylene glyclol: dichloroethane: ethanol (15 mL) containing 5,5’’-bis-[2,6-dimethyl-4-(2-propoxy-ethoxy)-phenyl]- 2,2’:6’,2’’-terpyridine macrocycle **1** (0.024 g, 1.87 × 10^{-5} moles) and dichlorotetrakis(dimethyl sulphoxide) ruthenium(II) (0.005 g, 9.33 × 10^{-6} moles) was heated at 125 ºC for 16 h. The reaction was cooled to room temperature and the dichloroethane and ethanol evaporated. The addition of aqueous potassium hexafluorophosphate induced precipitation of a red solid that was filtered over celite and washed with water and diethyl ether. The precipitate was dissolved with acetone into a clean flask, concentrated and diluted with methylene chloride. After drying over magnesium sulfate, filtering, and the solvent was removed to yield a red crystalline solid (0.030 g, 96%). mp 295 ºC dec.; ^{1}H NMR (500 MHz, CD_3CN, δ): 8.70 (4H, d, *J* = 8.4 Hz), 8.52 (4H, d, *J* = 8.4 Hz), 8.32 (2H, t, *J* = 8.4 Hz), 7.72 (4H, dd, *J* = 8.4, 1.2 Hz), 7.33 (4H, dd, *J* = 1.8 Hz), 6.86 (4H, bs), 6.60 (4H, bs), 4.44 (4H, m), 4.04 (4H, m), 3.59 (8H, m), 3.30 (4H, m), 3.13 (4H, m), 1.94 (12H, s), 1.26 (8H, m), 1.22 (12H, s), 1.08 (8H, m); ^{13}C NMR (125 MHz, CD_3CN, δ): 160.27, 157.29, 156.37, 153.94, 141.59, 141.31, 137.95, 137.33, 128.13, 125.02, 124.66, 117.88, 114.83, 73.28, 72.75, 68.26, 31.29, 28.04, 22.00, 20.86; ESI-MS: *m/z* for $[M]^{2+}$ calc. 694.3, found 694.2. HRMS (ESI) m/z: $[M]^{2+}$ calculated for ($C_{82}H_{90}N_6O_8Ru$): 694.29376; found: 694.29355.



1b

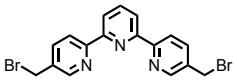
5’5’’-bis-(4-(2-(propoxy-ethoxy)-2,6-dimethyl-phenyl)-2,2’:6’,2’’-terpyridine) macrocycle ⊃ $Zn(OTf)_2$ (1b)

Zinc triflate (0.014 g, 3.89 × 10^{-5} moles) in ethanol (5.0 mL) was added drop wise to 5,5’’-bis-[2,6-dimethyl-4-(2-propoxy-ethoxy)-phenyl]-2,2’:6’,2’’-terpyridine macrocycle **1** (0.025 g, 1.94 × 10^{-5} moles) in methylene chloride (5.0 mL) and stirred for 6 h at room temperature. The solvent was removed to yield a white solid (0.038 g, 97 %). mp 195 – 201 ºC; ^{1}H NMR (500 MHz, CD_3CN, δ): 8.66 (d, *J* = 2.0 Hz, 4H), 8.59 (d, *J* = 8.5 Hz, 4H), 8.57 (d, *J* = 7.5 Hz, 4H), 8.51 (t, *J* = 8.5 Hz, 2H), 8.15 (dd, *J* = 8.0, 2.0 Hz, 4H), 6.81 (s, 8H), 4.15 (m, 8H), 3.75 (m, 8H), 3.51 (t, *J* =6.5 Hz, 8H), 2.07 (s, 24 H), 1.58 (m, 8H), 1.40 (m, 8H). ^{13}C NMR (125 MHz, CD_3CN, δ): 160.0, 150.6, 148.7, 146.8, 145.0, 144.0, 141.7, 138.9, 129.3, 123.7, 123.6, 114.8, 71.8, 69.9, 68.5, 30.5, 26.8, 21.2.; ESI-MS: *m/z* for $[M - 4OTf]^{4+}$ calc. 354.6, found 354.7; *m/z* for $[M - 4OTf + 2ACN]^{4+}$ calc. 375.1, found 375.2; *m/z* for $[M - 3OTf]^{3+}$ calc. 527.8, found 528.1; *m/z* for $[M - 4OTf + OH]^{3+}$ calc. 478.5, found 478.2. HRMS (ESI) m/z: calculated for $([M - 4OTf + HCOO]^{3+}$ ($C_{83}H_{90}N_6O_{10}Zn_2$): 486.51267; found: 486.51209.



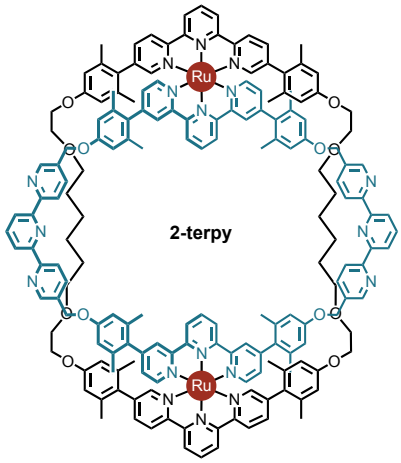
bis (5’5’’-bis-(4-(2-(propoxy-ethoxy)-2,6-dimethyl-phenyl) -2,2’:6’,2’’-terpyridine) macrocycle ⊂ bis-[Ru(II) [4,4’’-bis- (4-hydroxy-2,6-dimethyl-phenyl)- 2,2’:6’,2’’- terpyridine] $[PF_6]_4$ (2)

Prepared from modified literature procedures.[6] A 3:3:2 solution of dichloroethane : ethanol : ethylene glyclol (15 mL) containing 5,5’’-bis-[2,6-dimethyl-4-(2-propoxy-ethoxy)-phenyl]-2,2’:6’,2’’-terpyridine macrocycle **1** (0.100 g, 7.78×10^{-5} moles) and Ru[4,4’’-bis-(4-hydroxy-2,6-dimethyl-phenyl)-2,2’:6’,2’’-terpyridine}Cl_3 (0.110 g, 1.63×10^{-4} moles) was heated at 125 ºC for 24 h. The reaction was cooled to room temperature and the dichloroethane and ethanol evaporated. The addition of aqueous potassium hexafluorophosphate induced precipitation of a red solid that was filtered over celite and washed with water and diethyl ether. The precipitate was dissolved with acetone into a clean flask, concentrated and diluted with methylene chloride. After drying over magnesium sulfate, filtering, and the solvent was removed to yield a red solid. The crude solid was purified by column chromatography on silica gel with CH_3CN : H_2O : aq. KPF_6 (92: 8 : 0.8) as eluant to afford a red crystalline solid (0.166 g, 71%). Spectra matched literature values. ^{1}H NMR (500 MHz, $(CD_3)_2CO$, δ): 9.17 (4H, d, *J* = 8.4 Hz), 8.95 (4H, d, *J* = 8.4 Hz), 8.93 (4H, d, *J* = 8.4 Hz), 8.65 (2H, t, *J* = 8.4 Hz), 8.57 (4H, d, *J* = 1.2 Hz), 8.42 (2H, s), 8.27 (2H, t, *J* = 8.4 Hz), 7.99 (4H, dd, *J* = 8.4, 1.8 Hz), 7.89 (4H, d, *J* = 6 Hz), 7.60 (4H, d, *J* = 1.2 Hz), 7.23 (4H, ds, *J* = 6.0, 1.8 Hz), 6.63 (8H, s), 6.61 (8H, s), 4.07 (8, t, *J* = 4.8 Hz), 3.71 (8H, t, *J* = 4.8 Hz), 3.47 (8H, t, *J* = 6.6 Hz), 1.86 (24H, s), 1.63 (24H, s), 1.55 (8H, m), 1.37 (8H, m); ESI-MS: *m/z* for $[M]^{4+}$ calc. 609.2, found 609.1; *m/z* for $[M + PF_6^-]^{3+}$ calc. 860.6, found 860.9.



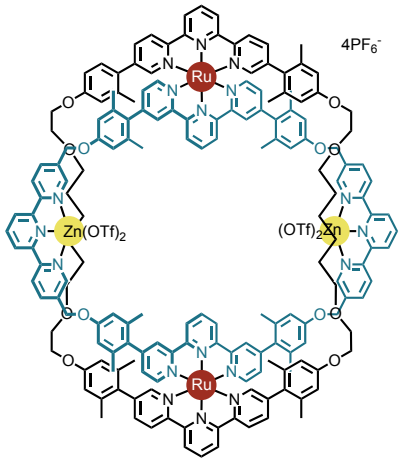
5,5’’-bis(bromomethyl)-2,2’:6’,2’’-terpyridine

Prepared from modified literature procedures.[9] A carbon tetrachloride solution (40 mL) containing 5,5’’-bis-methyl-2,2’:6’:2’’-terpyridine (0.500 g, 1.916×10^{-3} moles), *N*-bromosuccinimide (1.705 g, 9.579×10^{-3} moles), and catalytic benzoyl peroxide was placed in a hot oil bath at 80 ºC and heated for 3 h. The hot solution was filtered and the residue washed with carbon tetrachloride. Upon cooling the filtrate, a white precipitate forms and was collected, dissolved in methylene chloride, and washed with aqueous sodium thiolsulfate. The organic layers were combined, dried over magnesium sulfate, filtered and the solvent removed to give a white solid (0.413 g, 51%). Spectra matched the literature values. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.71 (2H, d, *J* = 2.8 Hz), 8.60 (2H, d, *J* = 8.4 Hz), 8.46 (2H, d, *J* = 7.8 Hz), 7.96 (1H, t, *J* = 7.8 Hz), 7.90 (2H, dd, *J* = 8.4, 2.4 Hz), 4.56 (4H, s); ESI-MS: *m/z* for $[M+Na^+]^+$ calc. 442.1, found 442.1.



[bis-(5''5''-bis-(4-(2-(propoxy-ethoxy)- 2,6-dimethyl-phenyl)-2,2':6',2''-terpyridine) macrocycle] ⊃ bis- (Ru(II) (*N,N'',N'''*- 4,4''-bis-(4-oxy- 2,6-dimethyl-phenyl)- 2,2':6',2''- terpyridine-5,5''-bis(methyl)-2,2':6',2''-terpyridine macrocycle)] $[PF_6]_4$ (2-terpy)

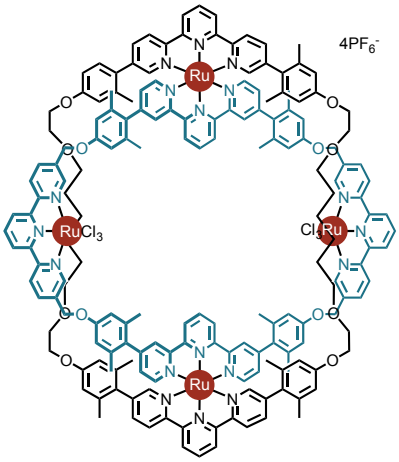
Cesium carbonate (0.032 g, 1.00×10^{-5} moles) was added to an anhydrous DMF solution (14 ml) under N_2 of bis Ru(II) tetraphenol macrocycle **2** (0.030 g, 1.00×10^{-5} moles), 5,5''-bis(bromomethyl)-2,2':6',2''-terpyridine (0.009 g, 2.00×10^{-5} moles). The contents were heated at 80° for 3.5 h then cooled to room temperature. Aqueous potassium hexafluorophosphate was added until a deep red precipitate formed. The precipitate was filtered over celite, washed with water and diethyl ether and dissolved into a clean flask with acetonitrile. The red solution was dried over magnesium sulfate, filtered and solvent evaporated to yield a red solid. The crude solid was purified by column chromatography on silica gel with CH_3CN : CH_2Cl_2 : H_2O : aqueous KPF_6 92 : 8 : 0.08 as the eluant to yield a red crystalline solid (0.020 g, 56%). m.p. > 350 °C. ^{1}H NMR (500 MHz, CD_3CN, δ): 8.82 (d, *J* = 8.2 Hz, 4H), 8.80 (d, *J* = 1.7 Hz, 4H), 8.62 (d, *J* = 7.8 Hz, 4H), 8.60 (d, *J* = 8.3 Hz, 4H), 8.54 (d, *J* = 8.3 Hz, 4H), 8.47 (t, *J* = 8.0 Hz, 2H), 8.47 (d, *J* = 7.8 Hz, 4H), 8.22 (d, *J* = 1.4 Hz, 4H), 8.11 (t, *J* = 8.2 Hz, 2H), 8.05 (t, *J* = 7.8 Hz, 2H), 7.94 (dd, *J* = 8.1, 2.2 Hz, 4H), 7.80 (dd, *J* = 8.3, 1.9 Hz, 4H), 7.49 (d, *J* = 5.8 Hz, 4H), 7.11 (d, *J* = 1.4 Hz, 4H), 7.08 (dd, *J* = 5.8, 1.7 Hz, 4H), 6.83 (s, 8H), 6.56 (s, 8H), 5.31 (s, 8H), 3.98 (t, *J* = 4.6 Hz, 8H), 3.65 (t, *J* = 4.6 Hz, 8H), 3.44 (t, *J* = 6.6 Hz, 8H), 1.86 (24H, s), 1.59 (24H, s), 1.57-1.49 (8H, m), 1.34 (8H, m). ^{13}C NMR (125 MHz, CD_3CN, δ) 159.7, 159.0, 158.9, 157.4, 156.5, 156.4, 156.2, 156.2, 153.6, 153.5, 152.3, 149.6, 141.3, 140.6, 139.3, 138.4, 138.0, 137.0, 136.4, 134.6, 131.1, 129.8, 128.5, 126.8, 125.1, 124.8, 124.5, 122.0, 121.6, 118.3, 115.1, 114.6, 71.8, 69.8, 68.3, 67.5, 30.3, 26.7, 20.9, 20.8. ESI-MS: *m/z* for $[M]^{4+}$calc. 737.9, found 738.1; *m/z* for $[M + PF_6]^{3+}$ calc. 1032.2, found 1032.3. HRMS (ESI) m/z: $[M]^{4+}$ calculated for ($C_{178}H_{166}N_{18}O_{12}Ru_2$): 737.77654; found: 737.77630.



2-terpy@[Zn(OTf)$_2$]$_2$

[bis-(5'5''-bis-(4-(2-(propoxy-ethoxy)-2,6- dimethyl-phenyl)-2,2':6',2''-terpyridine) macrocycle] ⊃ bis-(Ru(II) (*N,N'',N'''*-4,4''-bis-(4-oxy-2,6-dimethyl-phenyl)- 2,2':6',2''-terpyridine- 5,5''-bis(methyl)-2,2':6',2''-terpyridine macrocycle) ⊃ bis- Zn(OTf)$_2$][PF$_6$]$_4$ (2-Terpy⊃M$_2$-a)

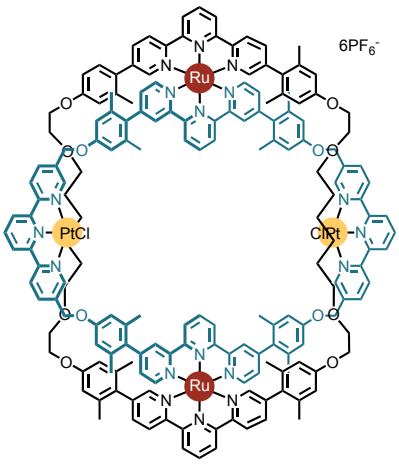
Prepared using an analogous literature procedure.[10] A solution of zinc triflate (0.003 g, 8.50 × 10^{-6} moles) in acetonitrile (0.5 mL) was added drop wise to a solution of two-ring complex **4** (0.015 g, 4.25 × 10^{-6} moles) in acetonitrile (0.5 mL). The red solution was stirred for 3 h at room temperature before removing the solvent to yield a red crystalline solid (0.017 g, 94 %). m.p. > 350 °C ^{1}H NMR (600 MHz, (CD_3CN, δ): 8.86 (4H, d, *J* = 7.8 Hz), 8.85 (4H, d, *J* = 1.8 Hz), 8.7 - 8.4 (22H, series of m), 8.25 (4H, d, *J* = 1.2 Hz), 8.19 (2H, t, *J* = 7.8 Hz), 8.18 (2H, t, *J* = 7.8 Hz), 7.80 (4H, dd, *J* = 8.4, 1.8 Hz), 7.52 (4H, d, *J* = 6.0 Hz), 7.14 (4H, d, *J* = 1.8 Hz), 7.13 (4H, dd, *J* = 6.0, 1.8 Hz), 6.88 (6H, s), 6.58 (10H, s), 5.39 (8H, s), 3.99 (8H, t, *J* = 4.8 Hz), 3.65 (8H, t, *J* = 4.8 Hz), 3.43 (8H, t, *J* = 6.6 Hz), 1.92 (24H, s), 1.62 (24H, s), 1.54 (8H, m), 1.34 (8H, m); ^{13}C NMR (125 MHz, CD_3CN, δ): 161.52, 160.01, 159.48, 157.46, 157.00, 156.36, 156.29, 155.27, 154.21, 153.26, 151.64, 150.35, 145.29, 142.22, 139.40, 138.48, 138.1, 137.22, 135.37, 134.79, 130.77, 128.90, 128.64, 127.53, 126.12, 124.84, 124.13, 122.26, 121.83, 115.20, 114.94, 72.58, 69.82, 68.55, 66.93, 31.18, 30.68, 26.02, 20.96, 20.9. ESI-MS: *m/z* for [M - 4OTf + 3H_2O]$^{8+}$ calc. 392.04, found 392.2; *m/z* for [M - 3OTf]$^{7+}$ calc. 464.0, found 464.4; *m/z* for [M - 2OTf]$^{6+}$ calc. 568.1, found 563.2.



2-terpy@[$RuCl_3$]$_2$

[bis-(5’5’’-bis- (4-(2-(propoxy-ethoxy)- 2,6-dimethyl-phenyl)-2,2’:6’,2’’-terpyridine) macrocycle] ⊃ bis- (Ru(II) (*N,N’’,N’’’*-4,4’’-bis-(4-oxy-2,6-dimethyl-phenyl)- 2,2’:6’,2’’- terpyridine-5,5’’-bis(methyl)-2,2’:6’,2’’- terpyridine macrocycle) ⊃bis-$RuCl_3$][PF_6]$_4$ (2-Terpy⊃M_2-b)

Ruthenium(III) trichloride hydrate (0.005 g, 2.04 × 10^{-5} moles) and two ring complex **1** (0.018 g, 5.10 × 10^{-6} moles) were combined in a 2:1 solution (1.5 mL) of ethanol : 1,2-dichloroethane. The red solution was heated for 16 h at reflux before reducing the solvent and adding aqueous potassium hexafluorophosphate until a dark red-brown precipitate formed. The precipitate was filtered over celite, washed with water and diethyl ether and dissolved into a clean flask with acetonitrile. The brown-red solution was dried over magnesium sulfate, filtered and solvent evaporated to yield a brown solid (0.020 g, 99%). m.p. > 350 °C; ESI-MS: *m/z* for [M - 4Cl + 4ACN]$^{6+}$ calc. 564.8, found 565.3; *m/z* for [M - 3Cl + 3ACN]$^{5+}$ calc. 676.6, found 676.6; *m/z* for [M]$^{4+}$ calc. 841.2, found 840.6.



2-terpy@[PtCl]$_2$

[bis-(5’5’’-bis- (4-(2-(propoxy-ethoxy)- 2,6-dimethyl-phenyl)-2,2’:6’,2’’-terpyridine) macrocycle] ⊃ bis- (Ru(II) (*N,N’’,N’’’*-4,4’’-bis-(4-oxy-2,6-dimethyl-phenyl)- 2,2’:6’,2’’- terpyridine -5,5’’-bis(methyl)-2,2’:6’,2’’-terpyridine macrocycle) ⊃ bis-PtCl][PF_6]$_6$ (2-Terpy⊃M_2-c)

Prepared using an analogous literature procedure.[2] Solid silver(I)tertrafluoroborate (0.003 g, 1.59 × 10^{-5} moles) was added to solution of dichloro (1,5-cyclooctadiene)-platinum(II)[11] (0.003 g, 7.55 × 10^{-6} moles) in acetone (0.250 mL) and the solution filtered through a celite pad into a solution of two ring complex **1** (0.013 g, 3.68 × 10^{-6} moles) in acetonitrile (1.0 mL). The red solution was stirred for 30 min at room temperature before adding a 10% solution of hydrochloric acid to cause a red precipitate. The precipitate was filtered over celite, washed with water and diethyl ether and dissolved into a clean flask with acetonitrile. Aqueous potassium hexafluorophosphate was added until a deep red precipitate formed and the precipitate was filtered over celite, washed with water and diethyl ether and dissolved into a clean flask with acetonitrile. The red solution was dried over magnesium sulfate, filtered and solvent evaporated to yield a red solid (0.011 g, 70 %). m.p. 320 °C dec.; ^{1}H NMR (600 MHz, (CD_3CN, δ): 9.08 (4H, d, *J* = 1.8 Hz), 8.62 (4H, d, *J* = 6.6 Hz), 8.62 (4H, d, *J* = 8.4 Hz), 8.5-8.4 (8H, m), 8.35-8.25 (8H, m), 8.19 (2H, t, *J* = 7.8 Hz), 7.80 (4H, dd, *J* = 8.4, 1.8 Hz), 7.52 (4H, d, *J* = 6.0 Hz), 7.16 (4H, d, *J* = 1.8 Hz), 7.14 (4H, dd, *J* = 6.0, 1.8 Hz), 6.86 (6H, s), 6.60 (10H, s), 5.30 (8H, s), 4.00 (8H, t, *J* = 4.8 Hz), 3.66 (8H, t, *J* = 4.8 Hz), 3.44 (8H, t, *J* = 6.6 Hz), 1.93 (24H, s), 1.61 (24H, s), 1.53 (8H, m), 1.33 (8H, m); ^{13}C NMR (125 MHz, (CD_3CN, δ): 162.34, 160.73, 159.02, 157.89, 156.89, 156.05, 155.97, 155.23, 154.31, 154.17, 151.02, 150.47, 145.68, 142.04, 140.19, 138.35, 138.12, 137.68, 135.49, 134.93, 131.21, 128.23, 128.01, 127.26, 126.24, 124.43, 124.04, 122.21, 121.90, 116.35, 115.27, 71.89, 70.66, 68.38, 66.23, 32.04, 30.73, 26.54, 21.01, 20.98. ESI-MS: *m/z* for $[M]^{6+}$ calc. 568.8, found 569.2.

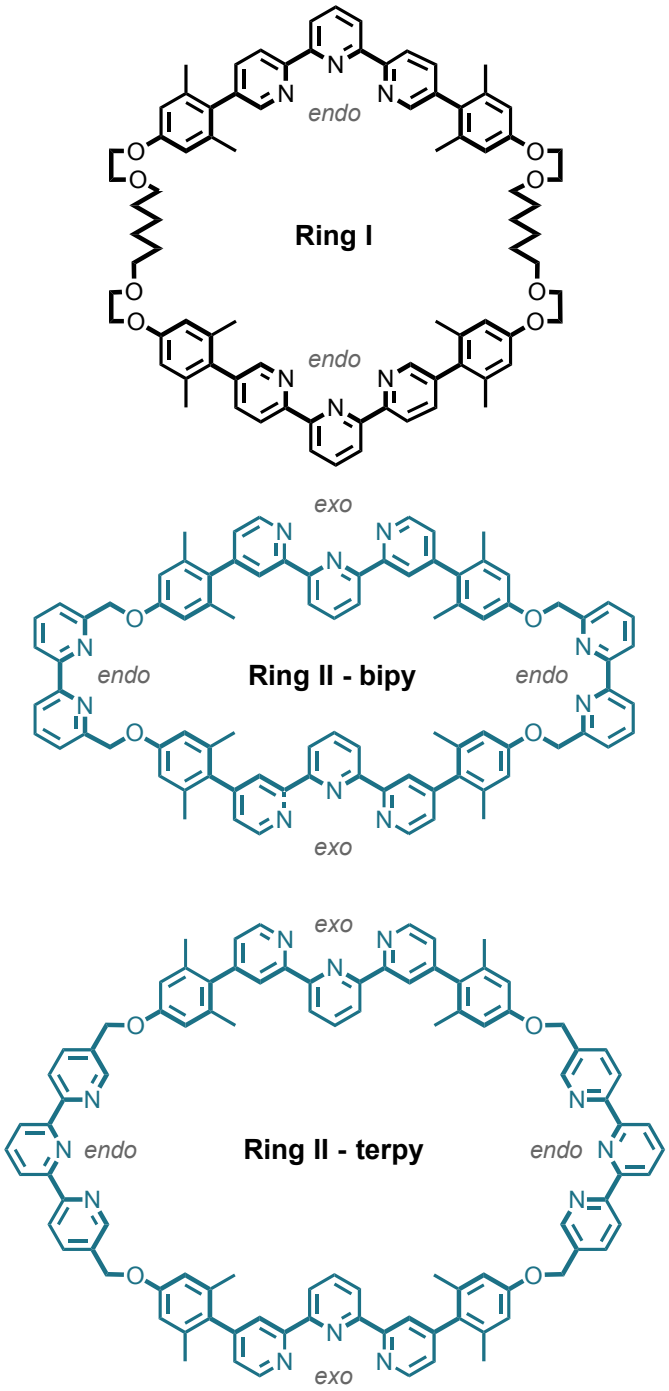


Figure S1. Chemdraw representations of polypyridyl macrocycles with exo- and endo- topic metal coordination sites labeled. **Ring I** is a 66 membered macrocycle, bipyridine **Ring II** is a 54 membered macrocyle, and terpyridine ring II is a 64 membered macrocycle.

3. NMR Spectra

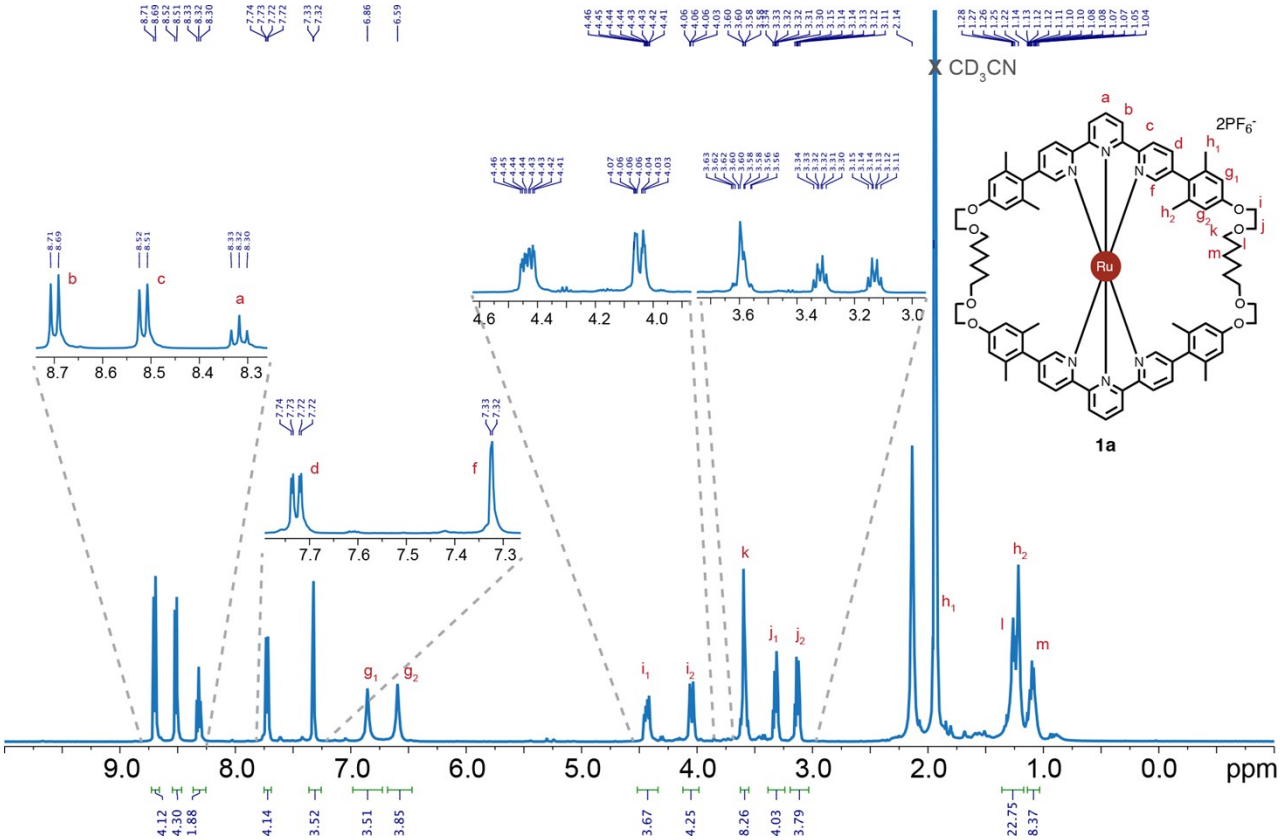


Figure S2. 500MHz ^{1}H NMR of Ring I complex **1a** in CD_3CN at RT. Protons g, h, i, and j are diastereotopic and appear as two peaks.

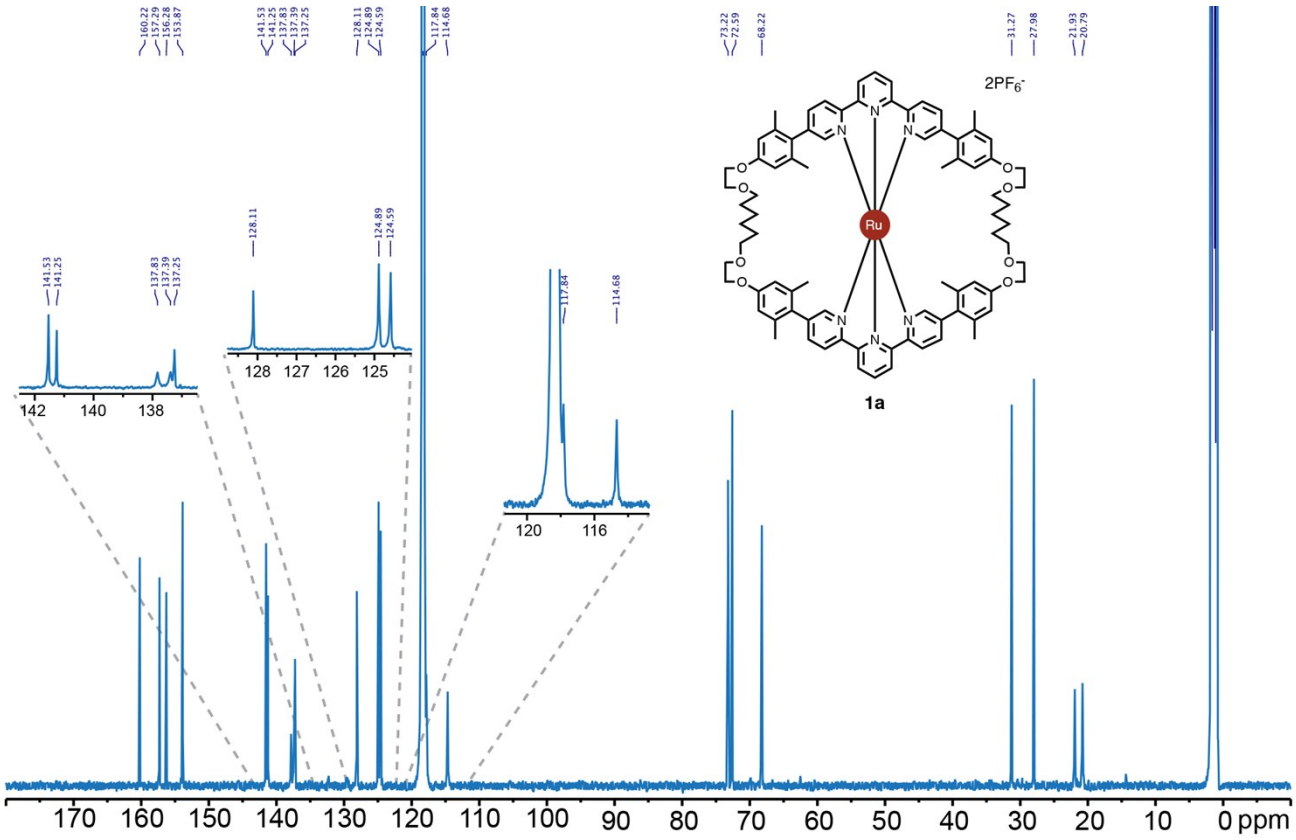


Figure S3. 125MHz ^{13}C NMR of Ring I complex **1a** in CD_3CN at RT.

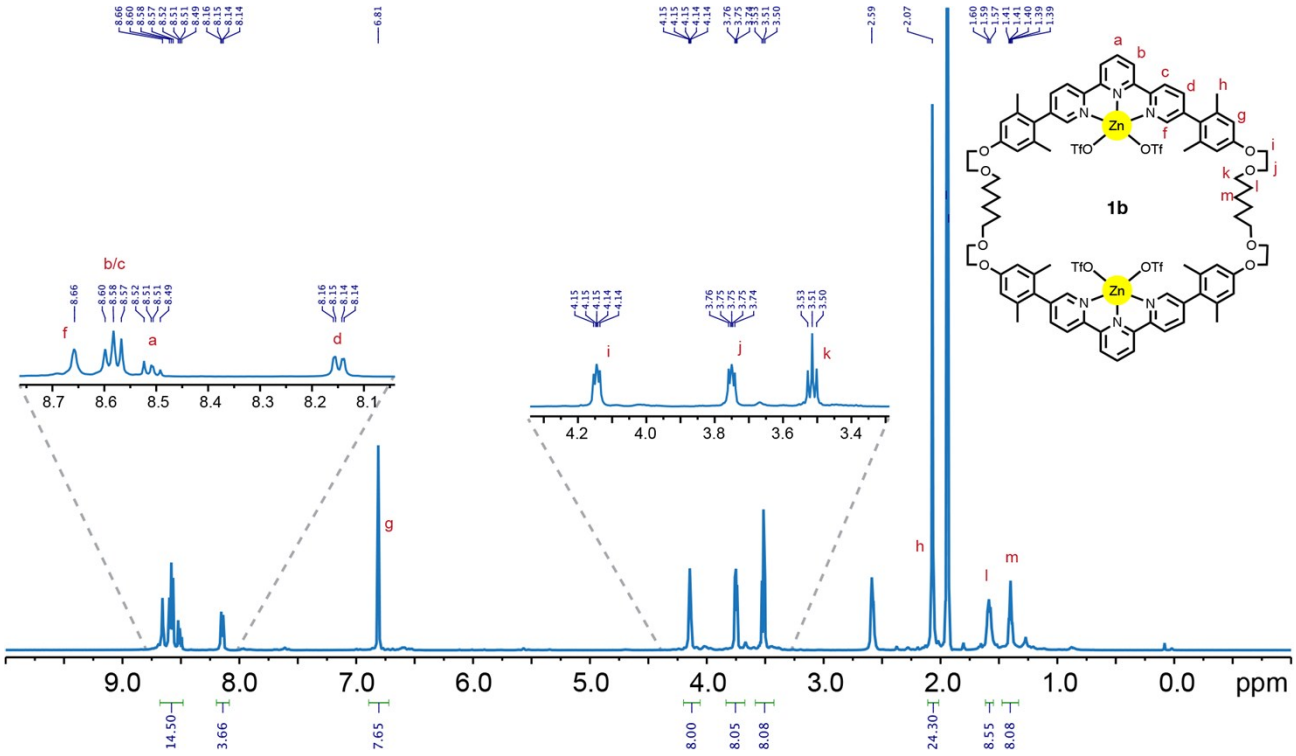


Figure S4. 500MHz ^{1}H NMR of Ring I complex **1b** in CD_3CN at RT.

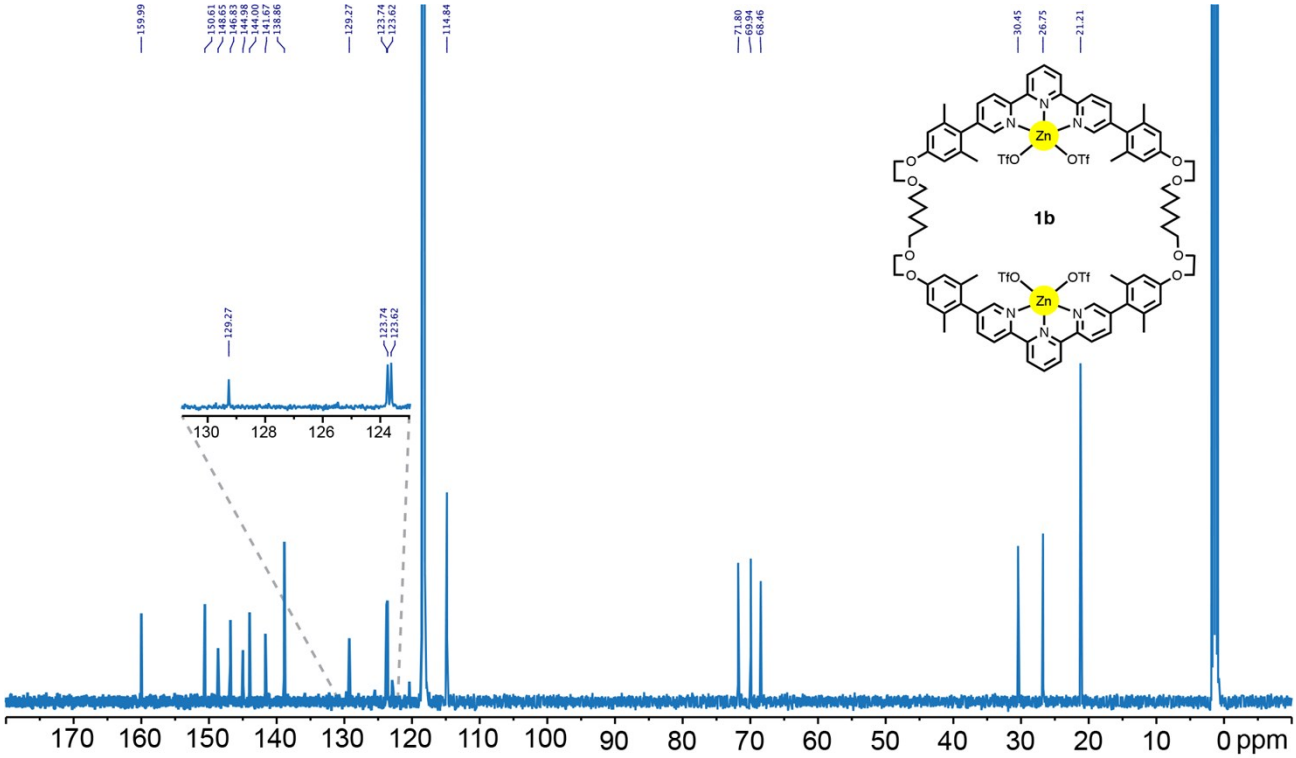


Figure S5. 125MHz ^{13}C NMR of Ring I complex **1b** in CD_3CN at RT.

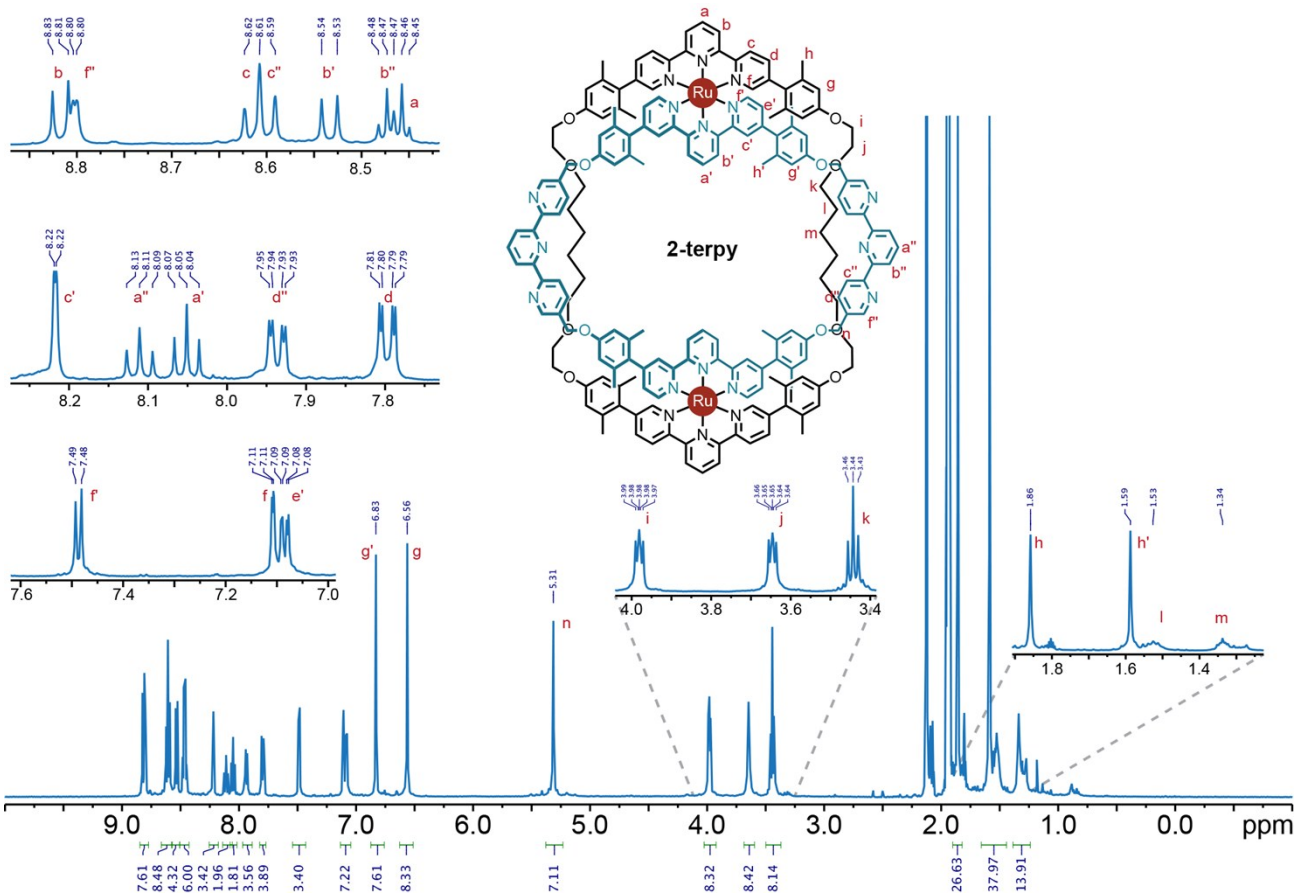


Figure S6. 500MHz ^{1}H NMR of two-ring complex **2-terpy** in CD_3CN at RT.

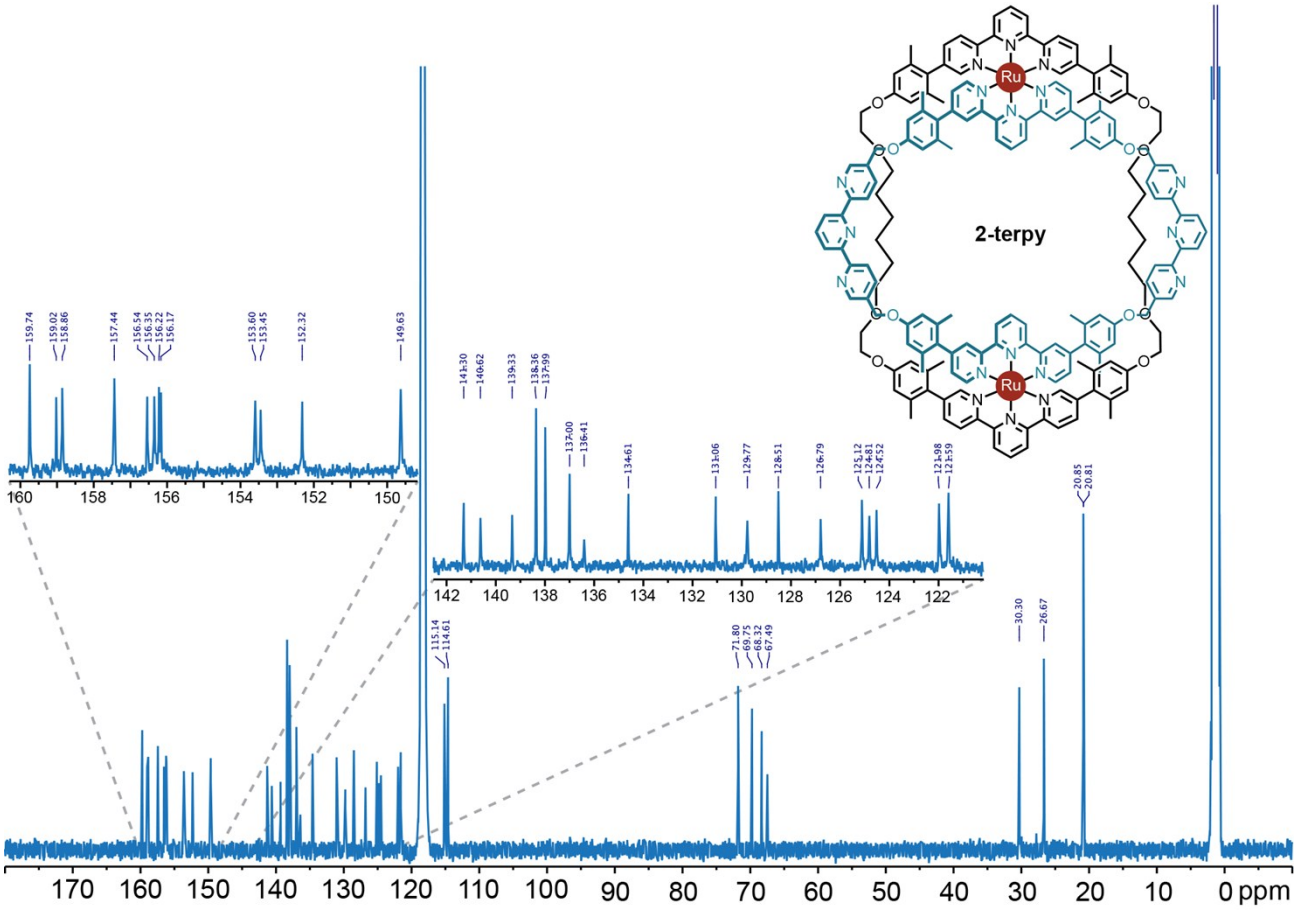


Figure S7. 125MHz ^{13}C NMR of two-ring complex **2-terpy** in CD_3CN at RT.

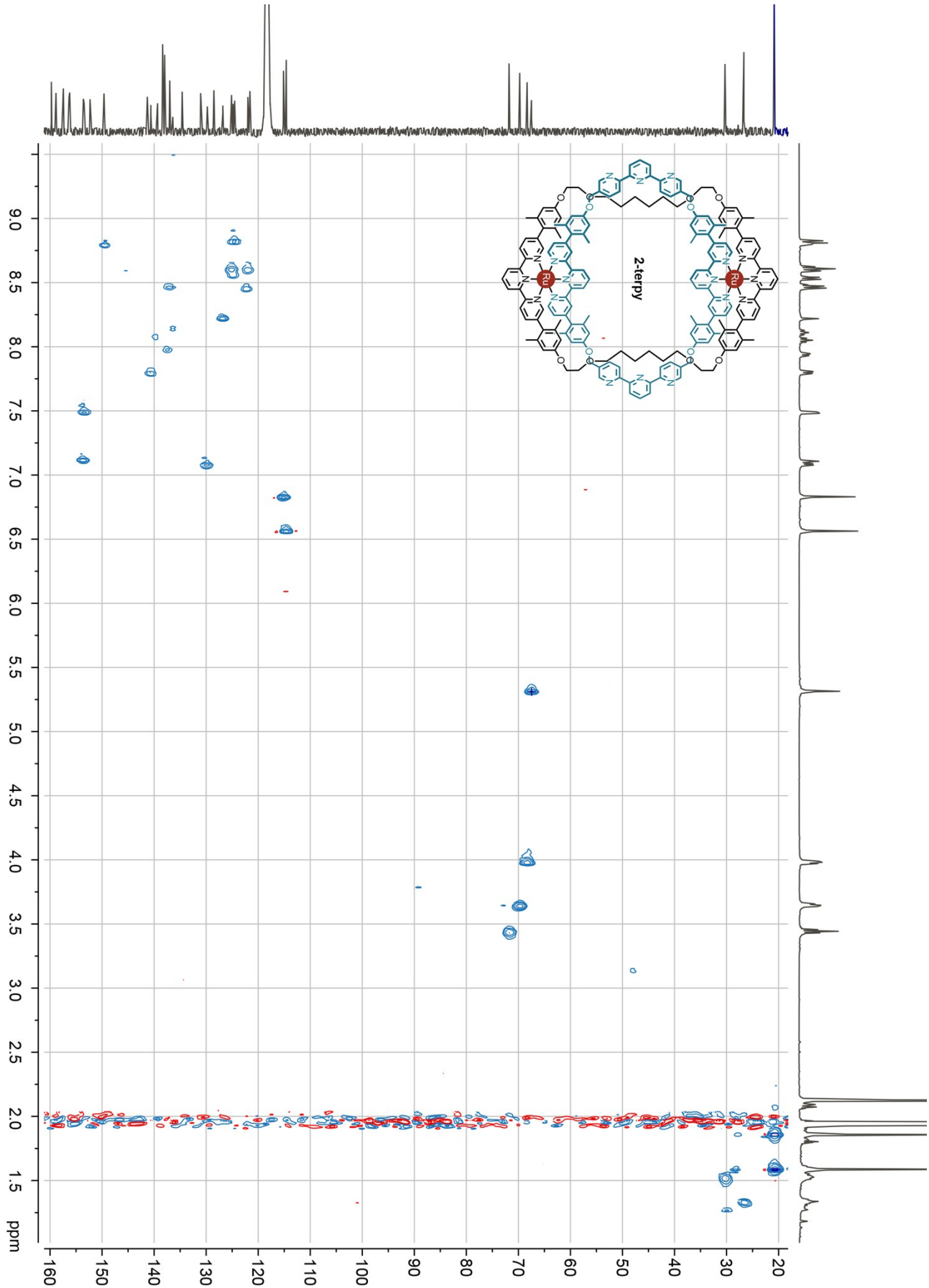


Figure S8. 500MHz HSQC NMR of two-ring complex **2-terpy** in CD_3CN at RT.

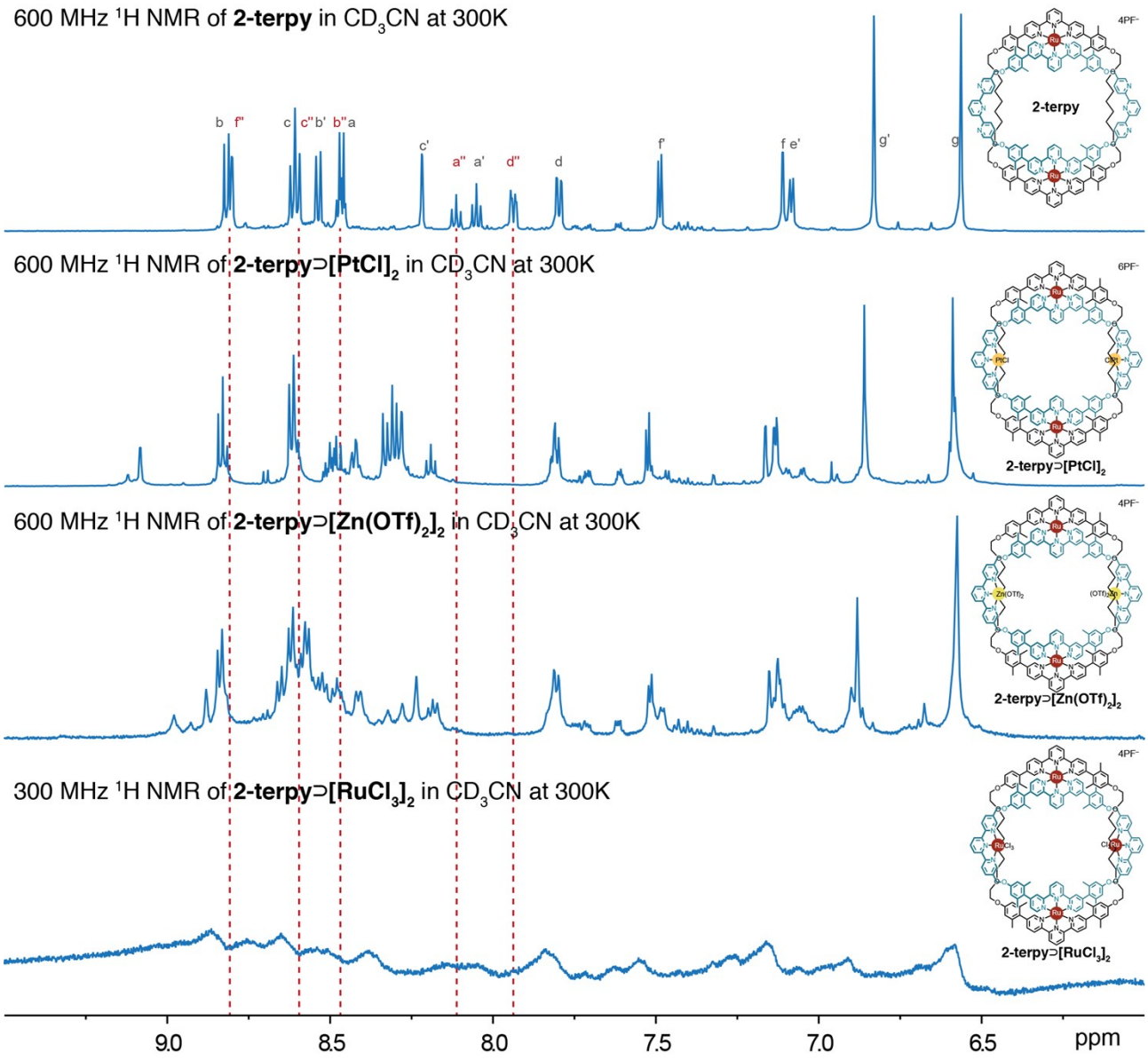


Figure S9. ^{1}H NMR Aromatic Region of **2-terpy** complexes **2-Terpy⊃M a – c** in CD_3CN at RT with peaks of the *endo*- terpyridine of Ring II highlighted to show shifts upon metal coordination. Note that the peaks of **2-Terpy⊃RuCl$_3$** are strongly broadened due to the hyperfine shift of two paramagnetic Ru(III) centers.

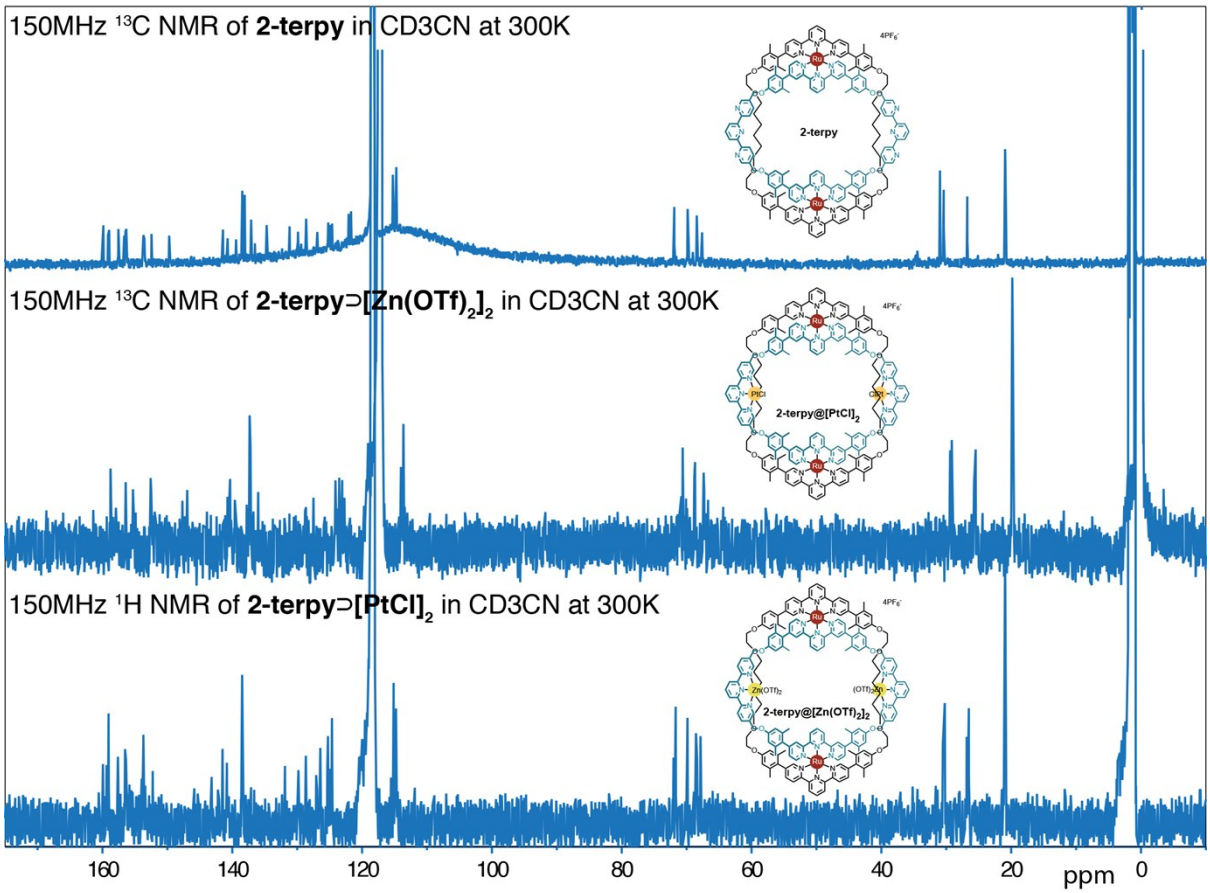


Figure S10. 150 MHz ^{13}C0NMR of two-ring complex **2-terpy** complexes **2-Terpy⊃M a – c** in CD_3CN at RT.

4. Mass Spectra

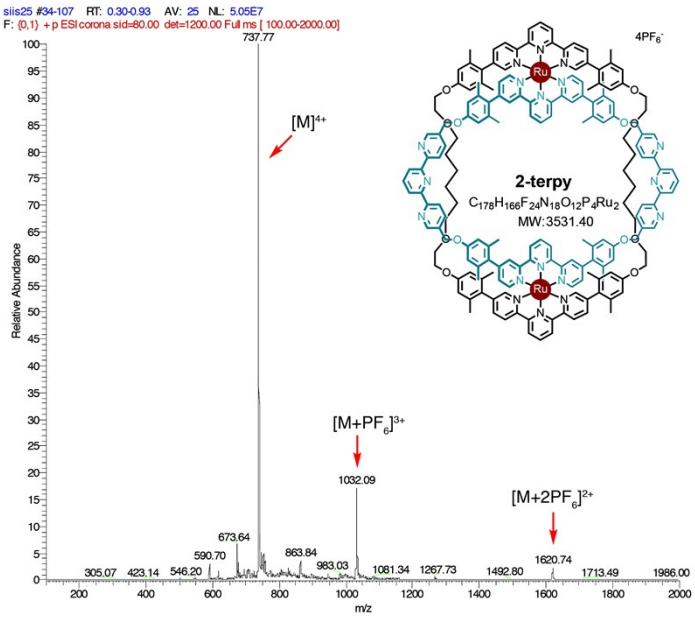


Figure S11. ESI-MS of two-ring complex **2-terpy.**

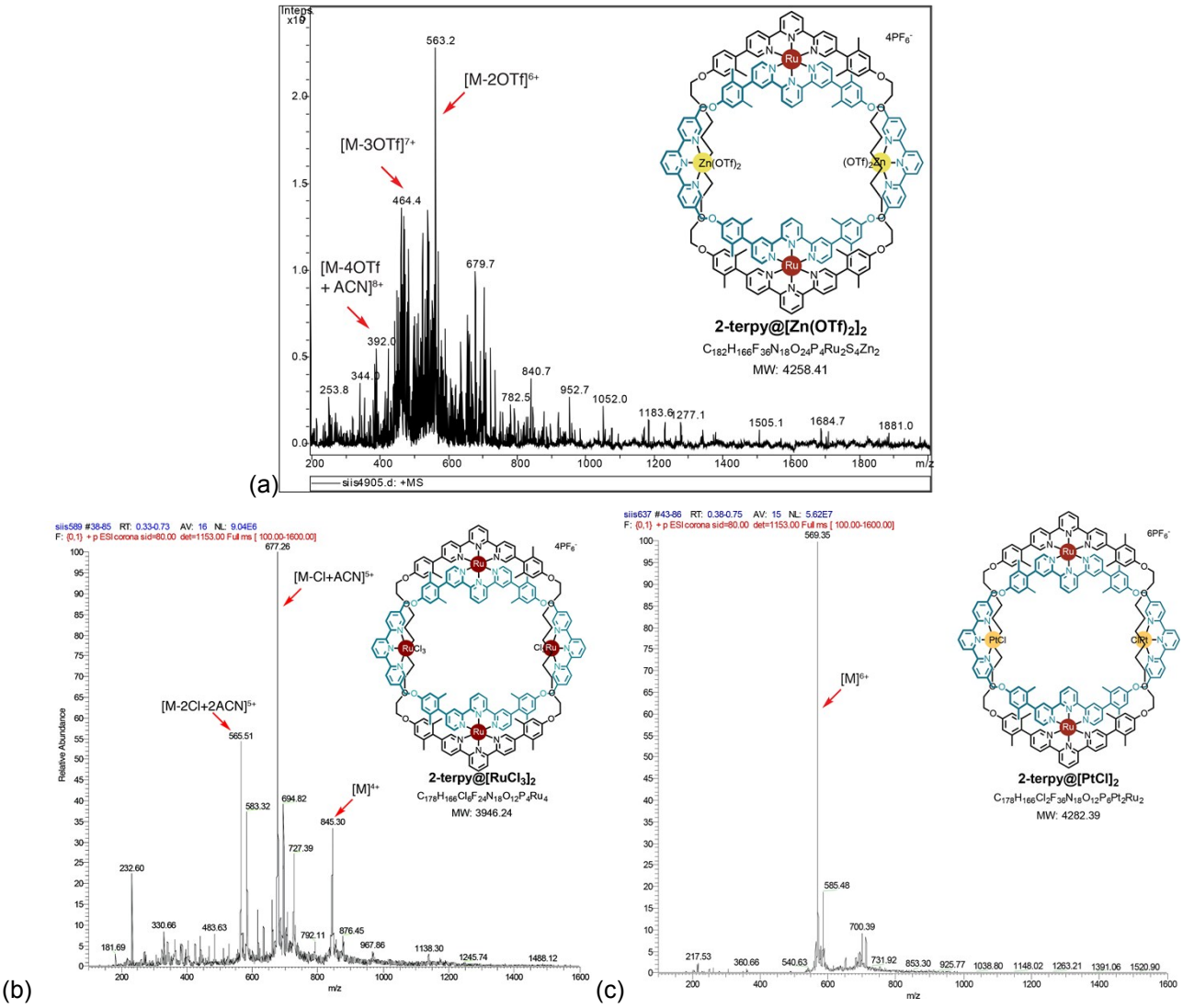


Figure S12. ESI-MS of two-ring complexes (a) **2-Terpy⊃M-a**,(b) **2-Terpy⊃M-b** and (c) **2-Terpy⊃M-c**

5. ORTEPs

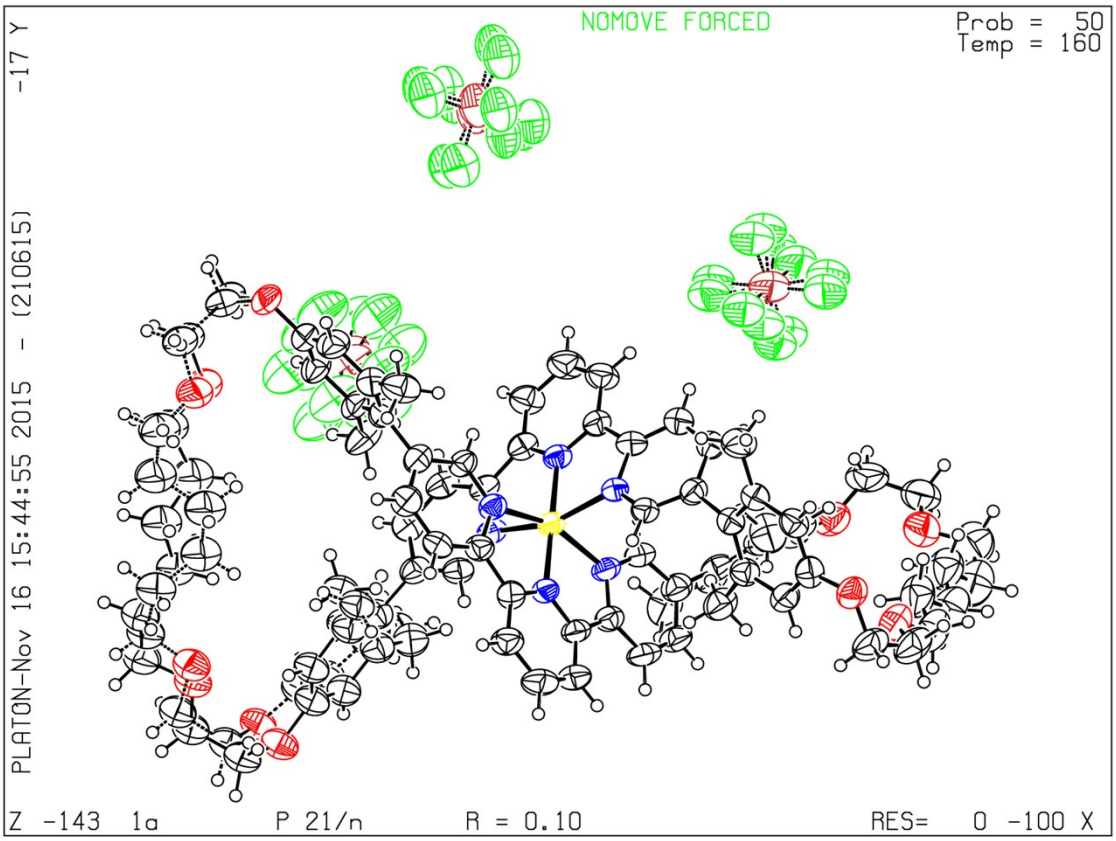


Figure S13. ORTEP (ellipsoids at 50% probability) for **1a**.

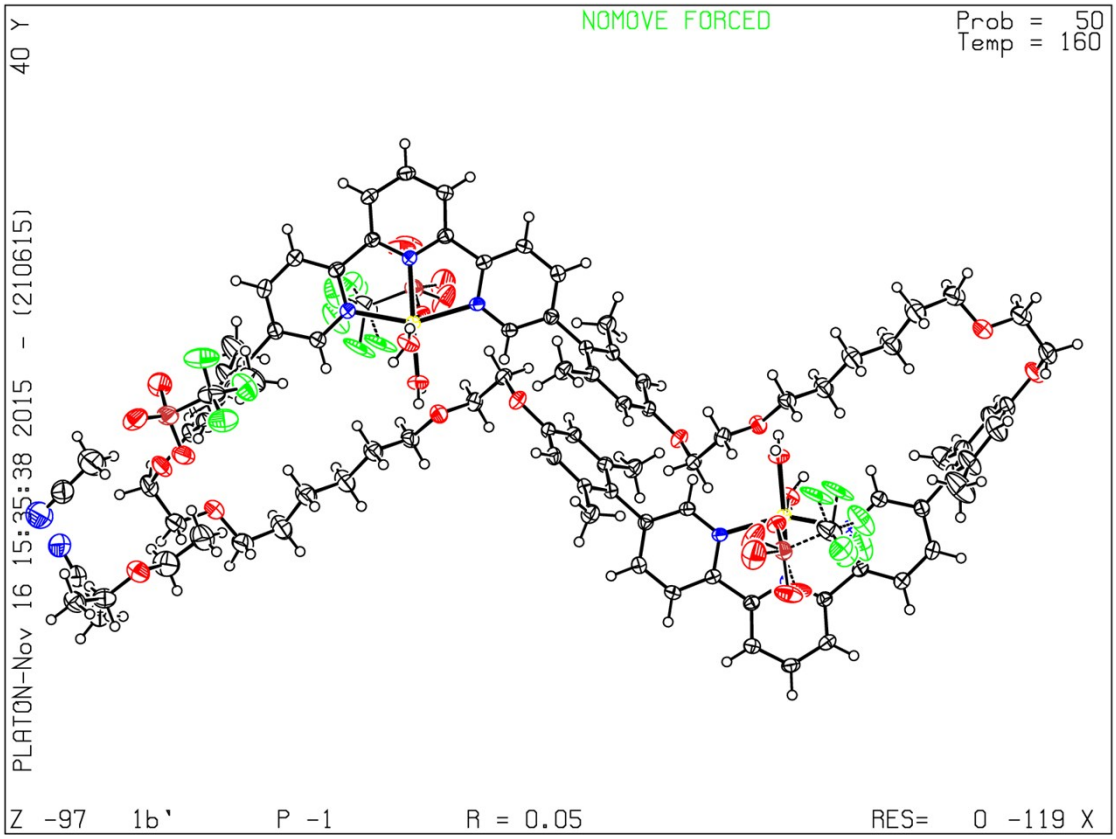


Figure S14. ORTEP (ellipsoids at 50% probability) for **1b**'.

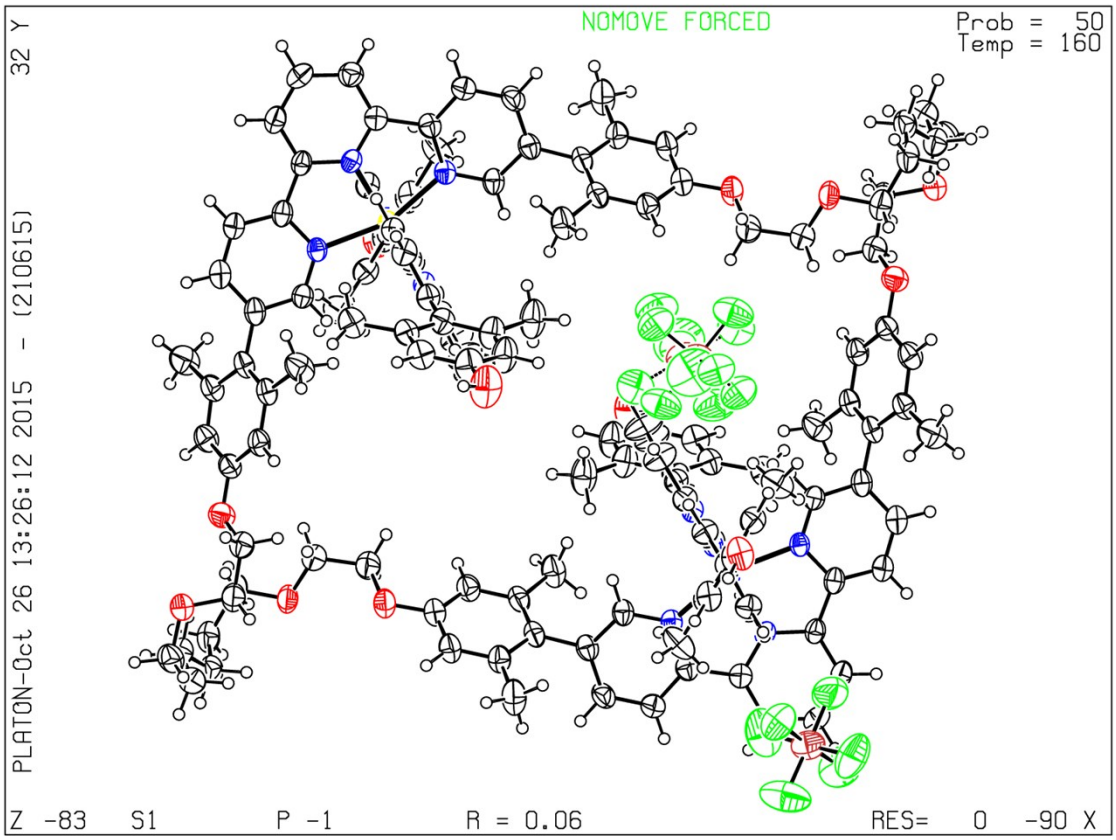


Figure S15. ORTEP (ellipsoids at 50% probability) for the double pseudo rotaxane **2**.

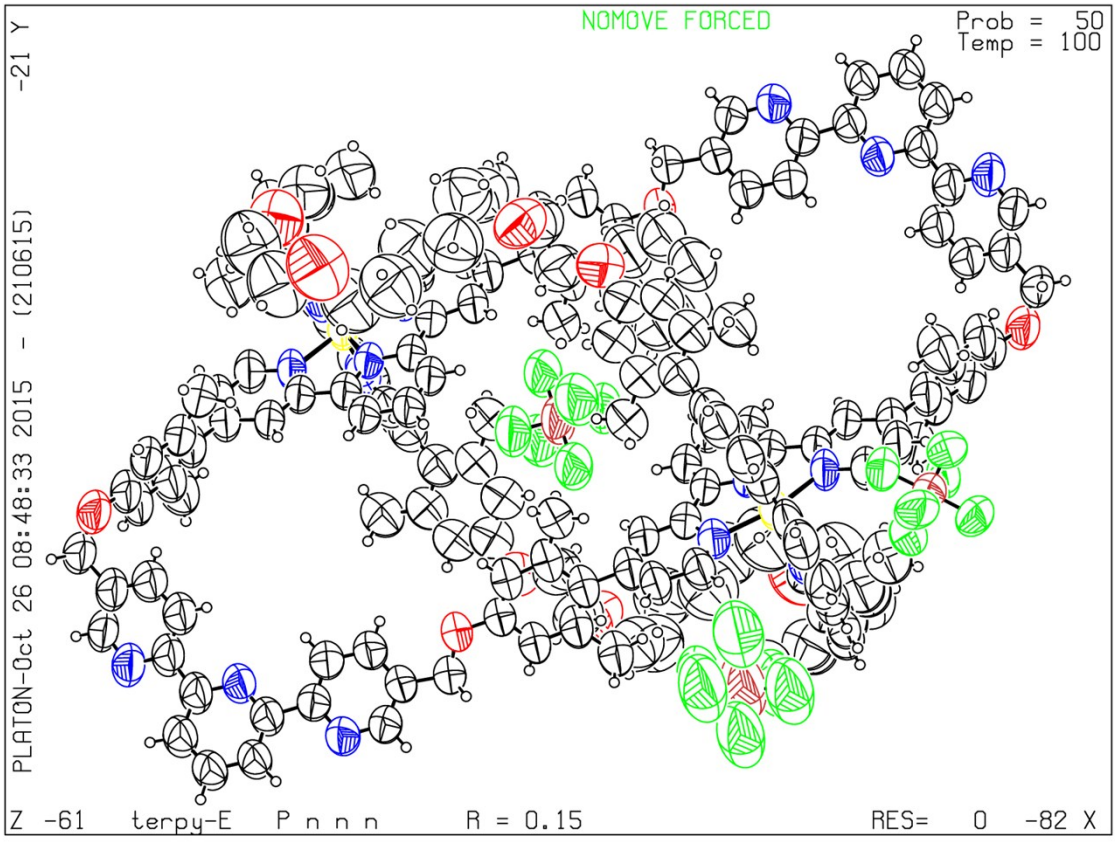


Figure S16 ORTEP (ellipsoids at 50% probability) for terpyridine two-ring **2-terpy**.

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