Electronic supplementary information

NEW PYRIDINE-CONTAINING AZACROWN CHELATORS PATPy AND PAPPy FOR Pb^{2+} IONS

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Experimental section

General remarks

All commercially available reagents and solvents were used without further purification. Compounds **1**, **2** and 2-(chloromethyl)pyridine hydrochloride were prepared as described earlier [1, 2]. Reaction progress was followed by TLC using aluminum oxide (Merck, 60 F_{254}, neutral). ^{1}H NMR spectra were recorded at 25°C on Varian Inova 400, Bruker Avance 400 spectrometers. Chemical shifts are reported in parts per million (δ) relative to the deuterated solvent used as the internal reference ($CDCl_3$ δ = 7.27, CD_3CN δ = 1.94). The coupling constant *J* is given in Hertz. Spectral assignments were based in part on two-dimensional NMR experiments COSY, HSQC and HMBC. Electrospray ionization mass spectrometry (ESI/MS) analyses were performed using a Shimadzu LCMS-2020 High Performance Liquid Chromatograph Mass Spectrometer with a single quadrupole detector, desolvation line/heat block temperature 250/400°C and an ionization voltage at 4.5 kV. Electrospray full scan spectra was obtained by infusion at 0.4 ml/min of MeCN solutions of the compounds and complexes. Elemental analysis was conducted on a Carlo Erba 1108 elemental analyzer at the Laboratory of Microanalysis of A. N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia.

Syntheses

3,6,9,12-tetraaza-1(2,6)-pyridinacyclotridecaphane (3). Compound **3** was prepared according to a modified procedure [3]. 1M BH_3·THF (14.5 ml, 14.5 mmol) was added to the compound **1** (200 mg, 0.72 mmol) in an argon atmosphere at 0°C. The mixture was stirred at 0°C for 45 hours. Then MeOH (5 ml) was added and the mixture stirred for 5 minutes. Then the solvent was evaporated in vacuum and MeOH (10 ml) was added and the mixture refluxed for 20 hours. The methanol was evaporated in vacuum and 0.5M HCl (4 ml) was added and the mixture refluxed for 10 hours. After cooling, the reaction mixture was washed with $CHCl_3$, adjusted to pH 10 by adding KOH and the product was extracted with $CHCl_3$. After evaporation $CHCl_3$ the product was obtained as a yellow oil (145 mg, 81%). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.52 (s, 4H, H(7)), 2.56 (t, 4H, H(6), *J*=3.5), 2.63 (t, 4H, H(5), *J*=3.2), 3.69 (s, 4H, H(4)), 6.82 (d, 2H, H(2), *J*=7.6), 7.33 (t, 1H, H(1), *J*=7.6). ^{13}C NMR ($CDCl_3$, 400 MHz): 48.24 (C-5), 48.40 (C-7), 48.48 (C-6), 53.71 (C-4), 120.56 (C-2), 136.61 (C-1), 158.59 (C-3). MS (ESI), m/z: calcd for $C_{13}H_{23}N_5$+H^+: 250.20 $[M+H]^+$; found: 249.98. Anal. Calcd for $C_{13}H_{23}N_5 \cdot H_2O$: C, 58.40; H, 9.42; N, 26.19. Found: C, 58.46; H, 9.40; N, 26.18.

3,6,9,12,15-pentaaza-1(2,6)-pyridinacyclohexadecaphane (4). 1M BH_3·THF (34 ml, 34 mmol) was added to the compound **2** (180 mg, 0.56 mmol) in an argon atmosphere at 0°C. The mixture was stirred at 0°C for 72 hours. Then MeOH (10 ml) was added and the mixture stirred for 5 minutes. Then the solvent was evaporated in vacuum and MeOH (15 ml) was added and the mixture refluxed for 20 hours. The methanol was evaporated in vacuum and 0.5M HCl (5 ml) was added and the mixture refluxed for 10 hours. After cooling, the reaction mixture was washed with $CHCl_3$, adjusted to pH 10 by adding KOH and the product was extracted with $CHCl_3$. After evaporation $CHCl_3$ the product was obtained as a yellow oil (118 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.66 (m, 4H, H(8)), 2.71 (m, 8H, H(5), H(7)), 2.75 (m, 4H, H(6)), 3.79 (s, 4H, H(4)), 7.00 (d, 2H, H(2), *J*=7.6), 7.48 (t, 1H, H(1), *J*=7.6). ^{13}C NMR ($CDCl_3$, 400 MHz): 49.00-49.11 (C-8, C-7, C-6, C-5), 54.79 (C-4), 120.69 (C-2), 136.49 (C-1), 158.68 (C-3). MS (ESI), m/z: calcd for $C_{15}H_{30}N_6$+H^+: 293.25 $[M+H]^+$; found: 293.07. Anal. Calcd for $C_{15}H_{30}N_6 \cdot 2H_2O$: C, 54.85; H, 9.82; N, 25.59. Found: C, 54.80; H, 9.80; N, 25.56.

3,6,9,12-tetrakis(pyridin-2-ylmethyl)-3,6,9,12-tetraaza-1(2,6)-pyridinacyclotridecaphane (PATPy). A solution of 2-(chloromethyl)pyridine (105 mg, 0.64 mmol) in MeCN (3 ml) was added to a mixture of **3** (40 mg, 0.16 mmol) and K_2CO_3 (177 mg, 1.28 mmol) dissolved in MeCN (3 ml). The reaction mixture was refluxed for 24 h, then solvent was evaporated under vacuum and the product was extracted with $CHCl_3$. The solvent was evaporated under vacuum to yield brown oil which was purified by column chromatography on Al_2O_{3basic} using $CHCl_3$/MeOH as eluent. The product was obtained as a brown oil; yield: 65 mg (67%). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.43 (s, 4H, H(7)), 2.54 (t, 4H, H(6), *J*=6.6, *J*=8.2), 2.71 (t, 4H, H(5), *J*=6.6, *J*=8.2), 3.59 (s, 4H, H(14)), 3.71 (s, 4H, H(8)), 3.80 (s, 4H, H(4)), 7.03 (t, 2H, H(17), *J*=6.2, *J*=5.8), 7.11 (t, 2H, H(12), *J*=6.2, *J*=5.0), 7.20 (d, 2H, H(10), *J*=7.8), 7.27 (d, 2H, H(15), *J*=8.2), 7.47 (t, 2H, H(16), *J*=7.4, *J*=5.8), 7.52 (d, 2H, H(2), *J*=7.8), 7.60 (m, 3H, H(1), H(11)), 8.40 (d, 2H, H(18), *J*=5.1), 8.48 (d, 2H, H(13), *J*=3.9). ^{13}C NMR ($CDCl_3$, 400 MHz): 50.61 (C-5), 51.64 (C-6), 51.86 (C-7), 60.05 (C-8), 61.74 (C-4), 61.88 (C-14), 121.57 (C-17), 121.83 (C-12), 122.47 (C-2, C-15), 122.90 (C-10), 136.08 (C-16), 136.25 (C-11), 136.37 (C-1), 148.66 (C-18), 148.87 (C-13), 158.17 (C-9), 159.72 (C-3), 160.02 (C-19). MS (ESI), m/z: calcd for $C_{37}H_{43}N_9+H^+$: 614.37 $[M+H]^+$; found: 614.48. Anal. Calcd for $C_{37}H_{43}N_9 \cdot 0.3CHCl_3$: C, 68.61; H, 6.68; N, 19.29. Found: C, 68.58; H, 6.61; N, 19.21.

3,6,9,12,15-pentakis(pyridin-2-ylmethyl)-3,6,9,12,15-pentaaza-1(2,6)-pyridinacyclohexadecaphane (PAPPy). A solution of 2-(chloromethyl)pyridine (132 mg, 0.80 mmol) in MeCN (5 ml) was added to a mixture of **4** (47 mg, 0.16 mmol) and K_2CO_3 (222 mg, 1.60 mmol) dissolved in MeCN (6 ml). The reaction mixture was refluxed for 24 h, then solvent was evaporated under vacuum and the product was extracted with $CHCl_3$. The solvent was evaporated under vacuum to yield brown oil which was purified by column chromatography on Al_2O_{3basic} using $CHCl_3$/MeOH as eluent. The product was obtained as a brown oil; yield: 75 mg (63%). ^{1}H NMR ($CDCl_3$, 400 MHz): 2.41 (s. br, 8H, H(7), H(8)), 2.58 (t, 4H, H(6), *J*=7.4, *J*=6.9), 2.65 (t, 4H, H(5), *J*=7.5, *J*=5.8), 3.54 (s, 2H, H(21)), 3.59 (s, 4H, H(15)), 3.79 (s, 8H, H(4), H(9)), 7.04-7.11 (m, 4H, H(12), H(18)), 7.22 (d, 2H, H(2), *J*=7.7), 7.30 (d, 2H, H(11), *J*=7.7), 7.35 (d, 2H, H(17), *J*=7.7), 7.46-7.53 (m, 5H, H(19), H(24), H(25), H(26)), 7.56-7.62 (m, 4H, H(1), H(13), H(23)), 8.40 (d, 2H, H(20), *J*=5.3), 8.46 (d, 2H, H(14), *J*=4.3). ^{13}C NMR ($CDCl_3$, 400 MHz): 51.54 (C-5), 52.28 (C-6), 52.47 (C-7, C-8), 60.43 (C-4), 60.66 (C-15), 61.04 (C-21), 61.31 (C-9), 121.35 (C-2), 121.56 (C-18, C-24), 121.75 (C-12), 122.52 (C-17, C-23), 122.69 (C-11), 136.08 (C-1, C-13), 136.20 (C-19, C-25, C-26), 136.37 (C-1), 148.53 (C-20), 148.73 (C-14), 158.72 (C-3, C-10), 159.38 (C-22), 159.68 (C-16). MS (ESI), m/z: calcd for $C_{45}H_{53}N_{11}+H^+$: 748.46 $[M+H]^+$; found: 748.75; calcd for $C_{45}H_{53}N_{11}+Na^+$: 770.44 $[M+Na]^+$; found: 770.75. Anal. Calcd for $C_{45}H_{53}N_{11} \cdot 1.6CHCl_3$: C, 59.19; H, 5.82; N, 16.27. Found: C, 59.16; H, 5.78; N, 16.20.

ESI/MS-experiments

The samples of the Pb^{2+} complexes for ESI/MS-experiment were prepared by mixing the solution of corresponding ligand (0.05 μmol) in 50 μl MeCN with the solution of $Pb(ClO_4)_2$ (0.05 μmol) in 50 μl MeCN and diluted to 1000 μl . The resulting solution was studied using ESI mass spectrometry.

Table S1. Pb^{2+} complex species detected by ESI MS and simulated m/z.

ligand	m/z experimental	m/z simulated
PATPy	410.50	410.67
PAPPy	477.80	477.71

NMR study

The samples of the Pb^{2+} complexes for the NMR measurements were prepared by dissolving the corresponding ligand (c_L = 0.02 M) and 1 eq. $Pb(ClO_4)_2$ in CD_3CN.

NMR spectra of compounds

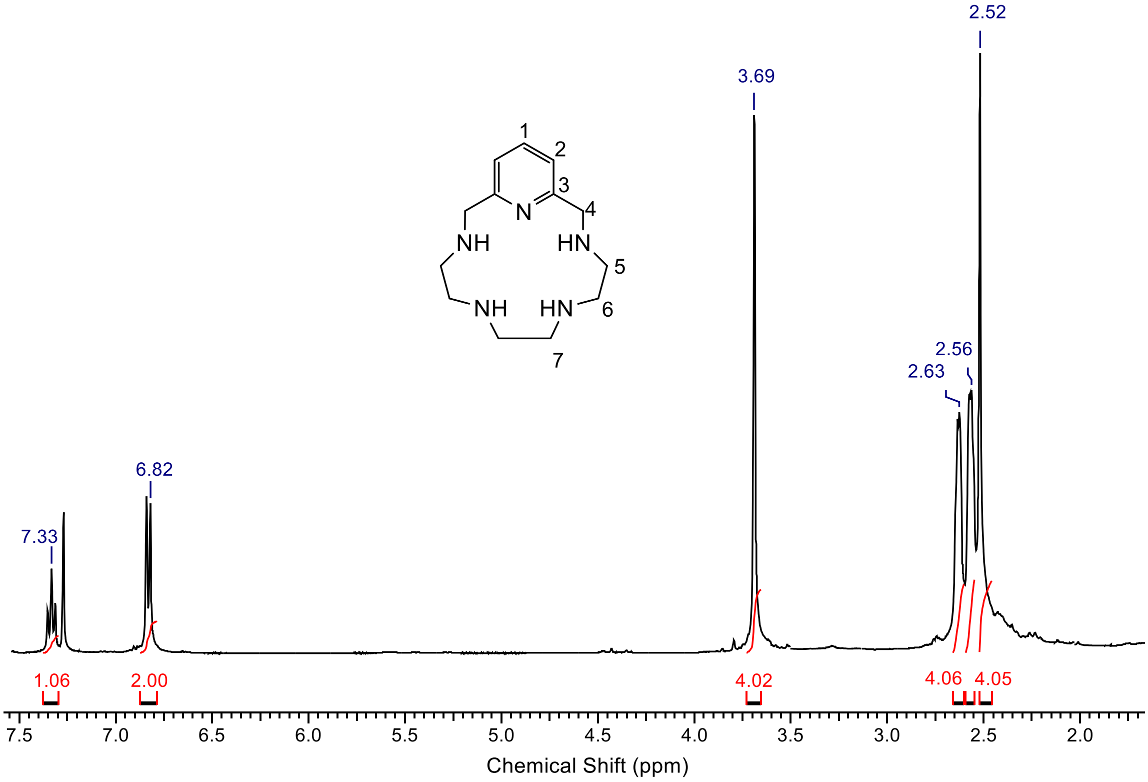


Figure S1: ^{1}H NMR spectrum of **3** in $CDCl_3$.

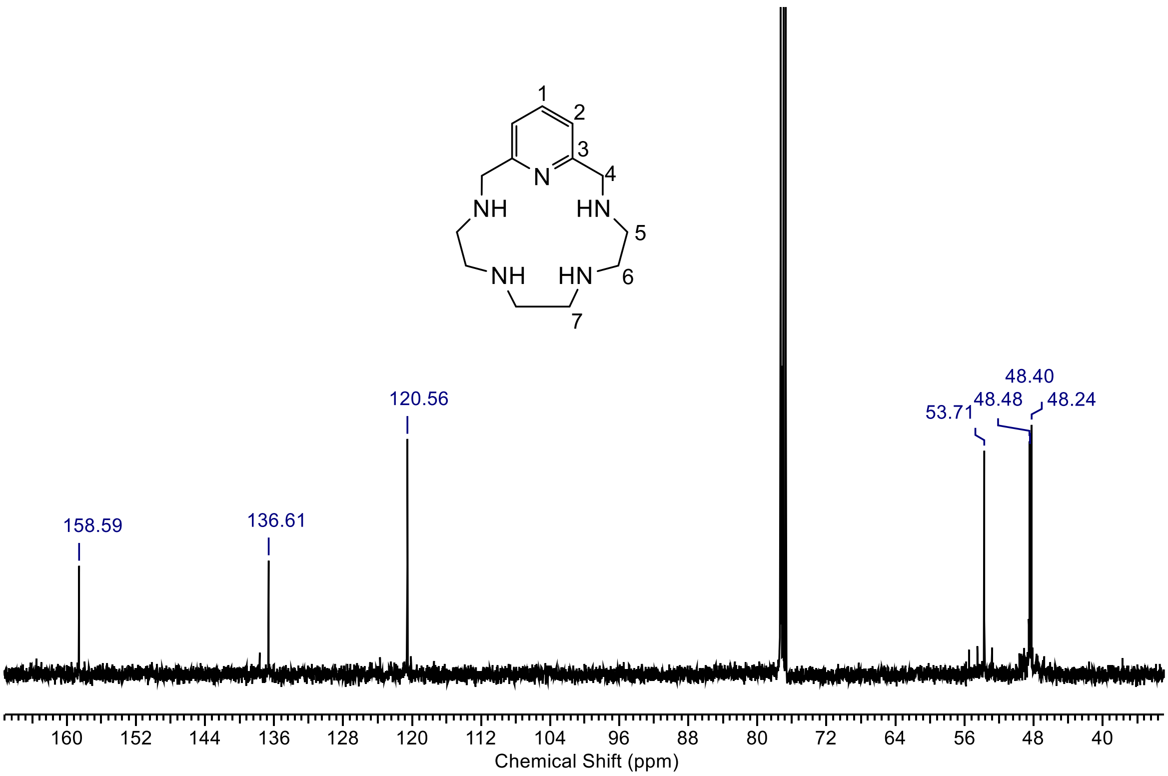


Figure S2: ^{13}C NMR spectrum of **3** in $CDCl_3$.

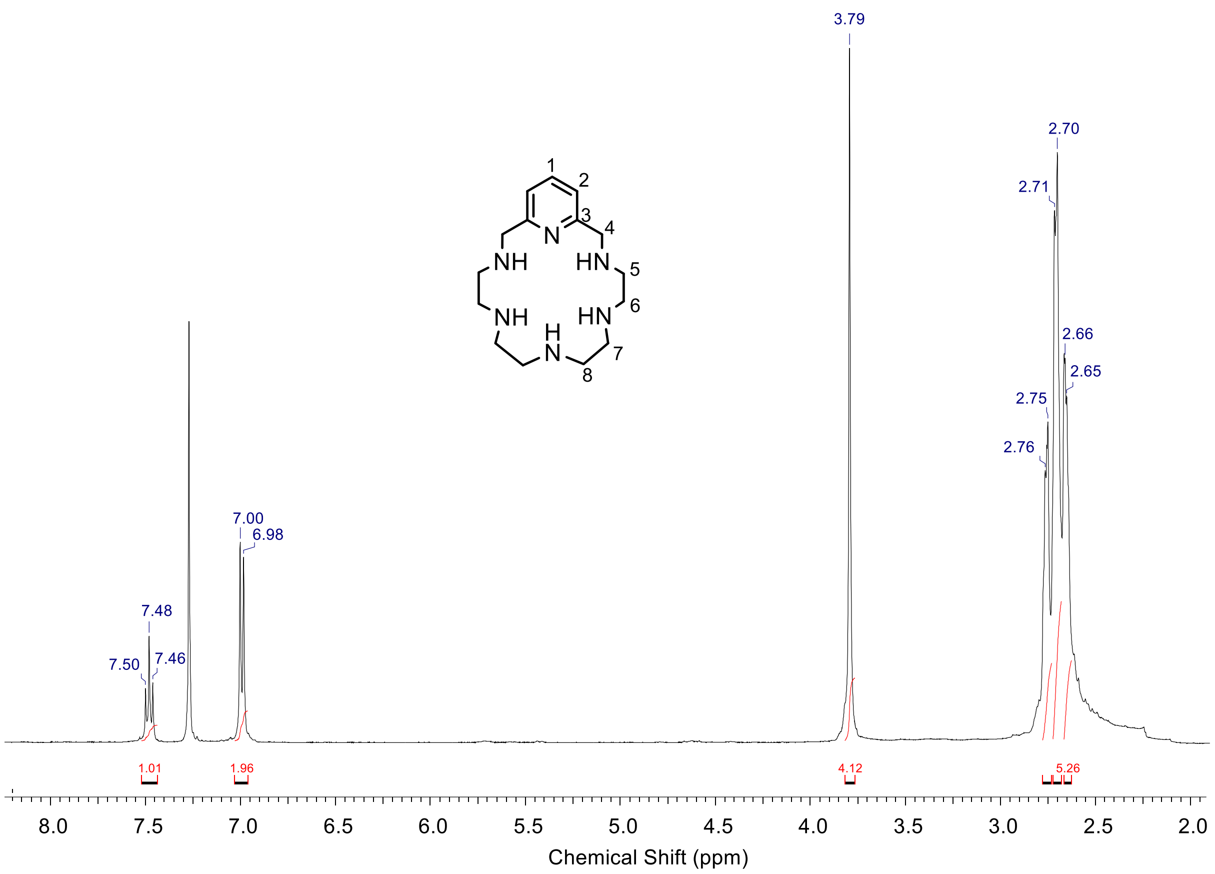


Figure S3: ^{1}H NMR spectrum of **4** in $CDCl_3$.

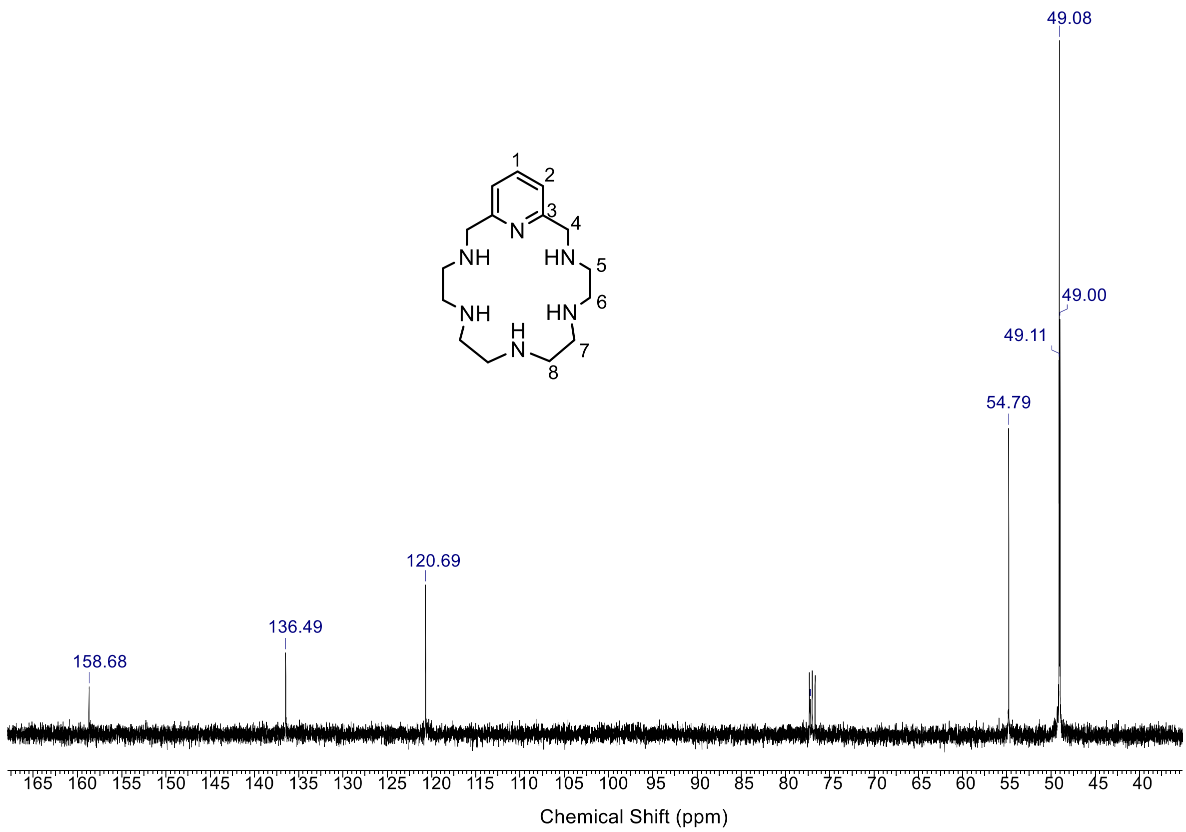
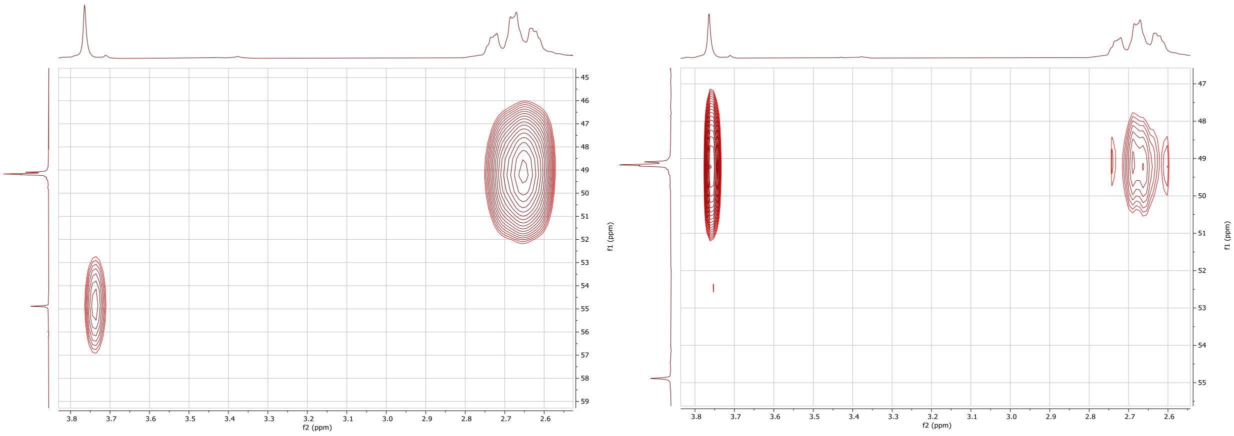


Figure S4: ^{13}C NMR spectrum of **4** in $CDCl_3$.

There are three signals in the ^{13}C NMR spectrum of compound **4** with chemical shifts of 49.00, 49.08, 49.11. The two-dimensional HSQC and HMBC NMR spectra are poorly resolved (fig. S5), making it difficult to relate signals to each other.



HSQC-NMR HMBC-NMR

Figure S5: HSQC-NMR (left) and HMBC-NMR (right) spectrum of **4** in $CDCl_3$ (aliphatic area).

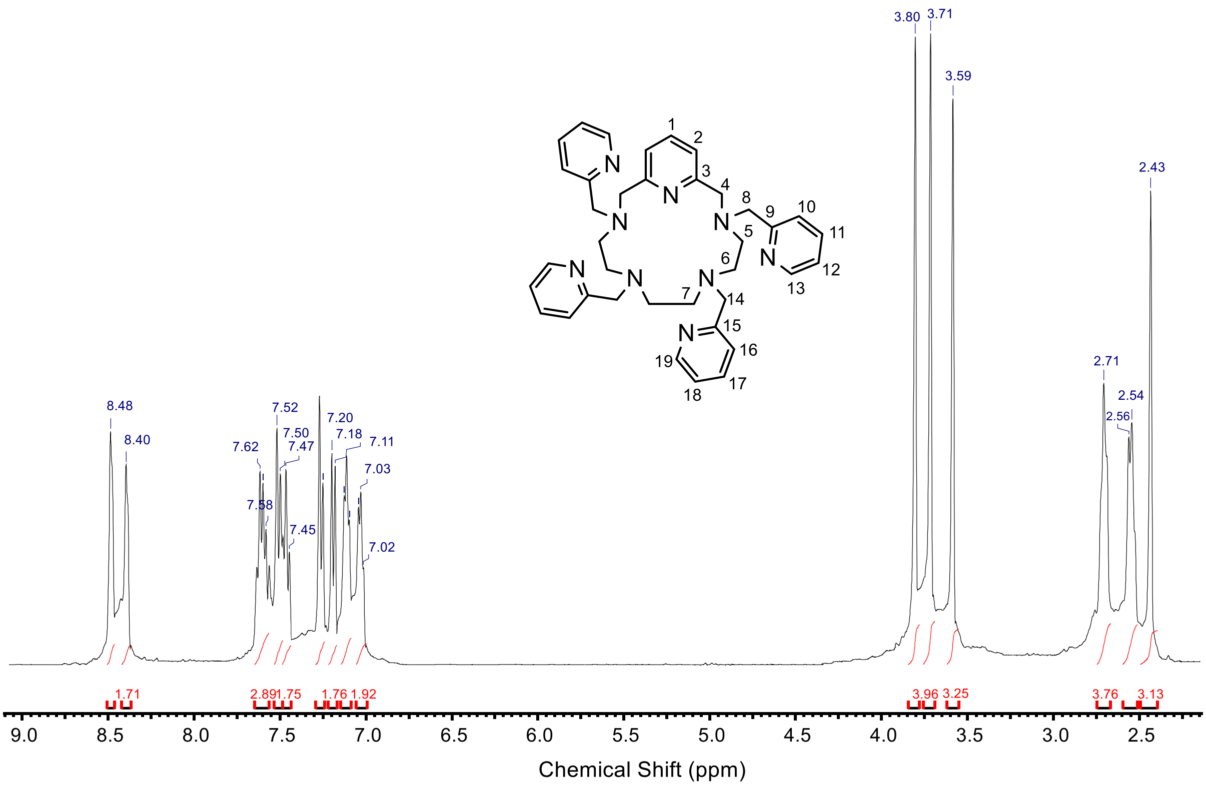


Figure S6: ^{1}H NMR spectrum of **PATPy** in $CDCl_3$.

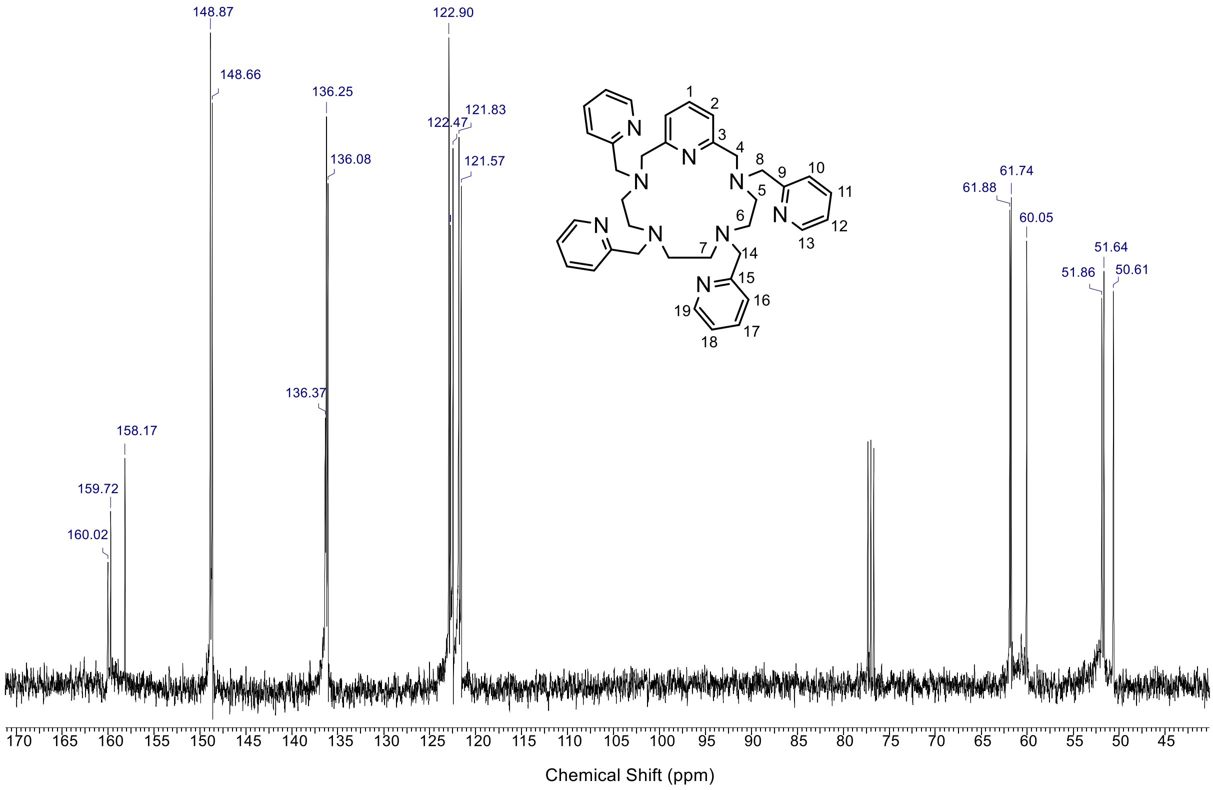


Figure S7: ^{13}C NMR spectrum of **PATPy** in $CDCl_3$.

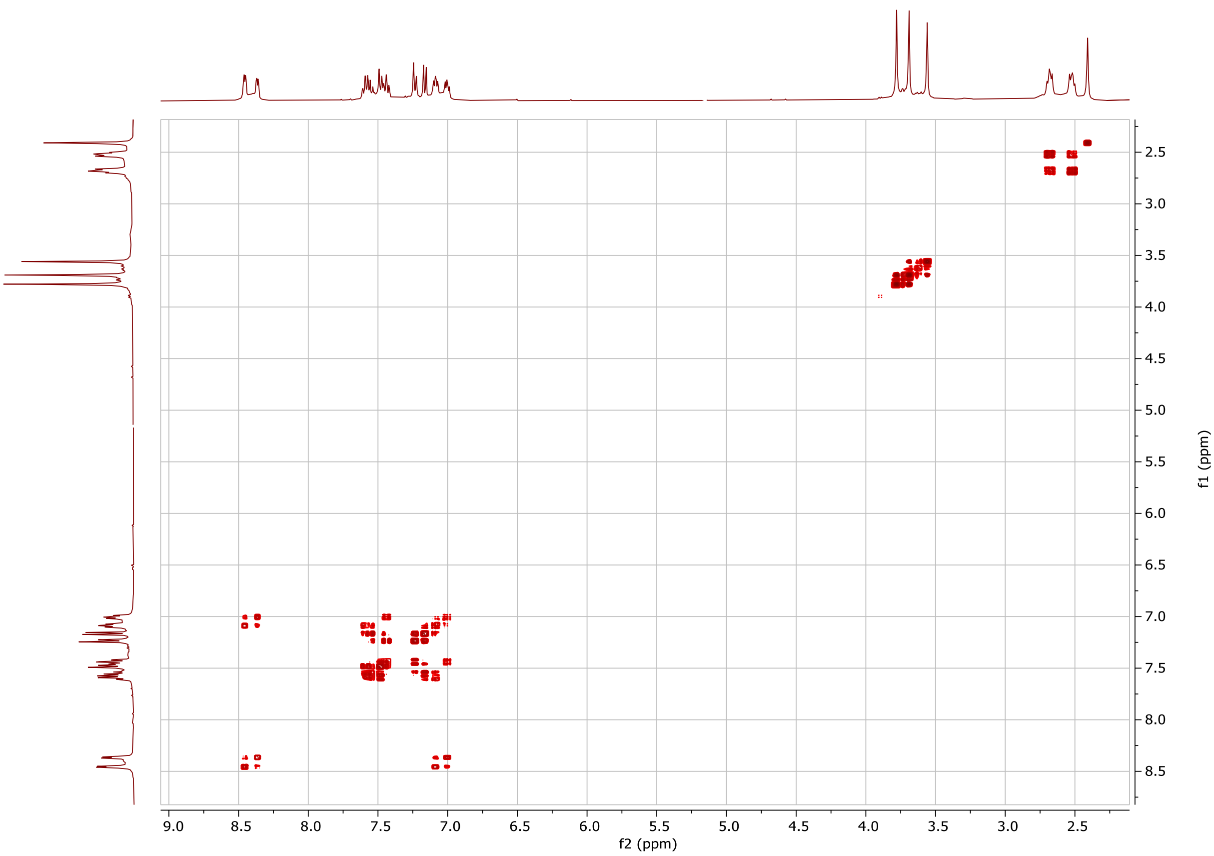


Figure S8: COSY-NMR spectrum of **PATPy** in $CDCl_3$.

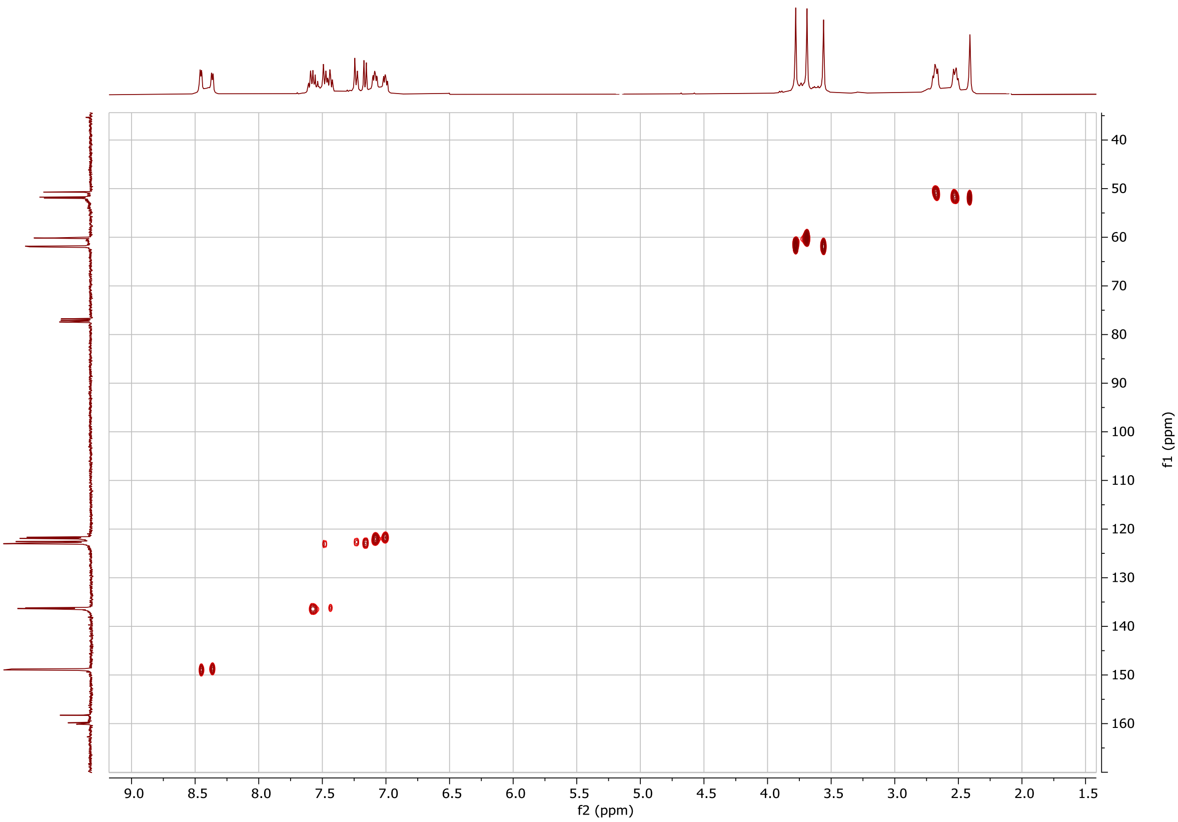


Figure S9: HSQC-NMR spectrum of **PATPy** in $CDCl_3$.

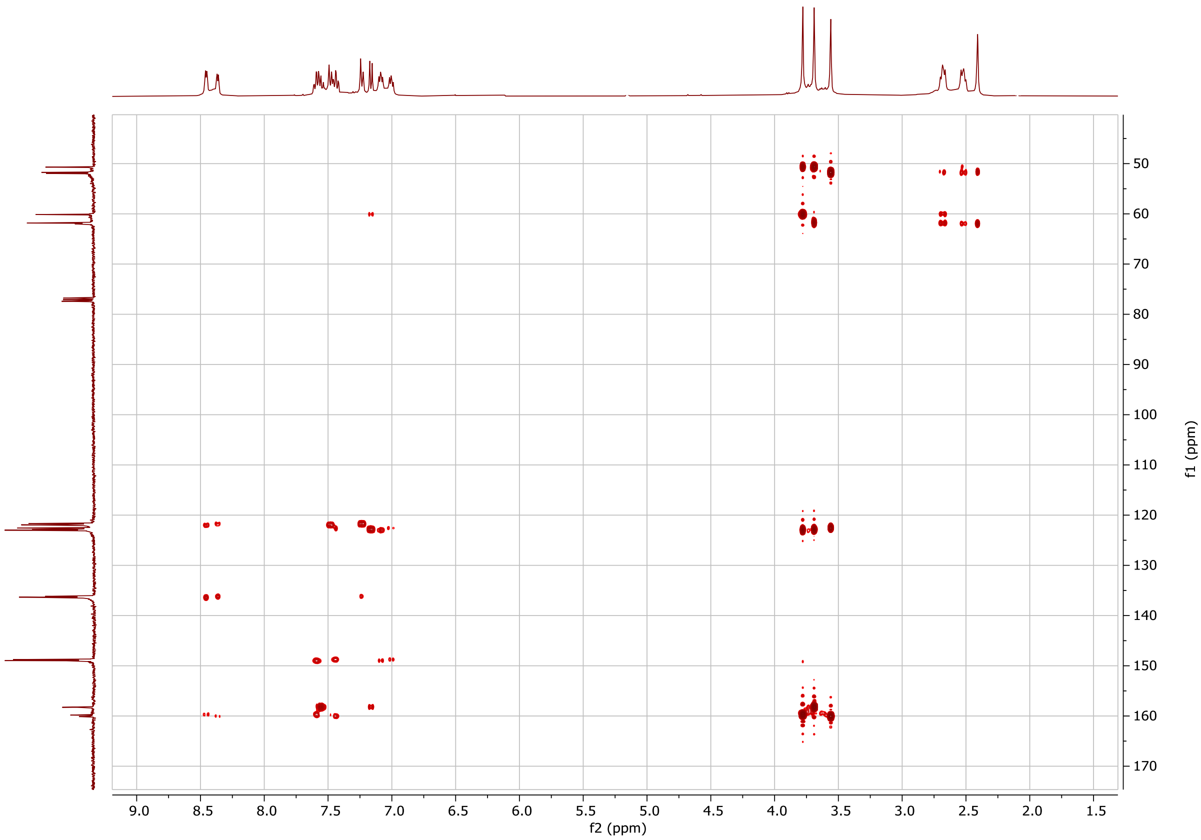


Figure S10: HMBC-NMR spectrum of **PATPy** in $CDCl_3$.

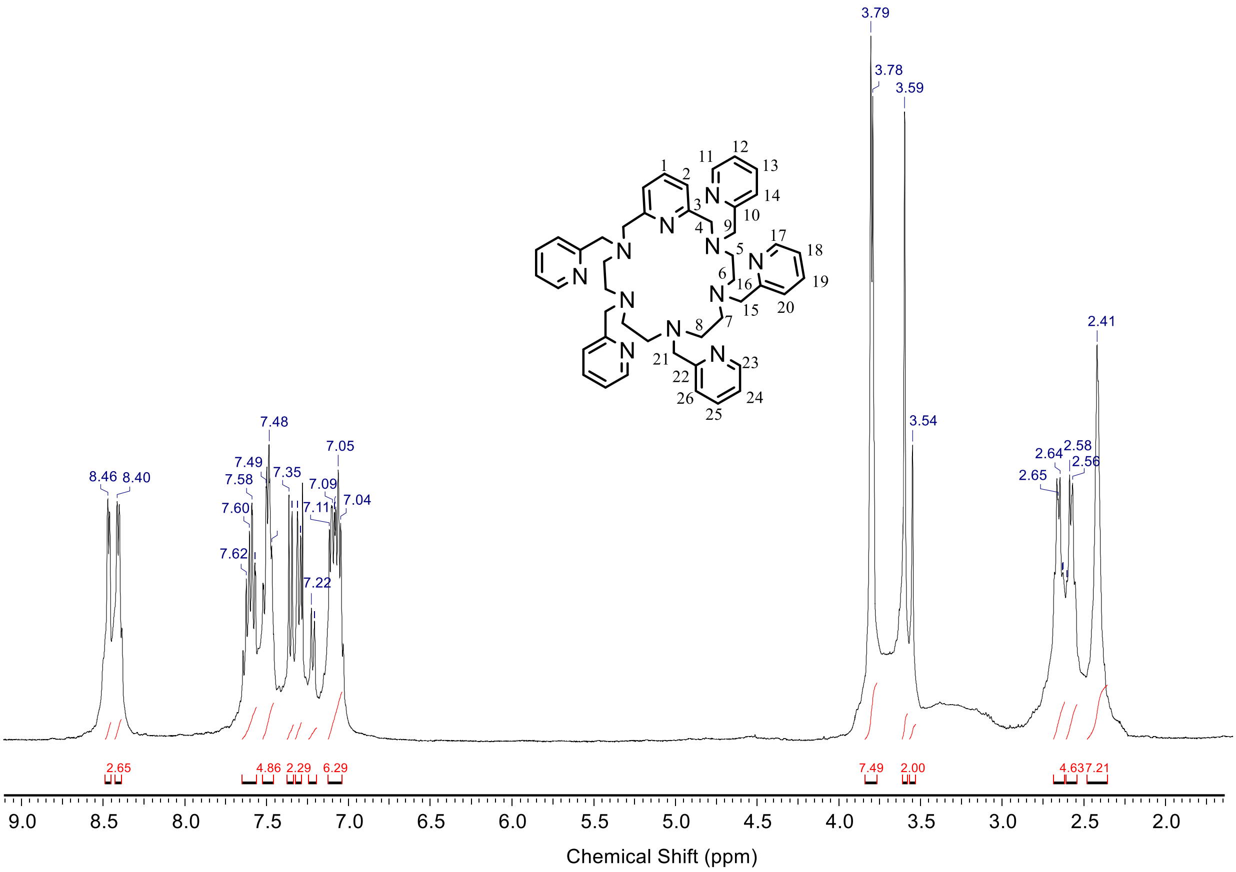


Figure S11: ^{1}H NMR spectrum of **PAPPy** in $CDCl_3$.

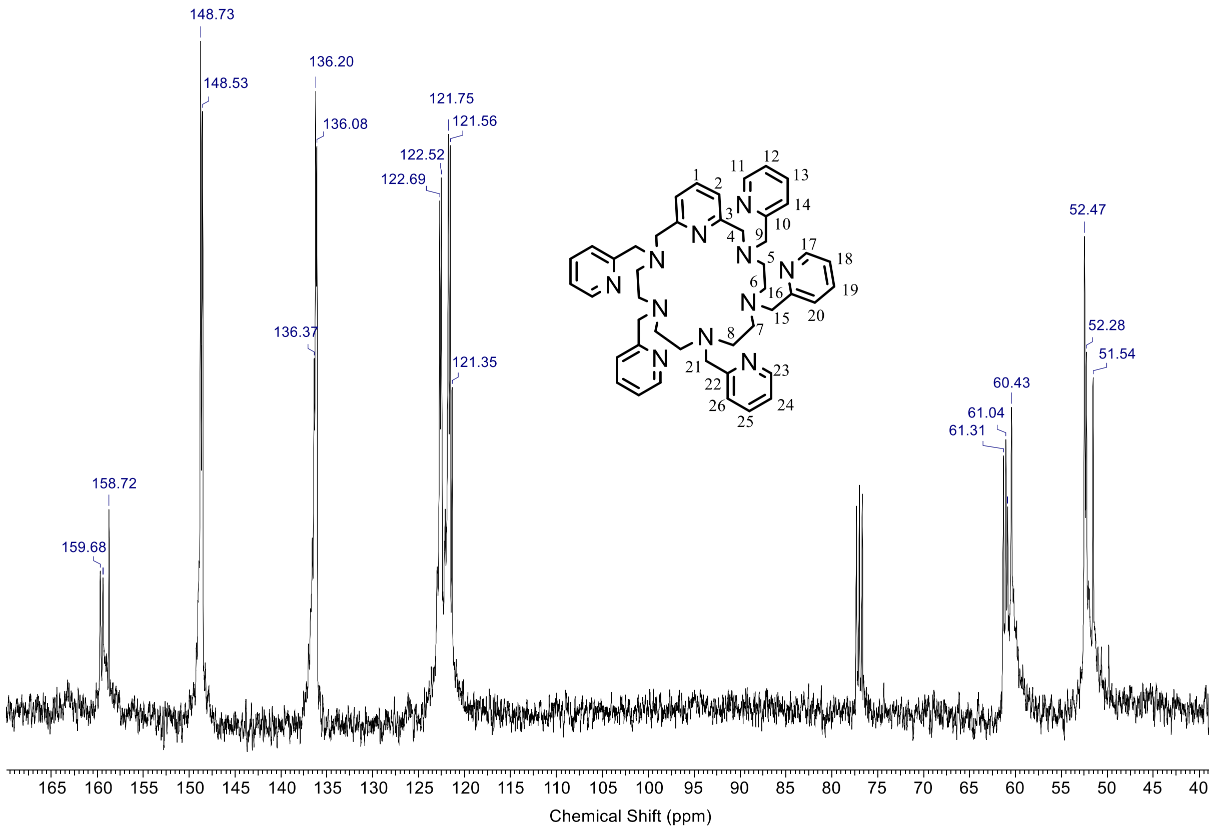


Figure S12: ^{13}C NMR spectrum of **PAPPy** in $CDCl_3$.

Figure S13: COSY-NMR spectrum of **PAPPy** in $CDCl_3$.

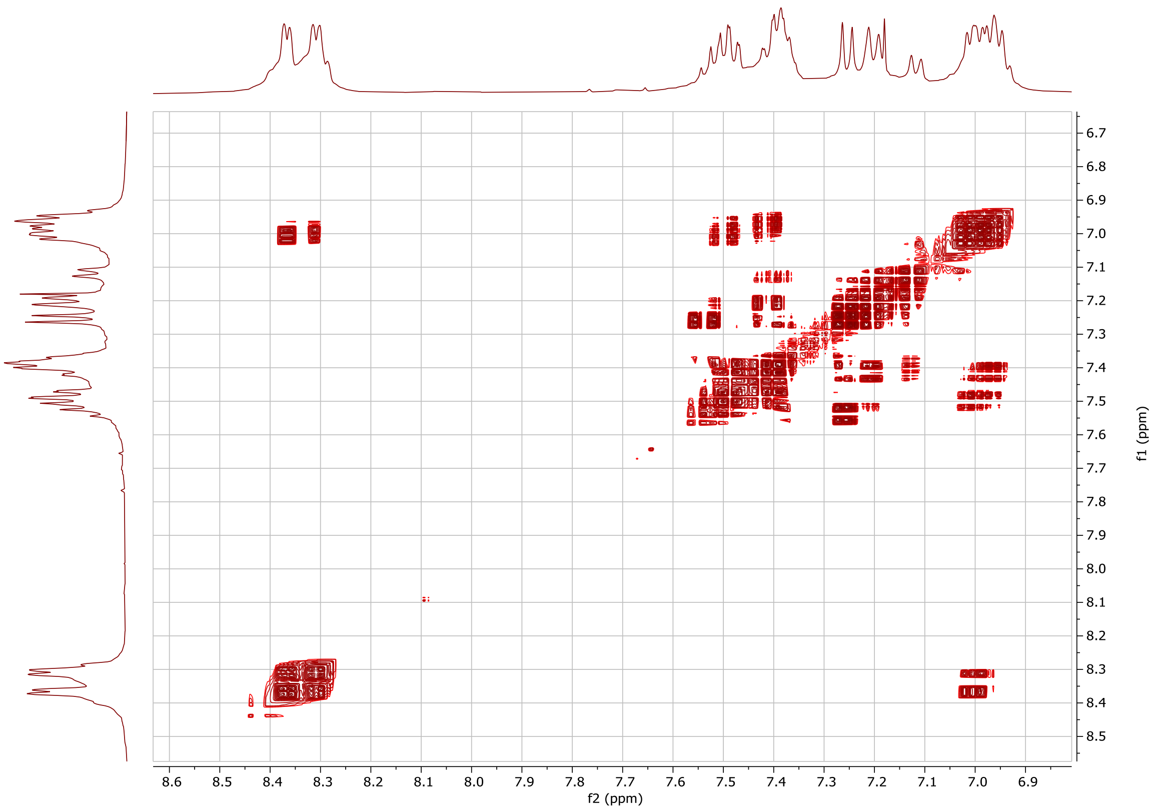


Figure S14: COSY-NMR spectrum of **PAPPy** in $CDCl_3$ (aromatic area).

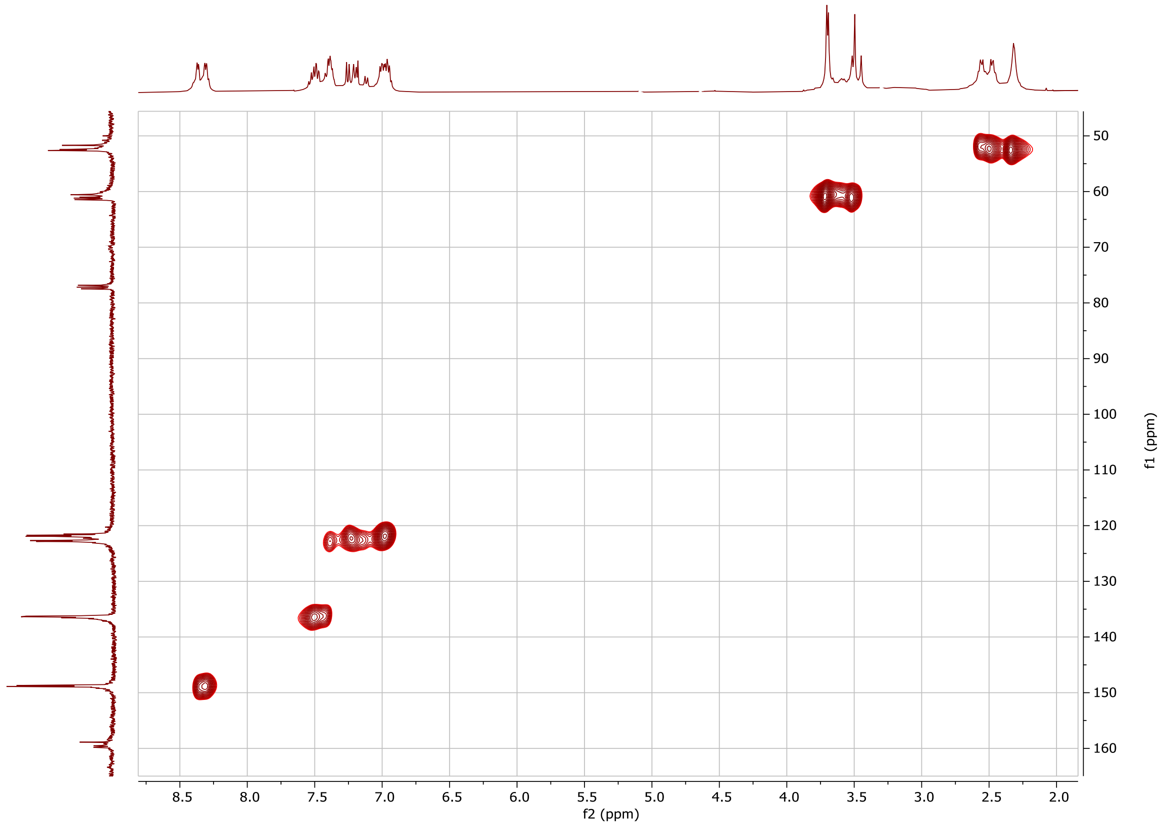


Figure S15: HSQC-NMR spectrum of **PAPPy** in $CDCl_3$.

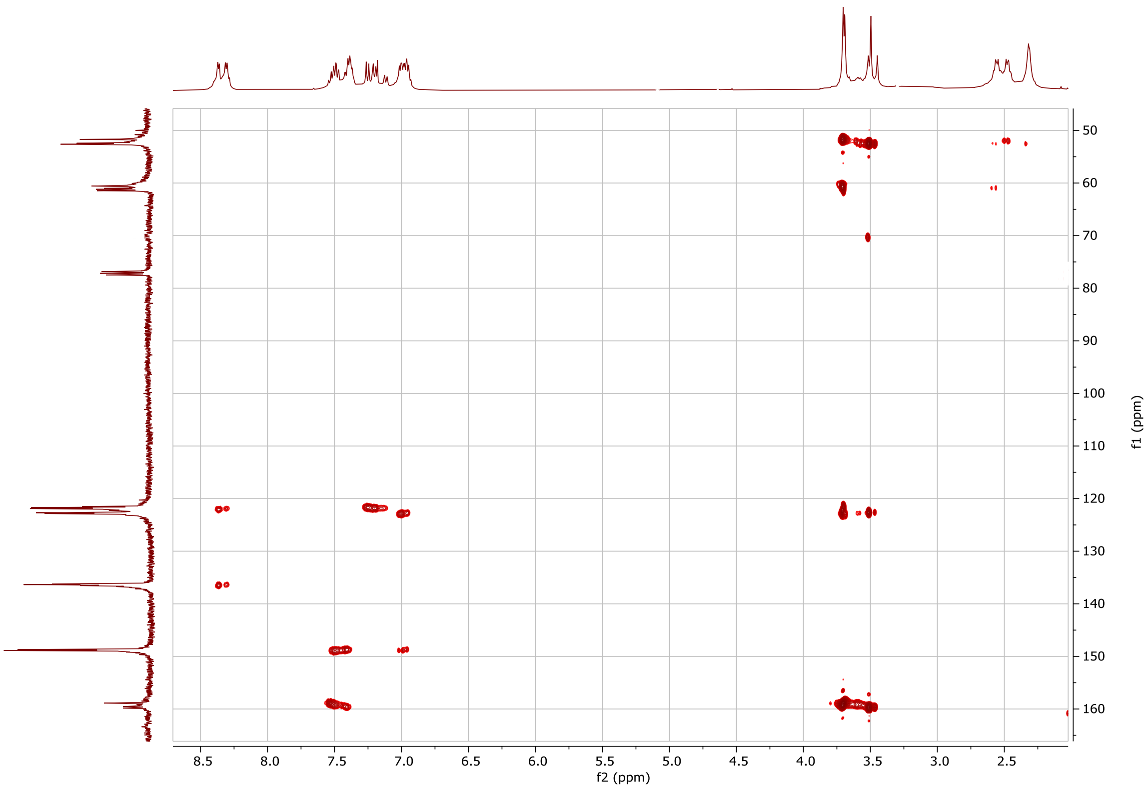


Figure S16: HMBC-NMR spectrum of **PAPPy** in $CDCl_3$.

NMR spectra of complexes

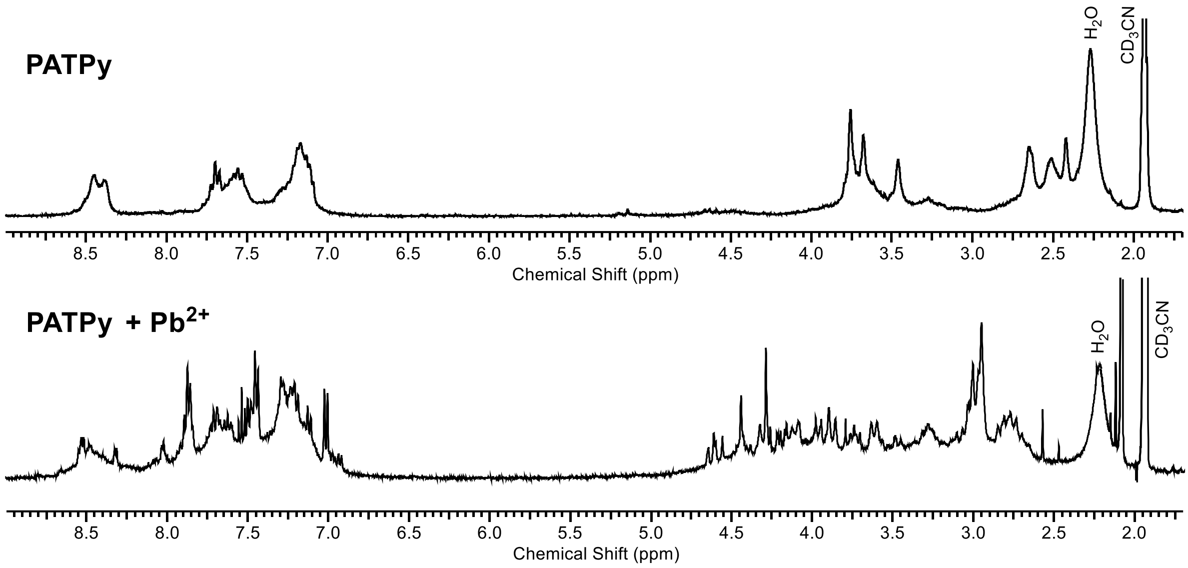


Figure S17: ^{1}H NMR spectra of free ligand **PATPy** and its Pb^{2+} complex in CD_3CN.

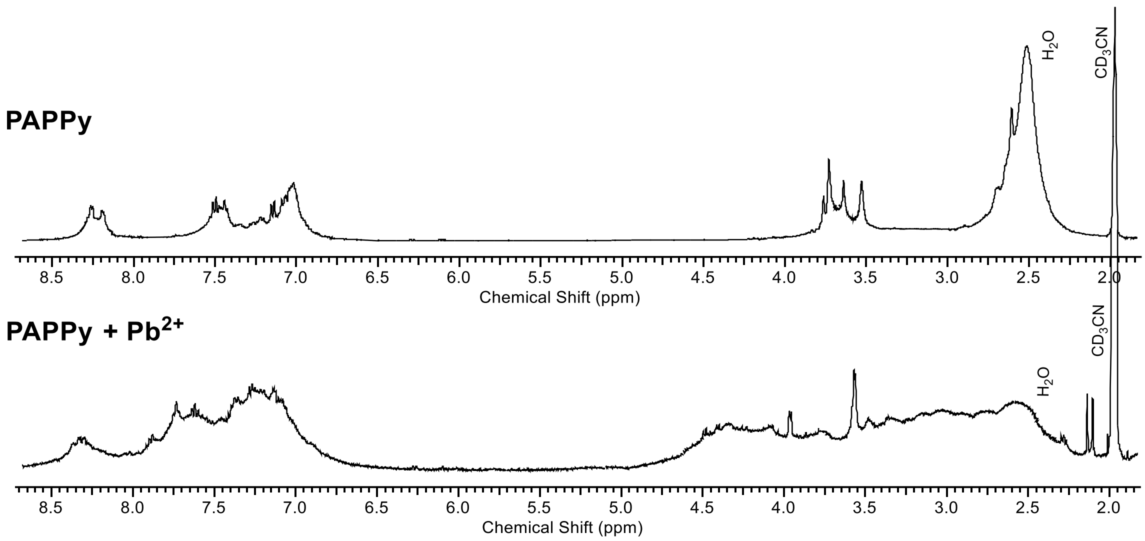


Figure S18: ^{1}H NMR spectra of free ligand **PAPPy** and its Pb^{2+} complex in CD_3CN.

References

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