Electronic Supplementary Information

Effects of subtle differences in ligand constitution and conformation in metallo-supramolecular self-assembled polygons

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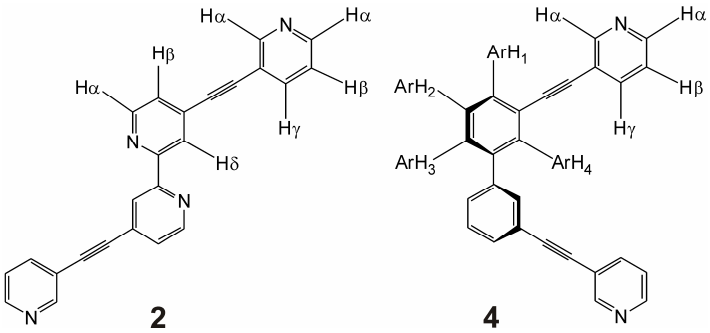
General: All chemicals were of reagent grade quality and used as obtained from commercial suppliers without further purification. Solvents were used as received or - if necessary - dried over 4 Å molecular sieves. Pt(dppp)OTf_2 **5** was prepared as described in the literature.[1] Ligands **2** and **4** were prepared by the established procedure for the ligands **1** and **3**.[2]

Instrumentation and methods: ^{1}H, ^{31}P and $^{1}H,H$ COSY NMR spectra were recorded with Bruker ECX 400, Jeol Eclipse 500 or Bruker Avance 700 MHz instruments at 293 K. All chemical shifts are reported in ppm with solvent signals taken as internal standards; coupling constants are in Hz. The electrospray-ionization Fourier-transform ion-cyclotron-resonance (ESI-FTICR) mass spectrometric experiments were performed with a Varian/IonSpec QFT-7 FTICR mass spectrometer equipped with a superconducting 7 Tesla magnet and a micromass Z-spray ESI ion source utilizing a stainless steel capillary with a 0.65 mm inner diameter. The sample solutions were introduced into the source with a syringe pump (Harvard Apparatus) at a flow rate of ca. 2.0 $\mu L \cdot min^{-1}$. Parameters were adjusted as follows: Source temperature: 40 °C; temperature of desolvation gas: 40 °C; parameters for capillary voltage, sample and extractor cone voltages are optimized for maximum intensities. No nebulizer gas was used for the experiments. The ions were accumulated in the instrument's hexapole for 2 to 5 s. Next, the ions were transferred into the FTICR analyzer cell by a quadrupole ion guide. The FTICR cell was operated at pressures below 10^{-9} mbar, and the ions were detected by a standard excitation and detection sequence. For tandem mass spectrometric experiments, the ions of interest were mass-selected and subsequently vibrationally excited for 1,000 ms with a CO_2 laser in the IR region (infrared multiphoton dissociation (IRMPD); 10.6 μm wavelength) to induce fragmentation. The maximum laser power is 25 W and can be controlled by the

instrument in percentages of 25 W. For each measurement, 10 to 20 scans were averaged to improve the signal-to-noise ratio.

Synthesis and analytical data of ligands 2 and 4



4,4'-bis(pyridin-3-ylethynyl)-2,2'-bipyridine (2): 4,4'-Diethynyl-2,2'-bipyridine[2] (113 mg, 0.55 mmol) and 3-iodopyridine (250 mg, 1.22 mmol) were dissolved under argon atmosphere in 15 ml DMF. After the addition of triethylamine (4 ml), PPh_3 (28.6 mg, 0.11 mmol), CuI (10.4 mg, 0.06 mmol) and $Pd(PPh_3)_2Cl_2$ (38.4 mg, 0.06 mmol), the reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel, mobile phase: CH_2Cl_2/MeOH = 25 : 1, R_f = 0.2) and afterwards recrystallized from MeOH. Yield: 93 mg, 47%. ^{1}H NMR (700 MHz, CD_2Cl_2): δ = 7.26 (ddd, ^3J = 7.8 Hz, ^4J = 4.9 Hz, ^5J = 0.9 Hz, 2H; pyH_β), 7.38 (dd, ^3J = 4.8 Hz, ^4J = 1.4 Hz, 2H; $bipyH_\beta$), 7.81 (dt, ^3J = 7.9 Hz, ^4J = 3.8 Hz, ^4J = 1.9 Hz, 2H; pyH_γ), 8.51 (br s, 4H; $bipyH_\delta$, pyH_α), 8.62 (d, ^3J = 4.8 Hz, 2H; $bipyH_\alpha$), 8.72 (dd, ^3J = 2.0 Hz, ^4J = 0.7 Hz, 2H; pyH_α); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 90.03, 90.44 (C≡C), 123.14, 123.28, 125.54, 138.74, 149.36, 149.44, 152.50 (CH), 119.44, 131.80, 155.68 (Cq); ESI-MS**:** *m/z* = 359.1 ($[M+H]^+$, 100%); HRMS (ESI) calculated mass 359.1291 ($C_{24}H_{14}N_4$ $(M+H)^+$); found 359.1291.

3,3'-Bis(pyridin-3-ylethynyl)biphenyl (4): 3,3'-Diethylnylbiphenyl[2] (30 mg, 0.15 mmol) and 3-iodopyridine (70 mg, 0.34 mmol) were dissolved under argon atmosphere in 2 ml DMF. After the addition of triethylamine (1 ml), PPh_3 (7.8 mg, 0.03 mmol), CuI (4.3 mg, 0.02 mmol) and $Pd(PPh_3)_2Cl_2$ (10.4 mg, 0.01 mmol), the reaction mixture was stirred for 12 h at room temperature. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (silica gel, mobile phase: CH_2Cl_2/MeOH = 90 : 1, R_f = 0.1). Yield: 9.2 mg, 17%. ^{1}H NMR: (500 MHz, CD_2Cl_2): δ = 7.29 (ddd, ^3J = 7.8 Hz, ^4J = 4.9 Hz, ^5J = 0.7 Hz, 2H; pyH_β), 7.47 (t, ^3J = 7.7 Hz, 2H; ArH_2), 7.56 (dt, ^3J = 7.7 Hz, ^4J = 2.6 Hz, ^4J = 1.3 Hz, 2H; ArH_3), 7.61 - 7.64 (m, 2H; ArH_1), 7.80 - 7.85 (m, 4H; ArH_4, pyH_γ), 8.53

(dd, ^3J = 4.8 Hz, ^4J = 1.5 Hz, 2H; pyH$_\alpha$), 8.76 (d, ^3J = 1.3 Hz, 2H; pyH$_\alpha$); ^{13}C NMR (126 MHz, CD_2Cl_2): δ = 86.64, 92.47 (C≡CH), 123.46, 127.90, 129.49, 130.63, 131.18, 138.73, 149.14, 152.56 (CH), 120.55, 123.58, 140.85 (Cq); ESI-MS: *m/z* = 357.1 ([M+H]$^+$, 100%); HRMS (ESI) calculated mass 357.1386 ($C_{26}H_{17}N_2$ (M+H)$^+$); found 357.1388.

General procedure for the preparation of Pt assemblies as their triflate salts: Ligand **1** (0.44 mg, 0.0012 mmol), ligand **2** (0.44 mg, 0.0012 mmol), ligand **3** (0.87 mg, 0.0024 mmol) or ligand **4** (0.87 mg, 0.0024 mmol), separately dissolved in CD_2Cl_2 (0.25 ml), were added to separate suspensions of Pt(dppp)OTf$_2$ **5** (2.00 mg, 0.0024 mmol) in CD_2Cl_2 (0.25 ml) in glass vials. The mixtures were stirred at room temperature and then transferred into NMR tubes for analysis. A sample for ESI-MS analysis was obtained from the NMR samples by diluting with a CH_2Cl_2/acetone mixture.

Analytical data obtained after 24 h: Ligand **1** + metal center **5**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.92 (d, $^3J_{HH}$ = 4.1 Hz; pyH$_\alpha$), 8.44 (br; bipyH$_\delta$), 8.07 (m; H$_{dppp\text{-}phenyl}$), 7.87 (m; bipyH$_\alpha$), 7.75-7.20 (m; H$_{dppp\text{-}phenyl}$ and pyH$_\beta$), 7.06 (d; $^3J_{HH}$ = 6.2 Hz, bipyH$_\beta$), 3.32 (m; H$_{dppp\text{-}alkyl}$), 2.58 (m; H$_{dppp\text{-}alkyl}$), 2.29 (m; H$_{dppp\text{-}alkyl}$) ppm; ^{31}P NMR (202 MHz, CD_2Cl_2): δ = -3.76 (s; P$_{dppp\text{-}bipy}$), -14.78 (s; P$_{dppp\text{-}py}$) ppm; ESI MS **(**ESI$^+$, CH_2Cl_2/acetone): *m/z* = 1114 (ML$^+$), 1297 ($M_4L_2^{3+}$), 2020 ($M_4L_2^{2+}$ and [$(M_4L_2)_2$]$^{4+}$); Ligand **2** + metal center **5**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.53 (d, $^3J_{HH}$ = 1.5 Hz; pyH$_\alpha$), 9.18 (s; pyH$_\alpha$), 9.15 (d, $^3J_{HH}$ = 1.6 Hz; pyH$_\alpha$), 8.88 (s; pyH$_\alpha$), 8.61 (s; bipyH$_\delta$), 8.59 (s; bipyH$_\delta$), 8.32-7.22 (m; pyH$_\beta$, pyH$_\gamma$, bipyH$_\alpha$ and H$_{dppp\text{-}phenyl}$), 6.97 (d, $^3J_{HH}$ = 2.2 Hz; bipyH$_\beta$), 3.36 (m; H$_{dppp\text{-}alkyl}$), 2.53 (m; H$_{dppp\text{-}alkyl}$), 2.31 (m; H$_{dppp\text{-}alkyl}$) ppm; ^{31}P NMR (202 MHz, CD_2Cl_2): δ = -4.58 (s; P$_{dppp\text{-}bipy}$), -14.81 (s; P$_{dppp\text{-}py}$), -15.07 (s; P$_{dppp\text{-}py}$) ppm; ESI MS **(**ESI$^+$, CH_2Cl_2/acetone): *m/z* = 1297 ($M_4L_2^{3+}$), 1478 ($M_6L_3^{4+}$), 1586 ([$(M_4L_2)_2$]$^{5+}$), 2020 ($M_4L_2^{2+}$ and $M_6L_3^{3+}$ and [$(M_4L_2)_2$]$^{4+}$), 2744 ([$(M_4L_2)_2$]$^{3+}$), 3105 ($M_6L_3^{2+}$); Ligand **3** + Metal center **4**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.91 (d, $^3J_{HH}$ = 6.3 Hz; pyH$_\alpha$), 7.80-7.30 (m; H$_{dppp\text{-}phenyl}$ and H$_{biaryl}$), 7.15 (d, $^3J_{HH}$ = 6.7 Hz; pyH$_\beta$), 3.32 (m; H$_{dppp\text{-}alkyl}$), 2.26 (m; H$_{dppp\text{-}alkyl}$) ppm; ^{31}P NMR (202 MHz, CD_2Cl_2): δ = -14.71 (s; P$_{dppp}$) ppm; ESI MS **(**ESI$^+$, CH_2Cl_2/acetone): *m/z* = 1112 ($M_2L_2^{2+}$), 1533 ([$(M_2L_2)_2$]$^{3+}$), 2373 ($M_2L_2^+$ and [$(M_2L_2)_2$]$^{2+}$); Ligand **4** + metal center **5**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 9.43 (d, $^3J_{HH}$ = 1.6 Hz; pyH$_\alpha$), 9.39 (br; pyH$_\alpha$), 8.76 (br; pyH$_\alpha$), 8.59 (s; pyH$_\alpha$), 8.23-7.34 (m; H$_{dppp\text{-}phenyl}$, H$_{biaryl}$ and pyH$_\beta$), 3.27 (m; H$_{dppp\text{-}alkyl}$), 2.33 (m; H$_{dppp\text{-}alkyl}$) ppm; ^{31}P NMR (202 MHz, CD_2Cl_2): δ = -14.99 (s; P$_{dppp\text{-}py}$), -15.51 (s; P$_{dppp\text{-}py}$) ppm; ESI MS **(**ESI$^+$, CH_2Cl_2/acetone): *m/z* = 1112 ($M_2L_2^{2+}$), 1533 ([$(M_2L_2)_2$]$^{3+}$), 1742 ($M_3L_3^{2+}$), 2373 ($M_2L_2^+$ and [$(M_2L_2)_2$]$^{2+}$).

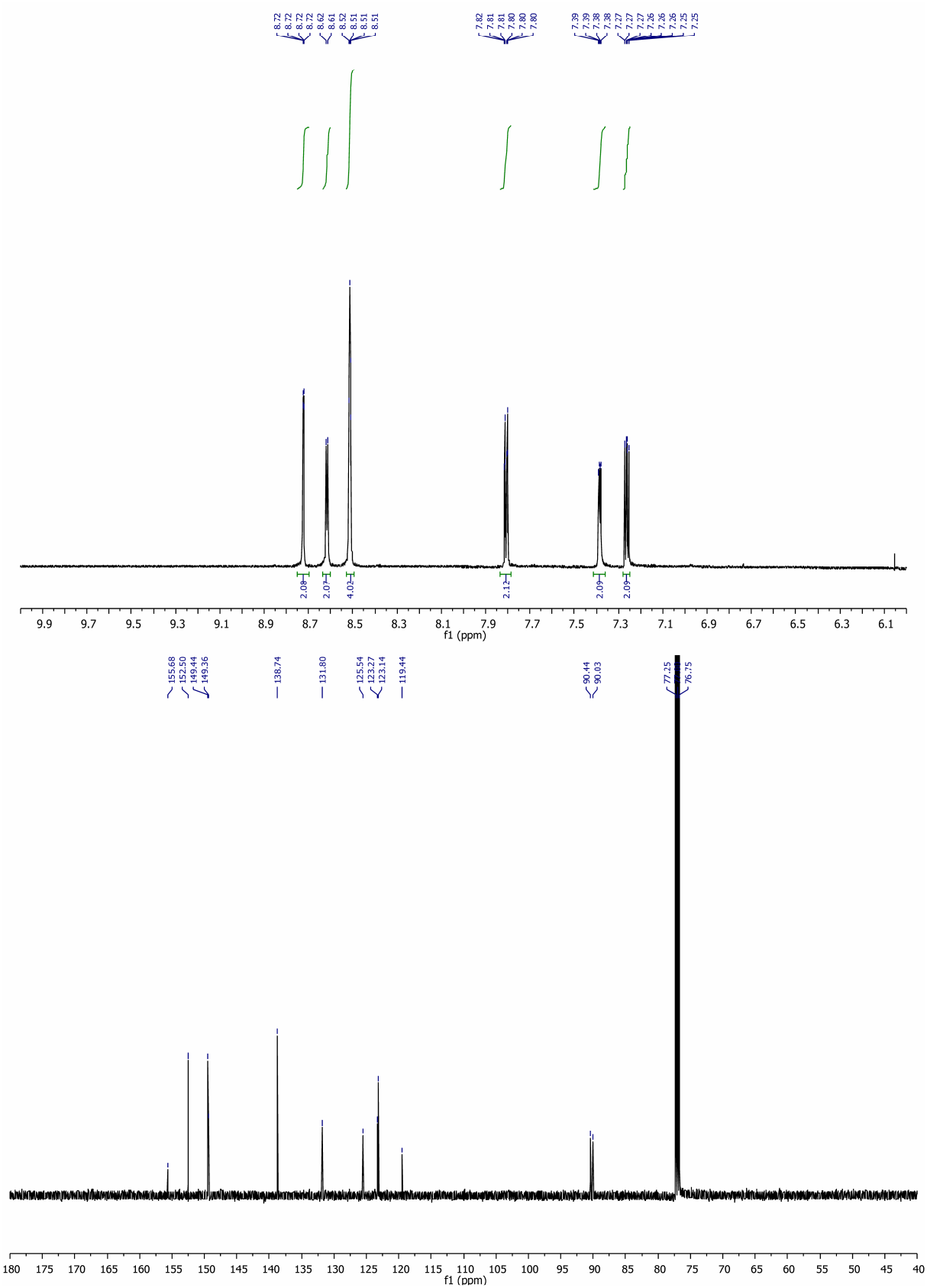


Figure S1. ^{1}H NMR and ^{13}C NMR spectra of ligand **2**.

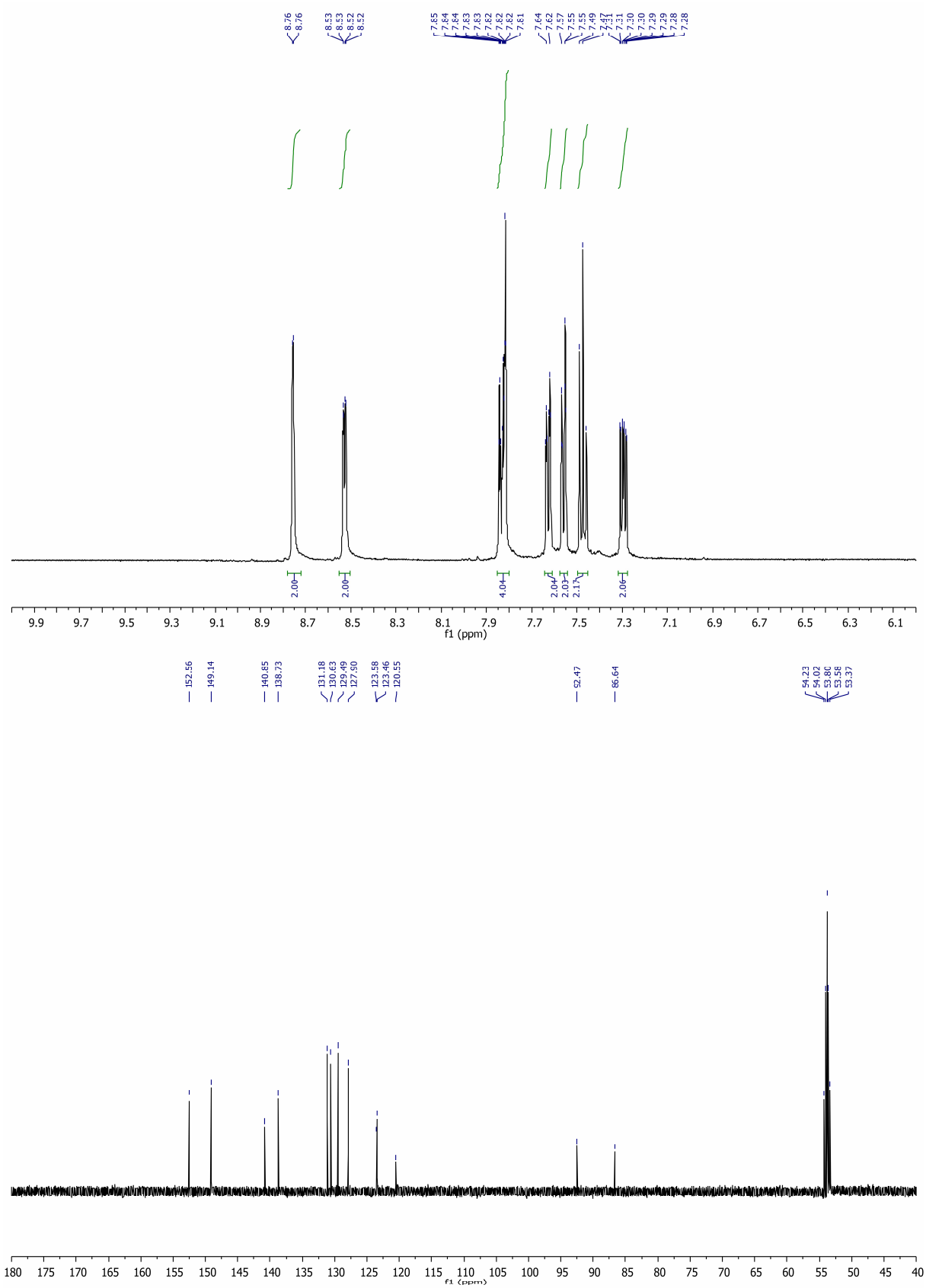


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of ligand **4**.

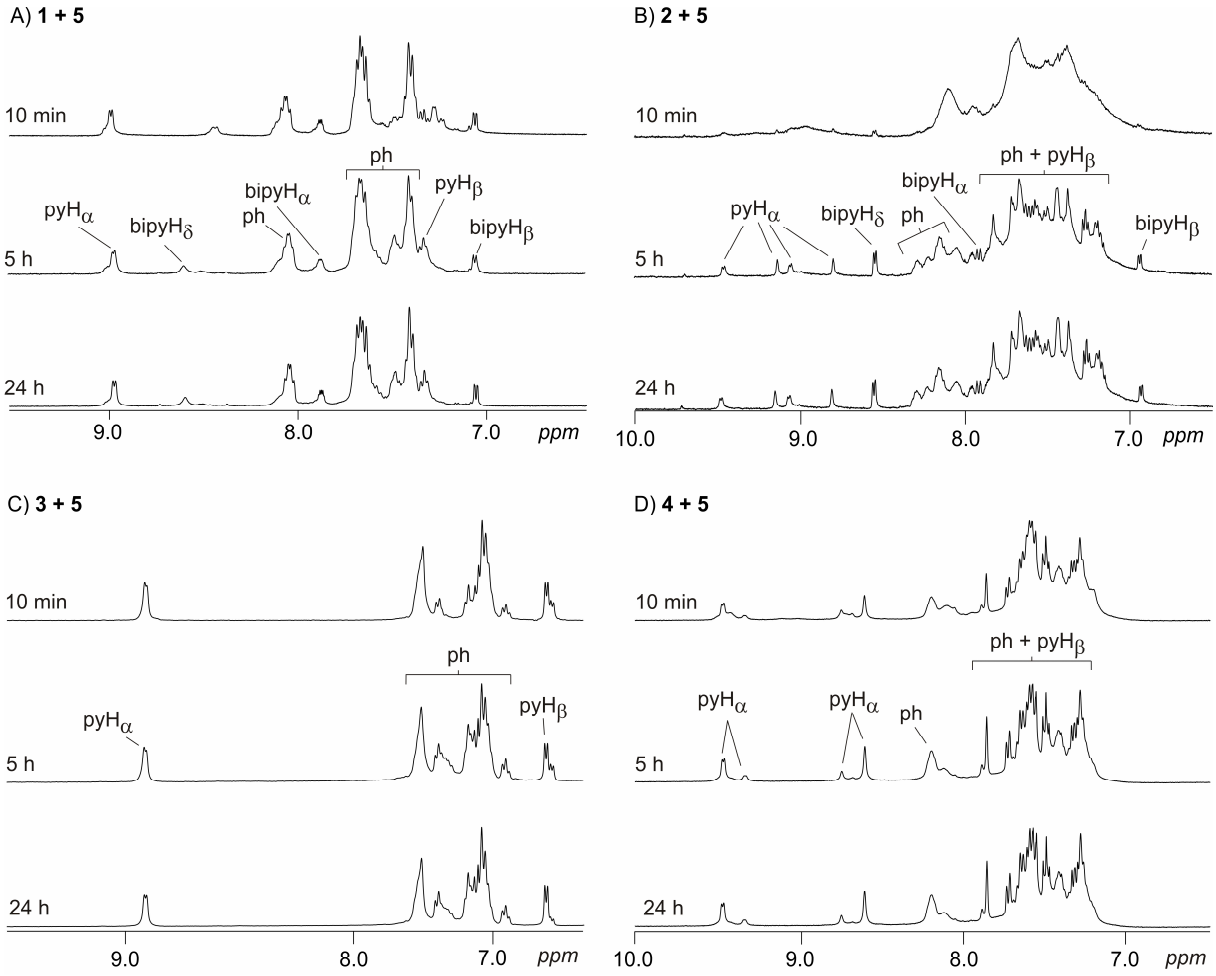


Figure S3. ^{1}H NMR spectra of the aromatic region for the separate mixtures of ligand A) **1**, B) ligand **2**, C) ligand **3** or D) ligand **4** with Pt metal center **5** ([**5**] = 4.9 mM) after 10 min, 5 h and 24 h stirring at room temperature.

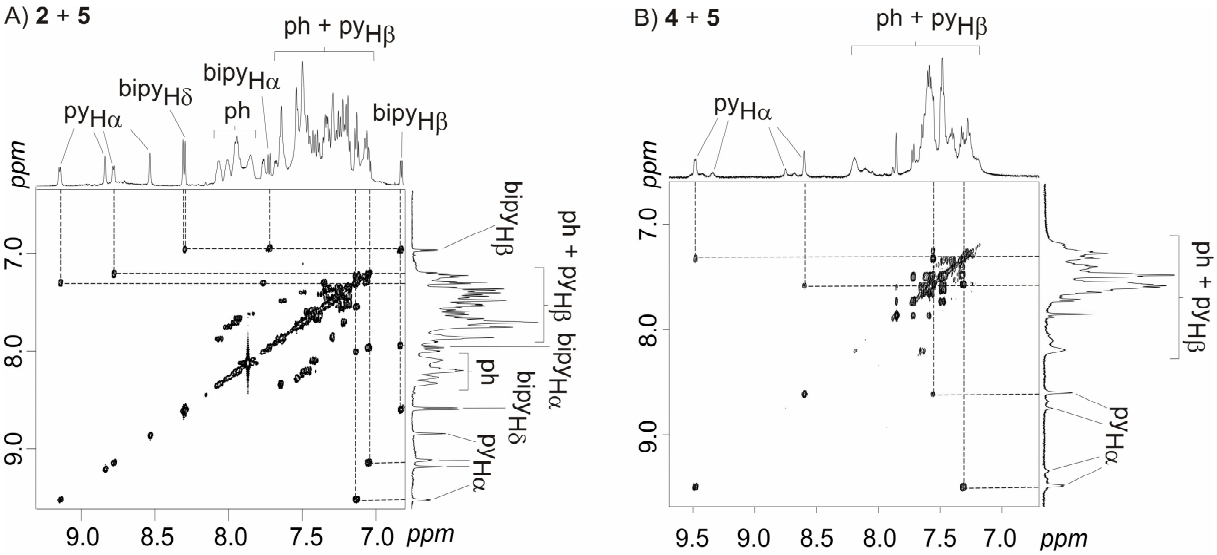


Figure S4. ^{1}H,^{1}H COSY NMR spectra of the aromatic region for the separate mixtures of ligand A) **2** and B) ligand **4** with Pt metal center **5** ([**5**] = 4.9 mM) after 24 h stirring at room temperature.

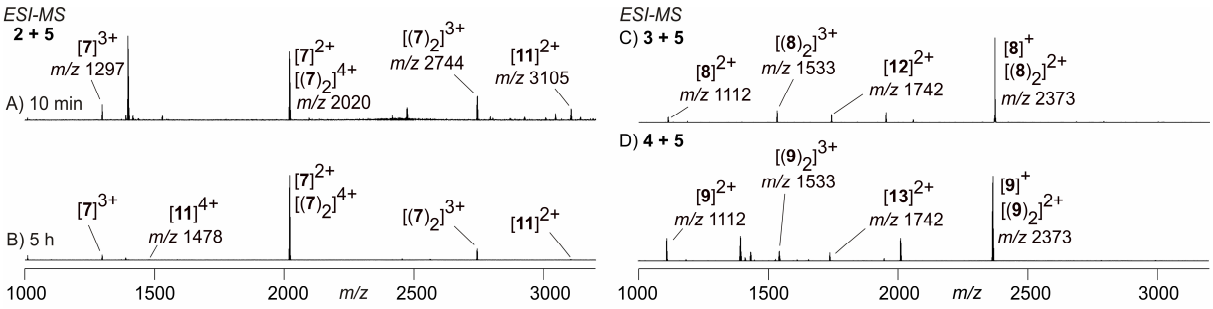


Figure S5. ESI mass spectra of the mixture of ligand **2** with Pt metal center **5** after A) 10 min and B) 24 h stirring at room temperature. Furthermore, the ESI mass spectra of the mixtures of C) ligand **3** and D) ligand **4** with Pt metal center **5** after stirring at room temperature for 10 min is shown.

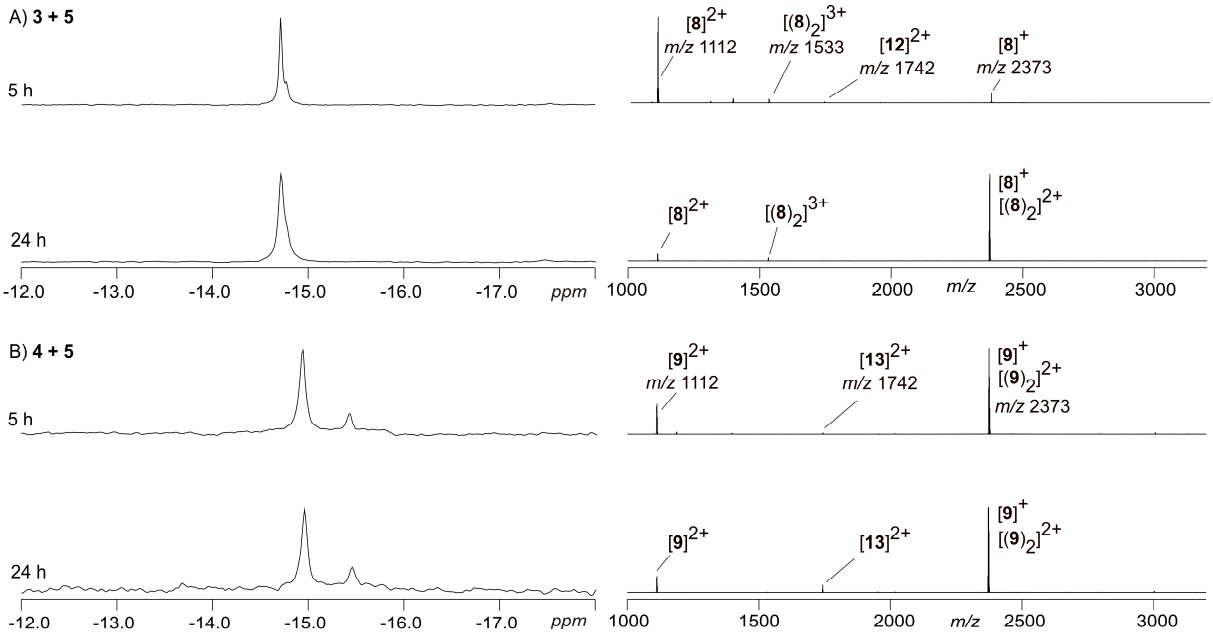


Figure S6. ^{31}P NMR and ESI mass spectra of the mixtures of A) ligand **3** and B) ligand **4** with Pt metal center **5** after 5 h and 24 h.

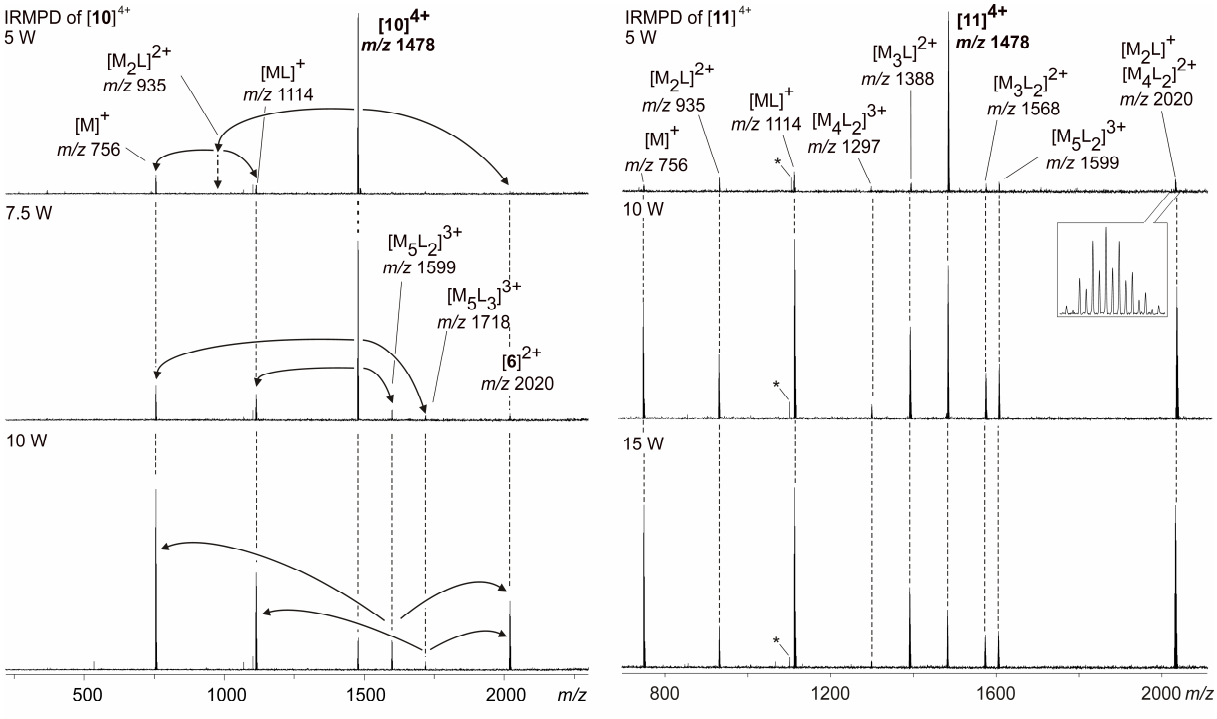


Figure S7. Tandem ESI mass experiments of the [**10**]$^{4+}$ and [**11**]$^{4+}$ ions with different IRMPD laser intensities for 500 ms (* = artefact due to stray radiation).

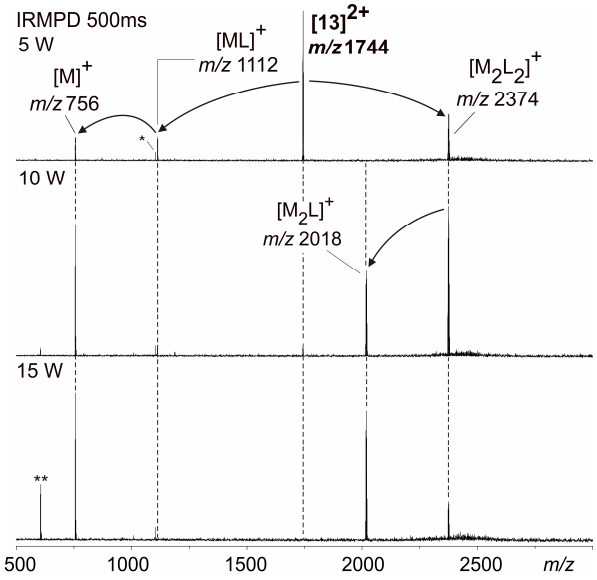


Figure S8. Tandem mass spectra of the [**13**]$^{2+}$ ion with different IRMPD laser intensities for 500 ms.

[1] P. J. Stang, D. H. Cao, *J. Am. Chem. Soc.* **1994**, *116*, 4981- 4982.

[2] B. Brusilowskij, C. A. Schalley, *Eur. J. Org. Chem.* **2011**, 469-477.