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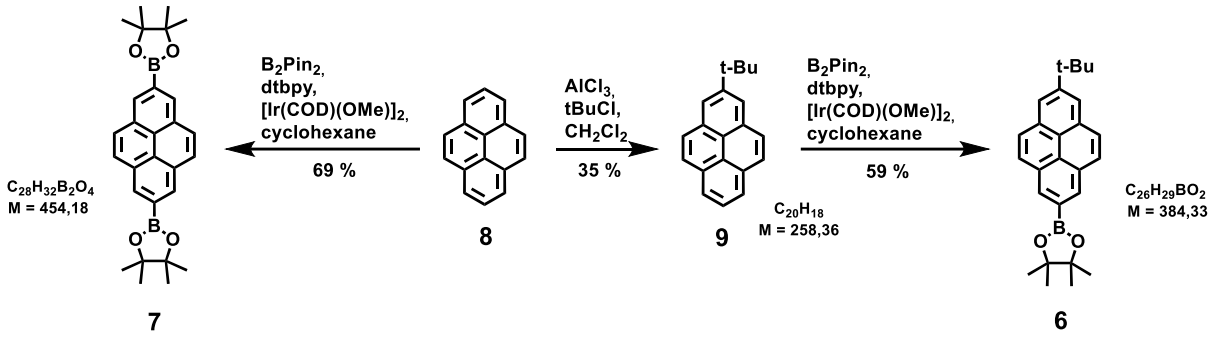
1 General Information

All chemicals were purchased from Sigma-Aldrich and used without any further purification. Solvents were distilled prior to usage. Dichloromethane was neutralized with K_2CO_3 before distillation. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F524, detected by UV-light (254 nm, 366 cnm). Column chromatography and flash column chromatography were performed on Macherey-Nagel silica gel 60 M (deactivated, 230−400 mesh, 0.04−0.063 mm). NMR spectroscopy was performed on Bruker Avance Neo Cryo-Probe DCH (^{1}H: 600 MHz, ^{13}C: 150 MHz), Bruker Avance Neo 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz) and Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C{^{1}H}: 101 MHz). Deuterated solvents were purchased from Sigma-Aldrich and used as received. Chemical shifts are referenced to residual protic impurities in the solvents (^{1}H: $CHCl_3$: 7.24 ppm) and (^{1}H: CH_2Cl_2: 5.32 ppm) or the deuterated solvent itself (^{13}C{^{1}H}: $CDCl_3$: 77.0 ppm) and (^{13}C{^{1}H}: CD_2Cl_2: 53.8 ppm). The resonance multiplicities are indicated as “s” (singlet), “d” (doublet), “t” (triplet), “q” (quartet) and “m” (multiplet). Signals referred to as “bs” (broad singlet) are not clearly resolved or significantly broadened. IR spectra were recorded on a Bruker FT-IR Tensor 27 spectrometer with a Pike MIRacle ATR unit. LDI/MALDI-ToF mass spectrometry was performed on a Bruker Ultraflex Extreme machine. In case of MALDI, the following matrix were used: 2,5-dihydroxybenzoic acid (DHB or *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyl-idene]malononitrile (DCTB). High resolution mass spectrometry was performed on an ESI/APPI-ToF mass spectrometer Bruker maXis 4G UHR MS/MS spectrometer, a Bruker micrOTOF II focus TOF MSspectrometer, or on a MALDI-ToF Bruker Ultraflex Extreme spectrometer. Microwave reactions were carried out in a monomode microwave reactor Biotage Initiator+ with an external IR surface temperature sensor. The microwave assisted reactions were carried out exclusively in the fixed hold time mode using an external IR temperature sensor. UV/vis spectroscopy was carried out on a Varian Cary 5000 UV−vis−NIR spectrometer.

2 Synthetic Procedures

2.1 Synthesis of Pyrene-Precursors



Scheme S1. Synthesis of borylated pyrene precursors **6** and **7**.

2-*tert*-butylpyrene 9

Adapting a procedure from Bédard *et al.*[1], pyrene **8** (5.00 g, 24.5 mmol, 1.0 equiv) was dissolved in CH_2Cl_2 in a 100 mL flask. The solution was cooled to 0 °C with an ice bath, and *tert*-butyl chloride (3.50 mL, 31.0 mmol, 1.3 equiv) was added. $AlCl_3$ (3.60 g, 27.0 mmol, 1.1 equiv) was added slowly in small portions, and the reddish, viscous, mixture was stirred for 3 h under slow warming to rt. The reaction was subsequently quenched by pouring the mixture into a beaker filled with ice water (200 mL). CH_2Cl_2 (100 mL) was added, and the phases separated. The aqueous phase was extracted with CH_2Cl_2 (3 x 100 mL), and the combined organic layers were washed with brine. After drying over Na_2SO_4, the solvent was removed, and the residue was recrystallized from hot MeOH. The precipitate was filtered off, the solvent removed under reduced pressure, and the crude recrystallized from hot hexanes. **9** was obtained as amber-colored, crystalline, plates in 35% yield (2.21 g, 8.56 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 8.22 (s, 2H), 8.14 (d, *J* = 7.6 Hz, 2H), 8.06 - 8.03 (m, 4H), 7.98 - 7.94 (m, 1H), 1.59 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 149.03, 131.00, 130.99, 127.60, 127.28, 125.52, 124.76, 124.64, 122.94, 122.24, 77.36, 77.04, 76.73, 35.27, 31.99.

HRMS (APPI, CH_2Cl_2) for $C_{20}H_{18}$ (M^+), calcd.: 258.1403, found: 258.1407.

2-(7-(*tert*-butyl)pyren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 6

Adapting a procedure from Bédard *et al.*[1], 2-*tert*-butylpyrene **8** (250 mg, 0.970 mmol, 1 equiv), B_2Pin_2 (270 mg, 1.06 mmol, 1.1 equiv) and dtbpy (26.0 mg, 97.0 µmol, 0.1 equiv) were added into a dry 25 mL Schlenk flask. Dry cyclohexane (3 mL) and $[Ir(COD)(OMe)]_2$ (32.0 mg, 51.0 µmol, 0.05 equiv) were added and the mixture heated to 80 °C for 20 h. The solvent was removed under reduced pressure and the crude purified by filtration through silica (SiO_2, hexanes/CH_2Cl_2 1:1 → CH_2Cl_2, Ø 3 cm x 12 cm). **6** was obtained as a colorless crystalline solid in 59% yield (220 mg, 0.57 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 8.58 (s, 2H), 8.19 (s, 2H), 8.03 (q, *J* = 8.9 Hz, 4H), 1.56 (s, 9H), 1.44 (s, 12H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 149.59, 131.48, 131.16, 130.25, 127.66, 127.45, 126.35, 122.85, 122.12, 84.12, 77.34, 77.03, 76.71, 35.30, 31.95, 25.09, 25.03.

HRMS (APPI, CH_2Cl_2) for $C_{26}H_{30}BO_2$ (MH^+), calcd.: 385.2333, found: 385.2348.

2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene 7

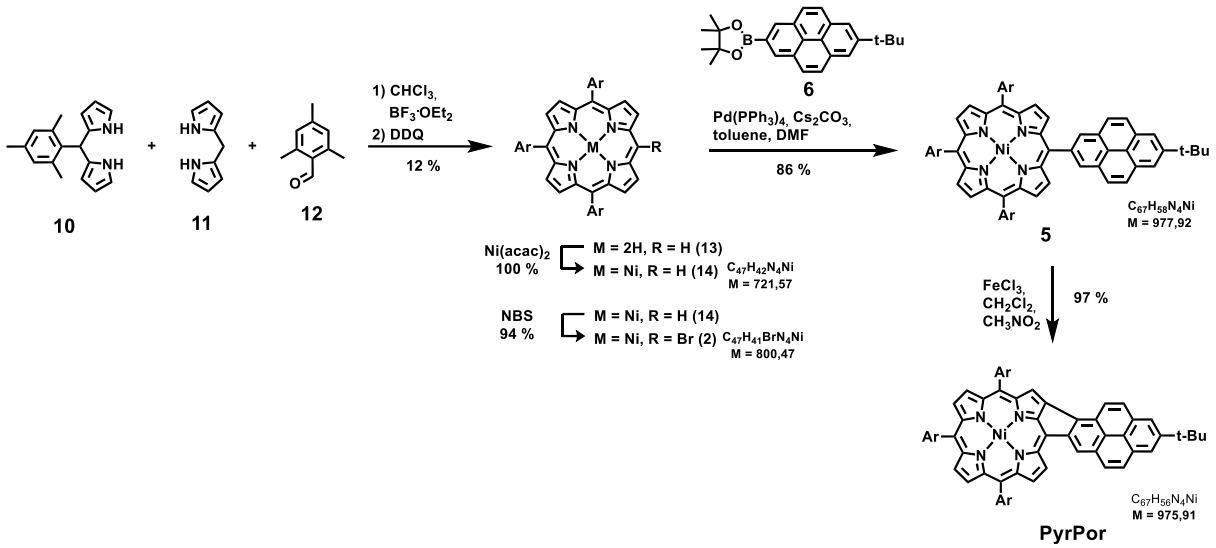
Adapting a procedure from Coventry *et al.*[2], pyrene **8** (789 mg, 3.90 mmol, 1 equiv), B_2Pin_2 (2.18 g, 8.60 mmol, 2.2 equiv) and dtbpy (105 mg, 0.4 mmol, 0.1 equiv) were added into a dry 50 mL Schlenk flask. Dry cyclohexane (15 mL) and $[Ir(COD)(OMe)]_2$ (129 mg, 0.195 mmol, 0.05 equiv) were added, and the mixture was heated to 80 °C for 20 h. The solvent was removed under reduced pressure, and the crude was purified by filtration through silica (SiO_2, CH_2Cl_2, Ø 3 cm x 12 cm). **7** was obtained after recrystallization from CH_2Cl_2/MeOH as a colorless crystalline solid in 69% yield (1.22 g, 2.69 mmol).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 8.60 (s, 4H), 8.06 (s, 4H), 1.44 (s, 24H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 131.21, 130.90, 127.65, 126.33, 84.19, 77.34, 77.02, 76.71, 25.02.

HRMS (APPI, CH_2Cl_2) for $C_{28}H_{33}B_2O_4$ (MH^+), calcd.: 455.2559, found:455.2582.

2.2 Synthesis of Fused Mono-Pyrene-Porphyrin



Scheme S2. Synthesis of fused Pyrene-Porphyrin **PyrPor**. Ar = mesityl.

Nickel-5,10,15-Trimesitylporphyrin 14

Ethanol (2 mL) stabilized $CHCl_3$ (775 mL) was degassed for 20 min (bubbling N_2 through the solution). dipyrromethane **11** (284 mg, 1.94 mmol, 0.5 equiv), mesitaldehyde **12** (572 µL, 3.88 mmol, 1 equiv) and mesityl-dipyrromethane **10** (513 mg, 1.94 mmol, 0.5 equiv) were added to the solution and the reaction was stirred for 5 min at rt. $BF_3{\cdot}OEt_2$ (316 µL, 2.57 mmol, 0.33 equiv) was added and the solution was stirred for 1 h at rt under the exclusion of light. DDQ (1.32 g, 5.81 mmol, 0.75 equiv) was added and the mixture was stirred for further 45 min. The acid was quenched via the addition of NEt_3 (3.60 mL, 25.7 mmol, 3.3 equiv) and the solvent was removed. The crude was purified by column chromatography (SiO_2, hexanes/CH_2Cl_2, 3:1, Ø 8 x 40 cm). The first isolated fraction contained both A_4-porphyrin and the target A_3B porphyrin which were subsequently separated by a second column (SiO_2, hexanes/toluene, 3:1, Ø 8 x 40 cm, 2nd band). The product was obtained as a purple solid. Free base porphyrin **13** (125 mg, 188 µmol, 1 equiv.) and $Ni(acac)_2$ (241 mg, 940 µmol, 5 equiv.) were dissolved in toluene (30 mL) and heated to reflux (heat-on temperature: 140 °C) for 5 h. The solvent was removed under reduced pressure, the product poured over a plug (SiO_2, CH_2Cl_2, Ø 3 x 6 cm) and afterwards recrystallized from CH_2Cl_2/MeOH yielding 12% of nickel-porphyrin **14** (136 mg, 188 µmol).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 9.79 (s, 1H), 9.07 (d, *J* = 4.8 Hz, 2H), 8.69 (d, *J* = 4.7 Hz, 2H), 8.57 (s, 4H), 7.22 (m, 6H), 2.56 (m, 9H), 1.79 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 142.93, 142.74, 142.59, 142.37, 139.11, 139.08, 137.88, 137.63, 137.59, 137.52, 137.44, 132.17, 131.24, 131.21, 131.15, 129.04, 128.23, 127.72, 127.69, 125.30, 117.32, 116.81, 104.26, 21.48, 21.39.

UV/Vis (CH_2Cl_2): *λ* [nm] (*ε* [$M^{-1}cm^{-1}$]): 407 (247000), 521 (18000), 553 (5000).

MS (MALDI, DCTB): m/z (rel. Int.): 720 (M^+, 100%).

HRMS (MALDI, CH_2Cl_2) for $C_{47}H_{42}N_4Ni$ (M^+) calcd.: 720.2757, found: 720.2775.

TLC: R_f [%]: 0.75 (hexanes/CH_2Cl_2 - 2:1).

Nickel-(5-Bromo)-10,15,20-Trimesitylporphyrin 2

To a solution of $CHCl_3$ (11 mL), pyridine (250 µL) and porphyrin **14** (130 mg, 180 µmol, 1 equiv) *N*-bromosuccinimide (32.0 mg, 180 µmol, 1 equiv) in $CHCl_3$ (3 mL) was added slowly at rt. The mixture was stirred for 15 min at rt before the reaction was quenched with acetone (3 mL). The solvents were removed under reduced pressure, and the crude was purified by silica plug filtration (hexanes/CH_2Cl_2 - 2:1, Ø 3 x 12 cm). The product **2** was obtained as a dark-orange solid in 94% yield (135 mg, 169 µmol).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 9.46 (d, *J* = 5.0 Hz, 2H), 8.60 (d, *J* = 5.0 Hz, 2H), 8.48 (s, 4H), 7.19 - 7.17 (m, 6H), 2.55 (m, 9H), 1.79 (m, 18H).

^{13}C NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 143.04, 143.00, 142.76, 142.43, 139.00, 138.95, 137.80, 137.75, 136.94, 133.20, 132.03, 131.84, 131.80, 127.77, 117.71, 117.54, 101.91, 21.46, 21.37.

UV/Vis (CH_2Cl_2): *λ* [nm] (*ε* [$M^{-1}cm^{-1}$]): 415 (225000), 530 (17000).

HRMS (MALDI, CH_2Cl_2) for $C_{47}H_{41}BrN_4Ni$ (M^+) calcd.: 798.1863, found: 798.1853.

TLC: R_f [%]: 0.80 (hexanes/CH_2Cl_2 - 2:1).

Nickel-Pyrene-Porphyrin 5

Nickel-(5-bromo)-10,15,20-trimesitylporphyrin **2** (50.0 mg, 62.5 µmol, 1 equiv), 2-(7-(*tert*-butyl)pyren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (25.3 mg, 65.5 µmol, 1.05 equiv), Cs_2CO_3 (60.5 mg, 188 µmol, 3 equiv) and $Pd(PPh_3)_4$ (14.5 mg, 12.5 µmol, 0.2 equiv) were dissolved in toluene (5 mL) and DMF (2.5 mL) and were degassed. The reaction was heated with an oil bath to 80 °C for 20 h. The solvent was removed, and the crude was purified by silica plug filtration (SiO_2, hexanes/CH_2Cl_2 - 1:1, Ø 3 cm x 8 cm). After recrystallization from CH_2Cl_2/MeOH the product **5** was obtained as a red crystalline solid in 86% yield (52.0 mg, 54.0 µmol).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 8.82 (s, 2H), 8.60 (d, *J* = 4.9 Hz, 2H), 8.55 - 8.53 (m, 6H), 8.34 (s, 2H), 8.26 - 8.14 (m, 4H), 7.22 - 7.15 (m, 6H), 2.56 - 2.52 (m, 9), 1.83 - 1.82 (m, 18H), 1.64 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 148.40, 142.28, 141.66, 141.59, 141.53, 138.06, 138.03, 137.55, 136.58, 136.57, 136.37, 136.34, 131.50, 130.35, 130.20, 129.89, 128.99, 128.29, 127.56, 126.70, 126.67, 126.40, 122.97, 121.94, 121.62, 117.57, 116.27, 115.93, 34.34, 30.99, 20.49, 20.38, 20.36.

UV/Vis (CH_2Cl_2): *λ* [nm] (*ε* [$M^{-1}cm^{-1}$]): 417 (260000), 527 (20000).

HRMS (MALDI, CH_2Cl_2) for $C_{67}H_{58}N_4Ni$ (M^+) calcd.: 976.4009, found: 976.3996.

TLC: R_f [%]: 0.75 (hexanes/CH_2Cl_2 - 3:1).

Fused-Nickel-Pyrene-Porphyrin PyrPor

A 20 mL vial was filled with a solution of nickel-pyrene-porphyrin **5** (20.0 mg, 20.5 µmol, 1 equiv) in CH_2Cl_2 (10 mL) and cooled with an ice bath. The solution was degassed (bubbling N_2 through the solution for 15 min). The N_2 flow through the solution was increased, and a solution of dry $FeCl_3$ (53.1 mg, 327 µmol, 16 equiv) in CH_3NO_2 (0.2 mL) was added. The N_2 bubbling through the solution was stopped 15 min after $FeCl_3$ was added and the solution was stirred under slow warming to rt for 1 h. MeOH (10 mL) was added to quench the reaction. After adding NEt_3 (1 mL), the solvent was removed, and the crude was purified by a silica plug (hexanes/ CH_2Cl_2 -

1:1, Ø 3 x 10 cm). The product was obtained as a dark-brown solid in 97% yield (19.5 mg, 19.9 µmol).

^{1}H NMR (601 MHz, CD_2Cl_2, rt): δ [ppm]: 9.29 (d, *J* = 4.8 Hz, 1H), 8.66 (s, 1H), 8.49 (d, *J* = 4.8 Hz, 1H), 8.14 – 8.05 (m, 5H), 8.06 – 8.02 (m, 2H), 7.99 - 7.98 (m, 1H), 7.93 - 7.91 (m, 2H), 7.88 – 7.87 (m, 1H), 7.25 (s, 2H), 7.22 (s, 2H), 7.18 (s, 2H), 2.59 (s, 3H), 2.56 (s, 3H), 2.52 (s, 3H), 1.99 (s, 6H), 1.86 (s, 12H), 1.55 (s, 9H)

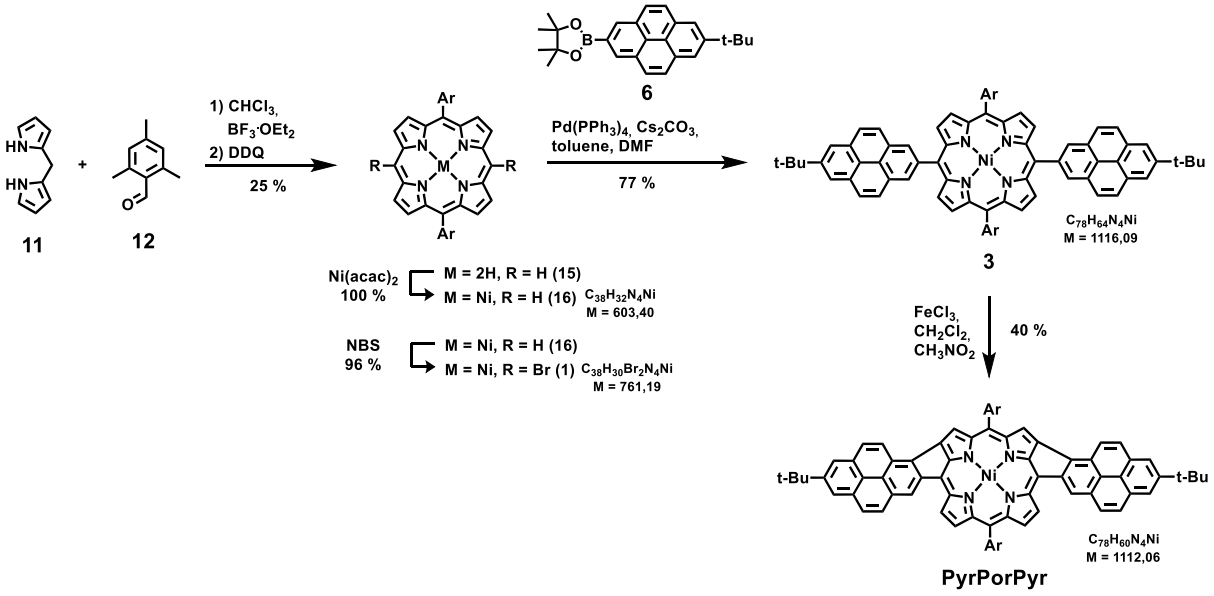
^{13}C NMR (151 MHz, CD_2Cl_2, rt): δ [ppm]: 156.32, 149.93, 147.66, 147.60, 146.88, 146.23, 145.23, 144.81, 144.07, 143.98, 142.03, 139.14, 139.00, 138.93, 138.32, 138.19, 138.16, 137.40, 137.10, 136.07, 134.14, 133.08, 132.58, 132.28, 132.11, 131.73, 131.10, 130.37, 130.09, 129.42, 128.24, 128.18, 128.15, 128.13, 128.10, 127.74, 127.09, 126.32, 124.83, 124.60, 123.83, 123.57, 122.26, 122.09, 121.73, 121.46, 118.40, 112.78, 31.80, 21.52, 21.46, 21.42, 21.36, 21.24.

UV/Vis (CH_2Cl_2): *λ* [nm] (*ε* [$M^{-1}cm^{-1}$]): 401 (58000), 473 (82000), 500 (84000), 586 (10000).

HRMS (MALDI, CH_2Cl_2) for $C_{67}H_{56}N_4Ni$ (M^+) calcd.: 974.3853, found: 974.3840.

TLC: R_f [%]: 0.50 (hexanes/CH_2Cl_2 - 4:1).

2.3 Synthesis of Double-Fused Bis-Pyrene-Porphyrin



Scheme S3. Synthesis of double-fused Bis-Pyrene-Porphyrin **PyrPorPyr**.

5,15-Dimesitylporphyrin 15

5,15-dimesitylporphyrin was synthesized adapting a procedure from Chen *et al.*.[3] Ethanol (4.5 mL) stabilized $CHCl_3$ (600 mL) was degassed for 15 min (bubbling N_2 through the solution). Dipyrromethane **11** (890 mg, 6.00 mmol, 1 equiv) and mesitaldehyde **12** (885 µL, 6.00 mmol, 1 equiv) were added to the solution, and the reaction was degassed for another 10 min. $BF_3{\cdot}OEt_2$ (500 µL) was added, and the solution was stirred for 3 h at rt under the exclusion of light. DDQ (2.04 g, 9.00 mmol, 3 equiv) was added, and the mixture was stirred for a further 30 min. The acid was quenched via the addition of NEt_3 (8 mL), and the solvent was removed under reduced pressure. The crude was purified by filtration through silica (SiO_2, hexanes/CH_2Cl_2, 1:1, Ø 13 x 8 cm). The product **15** was obtained as a purple crystalline solid in 25% yield (407 mg, 744 µmol).

^{1}H NMR (400 MHz, CD_2Cl_2, rt): δ [ppm]: 10.25 (s, 2H), 9.37 (d, *J* = 4.6 Hz, 4H), 8.86 (d, *J* = 4.6 Hz, 4H), 7.35 (s, 4H), 2.66 (s, 6H), 1.84 (s, 12H), -3.13 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 139.34, 138.00, 137.47, 131.85, 129.92, 127.80, 117.31, 104.45, 21.36, 21.19.

HRMS (MALDI, DCTB) for $C_{38}H_{34}N_4(M^+)$, calcd.: 546.2778, found: 546.2793.

Nickel-5,15-Dimesitylporphyrin 16

5,15-Dimesitylporphyrin **15** (350 mg, 640 µmol, 1 equiv) and $Ni(acac)_2$ (822 mg, 3.20 mmol, 5 equiv) were dissolved in toluene (60 mL). The mixture was heated to reflux for 7 h (heat-on temperature: 140 °C). The solvent was removed under reduced pressure, and the crude was purified by silica plug filtration (SiO_2, CH_2Cl_2, Ø 3.5 cm x 12 cm). After removal of the solvent, the residue was dissolved in CH_2Cl_2 (10 mL), and the product precipitated with MeOH (50 mL). The precipitate was filtered off and dried *in vacuo*. The product **16** was obtained as a red-brown solid in 100% yield (386 mg, 640 µmol).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 9.88 (s, 2H), 9.13 (d, *J* = 4.7 Hz, 4H), 8.76 (d, *J* = 4.7 Hz, 4H), 2.60 (s, 6H), 1.78 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 13 141.71, 141.65, 138.06, 136.68, 136.32, 131.31, 130.21, 126.74, 115.69, 103.70, 20.40, 20.33.

HRMS (MALDI, DCTB) for $C_{38}H_{32}N_4Ni$ (M^+), calcd.: 602.1975, found: 602.1961.

Nickel-5,15-Dibromo-10,20-Dimesitylporphyrin 1

To a solution of $CHCl_3$ (50 mL), pyridine (1.8 mL) and porphyrin **16** (372 mg, 616 µmol, 1 equiv) *N*-bromosuccinimide (219 mg, 1.23 mmol, 1 equiv) in $CHCl_3$ (9 mL) was added slowly at rt. The mixture was stirred for 15 min at rt before the reaction was quenched with acetone (3 mL). The solvents were removed under reduced pressure, and the crude was purified by silica plug filtration (CH_2Cl_2, Ø 3 x 12 cm). The product was obtained as a dark-orange solid in 96% yield (450 mg, 591 µmol).

^1H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 9.41 (d, *J* = 5.0 Hz, 4H), 8.56 (d, *J* = 5.0 Hz, 4H), 7.20 (s, 4H), 2.56 (s, 6H), 1.78 (s, 12H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 143.19, 142.91, 138.91, 138.07, 136.41, 133.86, 132.70, 127.88, 21.41, 21.31.

HRMS (MALDI, DCTB) for $C_{38}H_{30}N_4Br_2Ni$ (M^+), calcd.: 758.0185, found: 758.0190.

Nickel-Bis-Pyrene-Porphyrin 3

Nickel-5,15-dibromo-10,20-dimesitylporphyrin **1** (80.0 mg, 105 µmol, 1 equiv), 2-(7-(*tert*-butyl)pyren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **7** (85.0 mg, 221 µmol, 2.1 equiv), Cs_2CO_3 (103 mg, 316 µmol, 3 equiv) and $Pd(PPh_3)_4$ (49.0 mg, 42.0 µmol, 0.4 equiv) were dissolved in toluene (8 mL) and DMF (4 mL) and were degassed. The reaction was heated with an oil bath to 80 °C for 20 h. The solvent was removed, and the crude product separated from inorganics by silica plug filtration (SiO_2, hexanes/CH_2Cl_2 - 1:1, Ø 3 cm x 8 cm). Further purification was achieved by size exclusion chromatography (Biobeads SX1, toluene, Ø 5 cm x 130 cm) After recrystallization from CH_2Cl_2/MeOH the product was obtained as a red crystalline solid in 77% yield (90.0 mg, 81.0 µmol).

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ [ppm]: 8.85 (s, 4H), 8.64 (d, *J* = 5.0 Hz, 4H), 8.58 (d, *J* = 4.9 Hz, 4H), 8.34 (s, 4H), 8.25 - 8.18 (m, 8H), 7.17 (s, 4H), 2.52 (s, 6H), 1.83 (s, 12H), 1.64 (s, 18H).

^{13}C NMR (101 MHz, $CDCl_3$, rt): δ [ppm]: 149.48, 143.41, 142.71, 139.02, 138.47, 137.68, 137.33, 132.82, 131.25, 131.17, 130.07, 129.36, 128.65, 127.75, 127.44, 124.05, 122.98, 122.70, 118.82, 117.73, 35.39, 32.04, 21.41, 21.39.

UV/Vis (CH_2Cl_2): *λ* [nm] (*ε* [$M^{-1}cm^{-1}$]): 422 (300000), 529 (25000).

HRMS (MALDI, CH_2Cl_2) for $C_{78}H_{64}N_4Ni$ (M^+) calc.: 1114.4479, found: 1114.4473.

TLC: R_f [%]: 0.30 (hexanes/CH_2Cl_2 - 4:1).

Double-Fused Nickel-Bis-Pyrene-Porphyrin PyrPorPyr

A 20 mL vial was filled with a solution of nickel-bis-pyrene-porphyrin **3** (20.0 mg, 17.9 µmol, 1 equiv) in CH_2Cl_2 (10 mL) and cooled with an ice bath. The solution was degassed (bubbling N_2 through the solution for 15 min). The N_2 flow through the solution was increased, and a solution of dry $FeCl_3$ (46.5 mg, 287 µmol, 16 equiv.) in CH_3NO_2 (0.2 mL) was added. The N_2 bubbling through the solution was stopped 15 min after $FeCl_3$ was added and the solution was stirred under slow warming to rt for 1 h. MeOH (10 mL) was added to quench the reaction. After adding NEt_3 (1 mL), the solvent was removed, and the crude was separated from inorganics by a silica plug (hexanes/ CH_2Cl_2 - 1:1, Ø 3 x 10 cm). Further purification was achieved by column chromatography (hexanes/ CH_2Cl_2 - 4:1, Ø 7 x 40 cm). The product was obtained as a dark-purple solid in 40% yield (7.96 mg, 7.16 µmol).

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 80 °C): δ [ppm]: 8.93 (d, *J* = 5.0 Hz, 2H), 8.50 (s, 2H), 8.10 (d, *J* = 4.9 Hz, 2H), 8.02 - 7.81 (m, 13H), 7.55 (s, 2H), 7.24 (s, 2H), 7.17 (s, 2H), 2.62 (s, 3H), 2.54 (s, 3H), 2.16 (s, 6H), 1.89 (s, 6H), 1.53 (s, 18H).

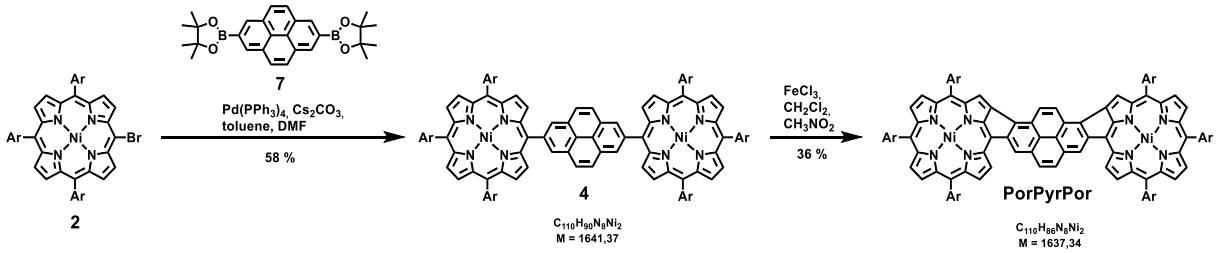
^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 80 °C): δ [ppm]: 139.05, 138.83, 138.24, 138.09, 137.03, 134.71, 134.28, 129.99, 128.34, 128.19, 128.07, 127.79, 127.79, 125.57, 124.83, 124.56, 124.52, 123.71, 123.25, 122.02, 121.70, 120.62, 74.54, 74.46, 32.00, 21.76, 21.71, 21.63, 21.40, 14.27.

UV/Vis (CH_2Cl_2): λ [nm] (ε [$M^{-1}cm^{-1}$]): 300 (29000), 415 (47000), 522 (62000), 600 (150000).

HRMS (MALDI, CH_2Cl_2) for $C_{78}H_{60}N_4Ni$ (M^+) calcd.: 1110.4166, found:1110.4194.

TLC: R_f [%]: 0.40 (hexanes/CH_2Cl_2 - 3:1).

2.4 Synthesis of Doubled-Fused Bis-Porphyrin-Pyrene



Scheme S4. Synthesis of fused bis-porphyrin-pyrene **PorPyrPor**.

Bis-Porphyrin-Pyrene 4

Nickel-(5-bromo)-10,15,20-trimesitylporphyrin **2** (20.0 mg, 25.0 µmol, 2 equiv), 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (5.70 mg, 12.5 µmol, 1 equiv), Cs_2CO_3 (12.2 mg, 37.5 µmol, 3 equiv) and $Pd(PPh_3)_4$ (2.90 mg, 2.50 µmol, 0.2 equiv) were dissolved in toluene (2 mL) and DMF (1 mL) and were degassed. The reaction was heated with an oil bath to 80 °C for 20 h. The solvent was removed, and the crude product separated from inorganics by silica plug filtration (SiO2, hexanes/CH_2Cl_2 - 1:1, Ø 3 cm x 8 cm). Further purification was achieved by size exclusion chromatography (Biobeads SX1, toluene, Ø 3 cm x 30 cm). After recrystallization from CH_2Cl_2/MeOH the product was obtained as a red crystalline solid in 58% yield (23.8 mg, 14.5 µmol).

^{1}H NMR (500 MHz, CS_2/$CDCl_3$, rt): δ [ppm]: 8.98 (s, 4H), 8.67 (d, *J* = 4.8 Hz, 4H), 8.59 (d, *J* = 4.8 Hz, 4H), 8.56 (s, 8H), 8.39 (s, 4H). 7.20 - 7.19 (m,.12H), 2.57 (s, 6H), 2.56 (s, 12H), 1.86 (s, 36H).

^{13}C NMR (126 MHz, CS_2/$CDCl_3$, rt): δ [ppm]: 143.21, 142.61, 142.52, 142.47, 139.30, 138.95, 138.93, 137.54, 137.32, 137.27, 132.46, 131.37, 131.34, 130.96, 130.51, 129.72, 128.61, 127.73, 124.08, 118.33, 117.27, 116.99, 21.48, 21.41.

UV/Vis (CH_2Cl_2): λ [nm] (ε [$M^{-1}cm^{-1}$]): 425 (476000), 529 (47000).

HRMS (MALDI, CH_2Cl_2) for $C_{110}H_{90}N_8Ni_2$ (M^+) calcd.: 1638.5990, found: 1638.6003.

TLC: R_f [%]: 0.50 (hexanes/CH_2Cl_2 - 2:1).

Double-Fused Nickel-Bis-Porphyrin-Pyrene PorPyrPor

A 20 mL vial was filled with a solution of nickel-bis-porphyrin-pyrene **4** (20.0 mg, 12.2 µmol, 1 equiv) in CH_2Cl_2 (8 mL) and CS_2 (2 mL) and cooled with an ice bath. The solution was degassed (bubbling N_2 through the solution for 15 min). The N_2 flow through the solution was increased, and a solution of dry $FeCl_3$ (32.0 mg, 195 µmol, 16 equiv) in CH_3NO_2 (0.2 mL) was added. The N_2 bubbling through the solution was stopped 15 min after $FeCl_3$ was added and the solution was stirred under slow warming to rt for 24 h. MeOH (10 mL) was added to quench the reaction. After adding NEt_3 (1 mL), the solvent was removed, and the crude was separated from inorganics by a silica plug (hexanes/ CH_2Cl_2 - 1:1, Ø 3 x 10 cm). Further purification was achieved by column chromatography (hexanes/CH_2Cl_2 - 4:1, Ø 7 x 40 cm). The product was obtained as a dark-purple solid in 36% yield (7.19 mg, 4.39 µmol).

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 80 °C): δ [ppm]: 9.21 (d, *J* = 5.0 Hz, 2H), 8.49 (d, *J* = 4.8 Hz, 2H), 8.47 (s, 2H), 8.13 - 8.04 (m, 10H), 7.96 (s, 2H), 7.81 (s, 2H), 7.23 (s, 4H), 7.17 (s, 4H), 7.11 (s, 4H), 2.62 (s, 6H), 2.54 (s, 6H), 2.49 (s, 6H), 1.97 (s, 12H), 1.84 (s, 12H), 1.82 (s, 12H).

^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 80 °C): δ [ppm]: 147.99, 147.61, 146.24, 146.21, 145.94, 145.39, 144.75, 144.35, 144.22, 141.90, 139.16, 139.03, 138.91, 137.96, 137.92, 137.45, 137.17, 136.15, 134.16, 132.06, 131.19, 130.50, 130.23, 128.71, 128.24, 128.08, 128.02, 126.73, 126.44, 122.61, 121.68, 120.63, 118.69, 29.88, 21.76, 21.65, 21.53, 21.39.

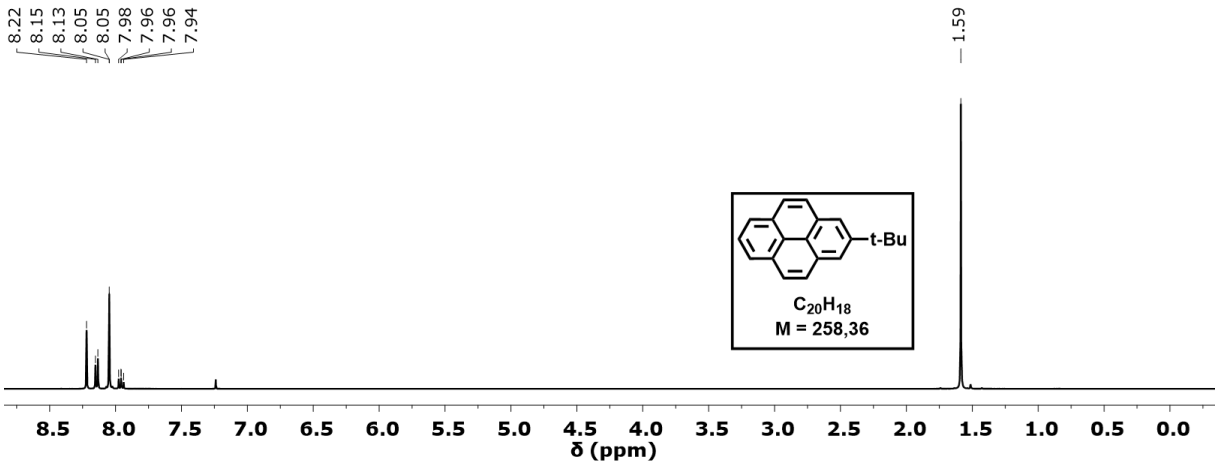
UV/Vis (CH_2Cl_2): λ [nm] (ε [$M^{-1}cm^{-1}$]): 391 (48000), 451 (42000), 554 (76000), 630 (21000), 688 (11000).

HRMS (MALDI, CH_2Cl_2) for $C_{110}H_{86}N_8Ni_2$ (M^+) calcd.: 1634.5677, found: 1634.5668.

TLC: R_f [%]: 0.40 (hexanes/CH_2Cl_2 - 3:1).

3 Spectral Appendix

^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (101 MHz, $CDCl_3$, rt)

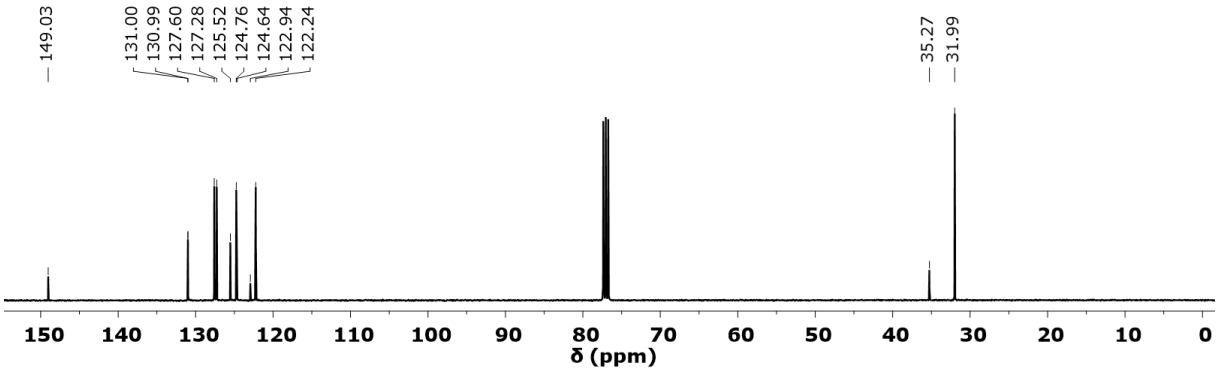
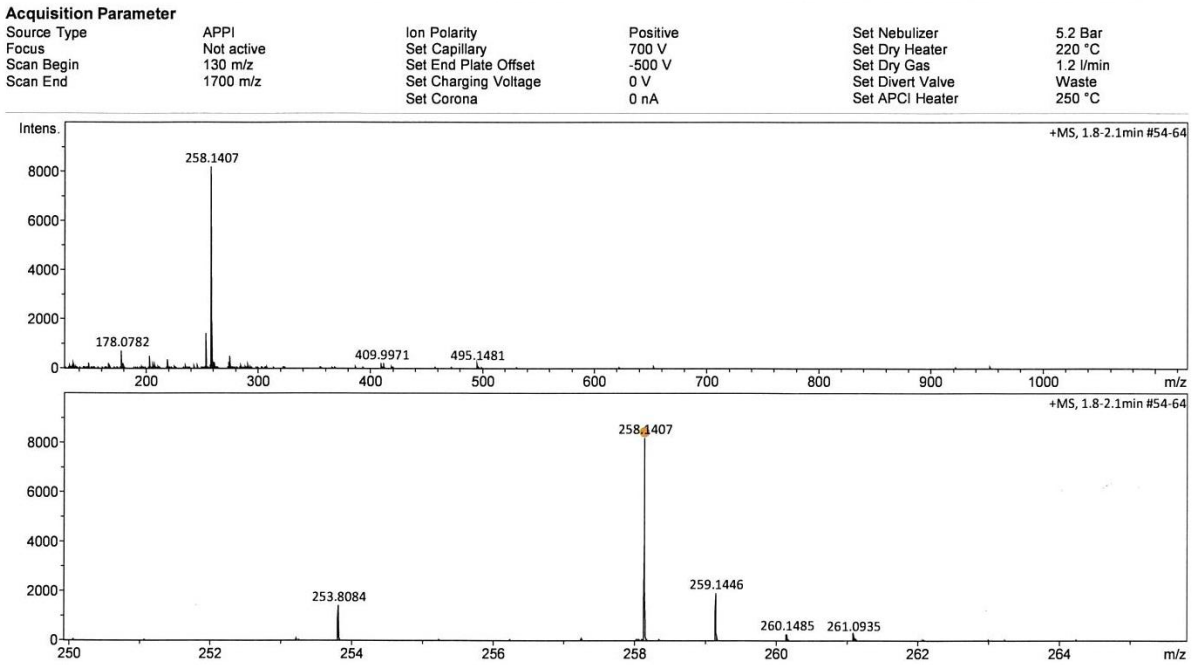


Figure S1. ^{1}H and ^{13}C NMR of **9**.

MS (APPI)



HRMS (APPI)

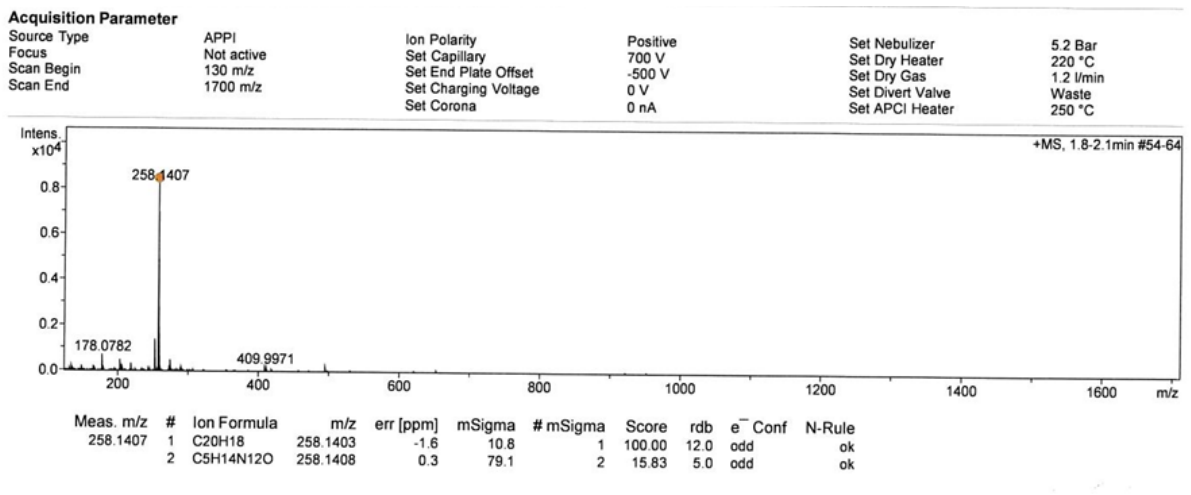


Figure S2. MS/HRMS (APPI) of **9**.

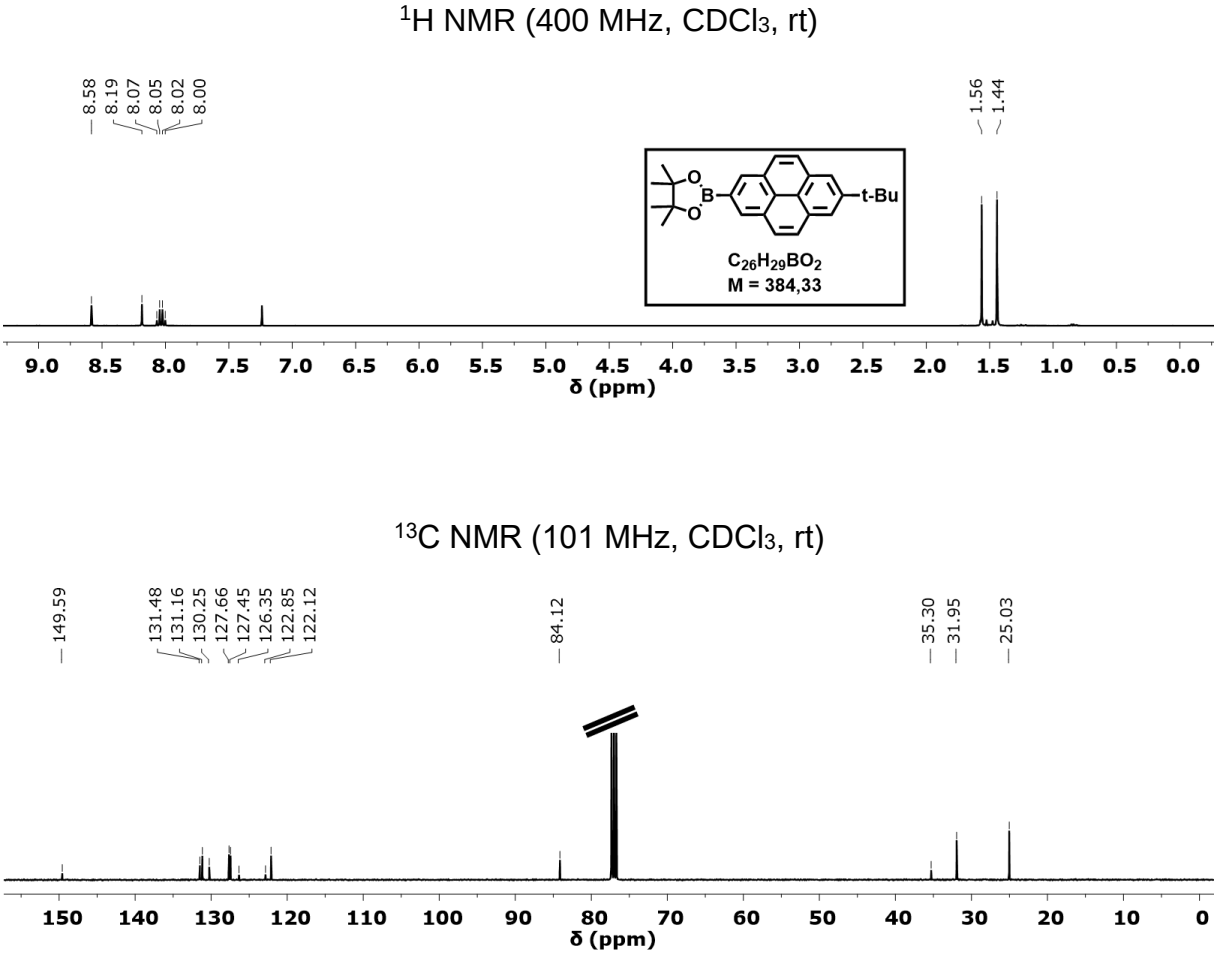
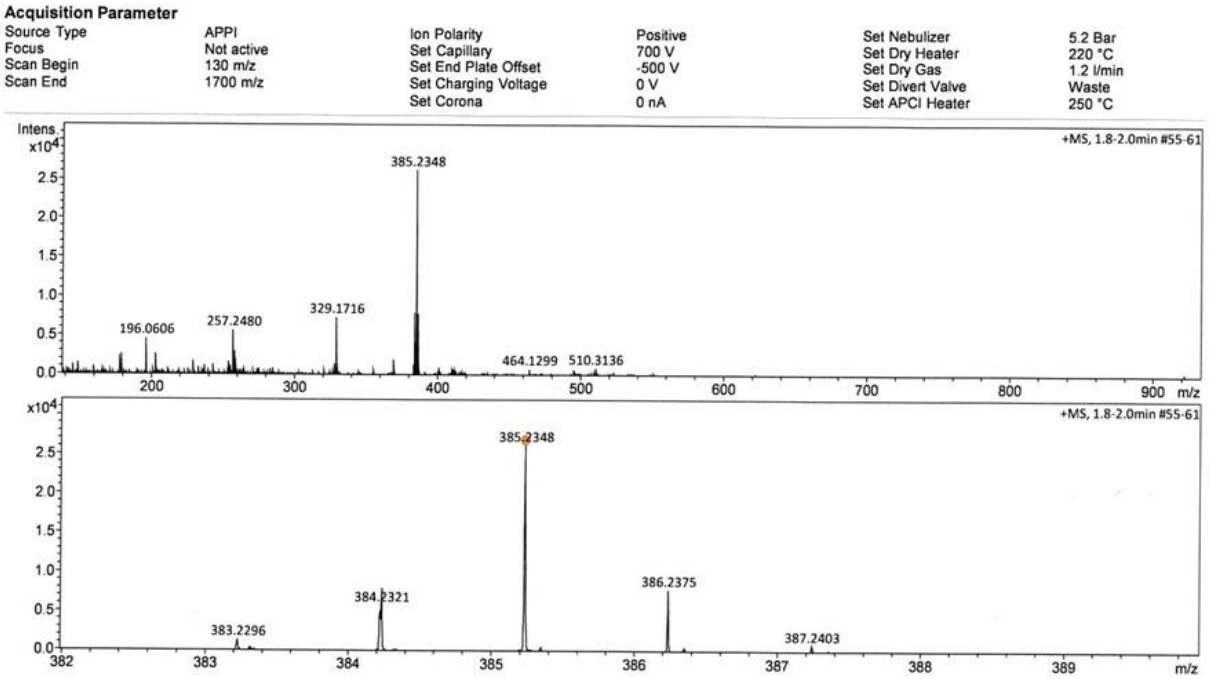


Figure S3. ^{1}H and ^{13}C NMR of **6**.

MS (APPI)



HRMS (APPI)

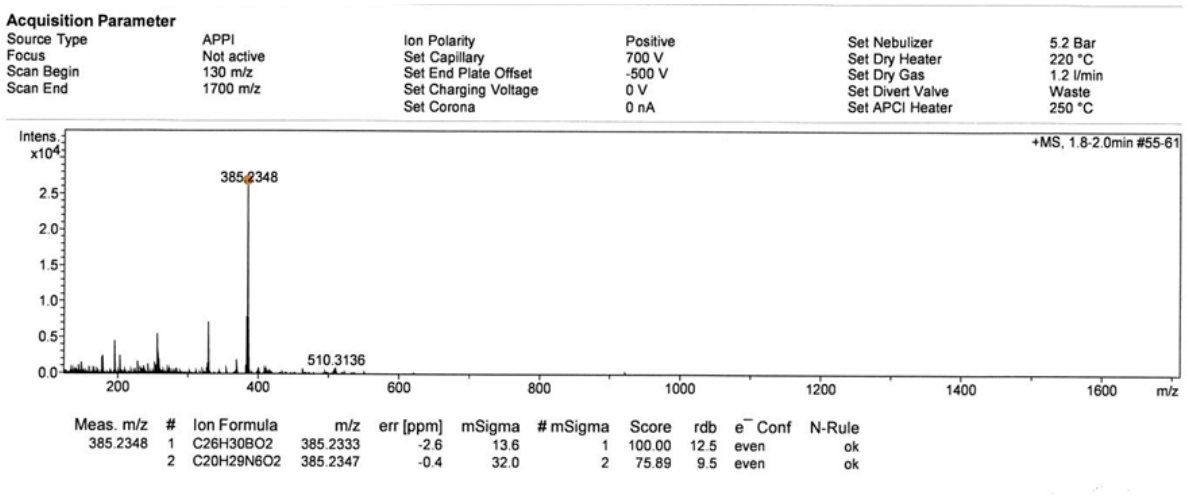
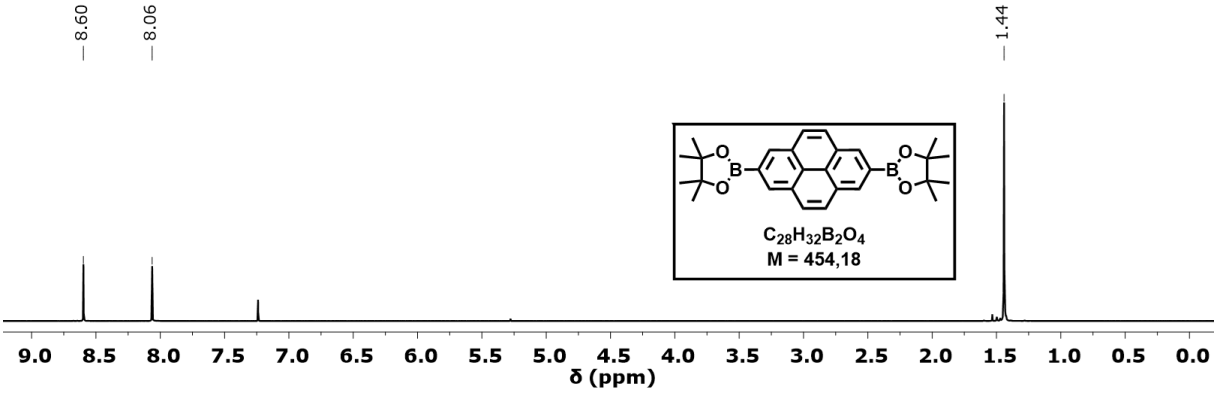


Figure S4. MS/HRMS (APPI) of **6**.

^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (101 MHz, $CDCl_3$, rt)

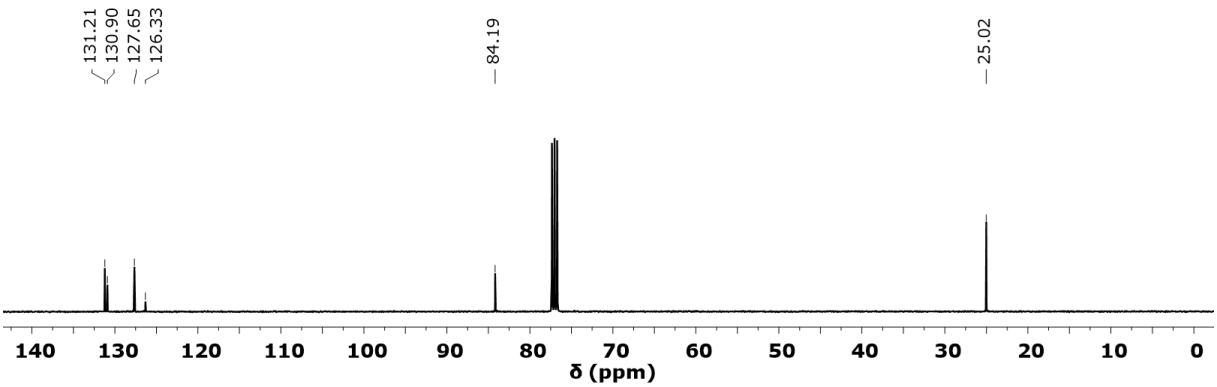
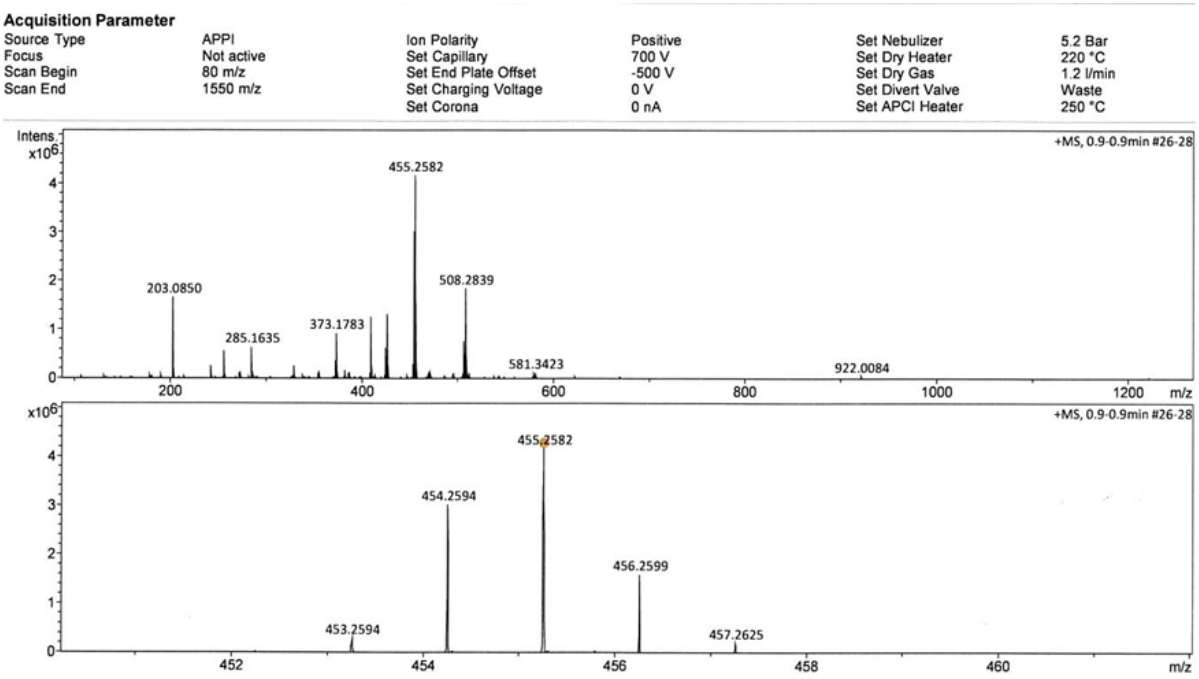


Figure S5. ^{1}H and ^{13}C NMR of **7**.

MS (APPI)



HRMS (APPI)

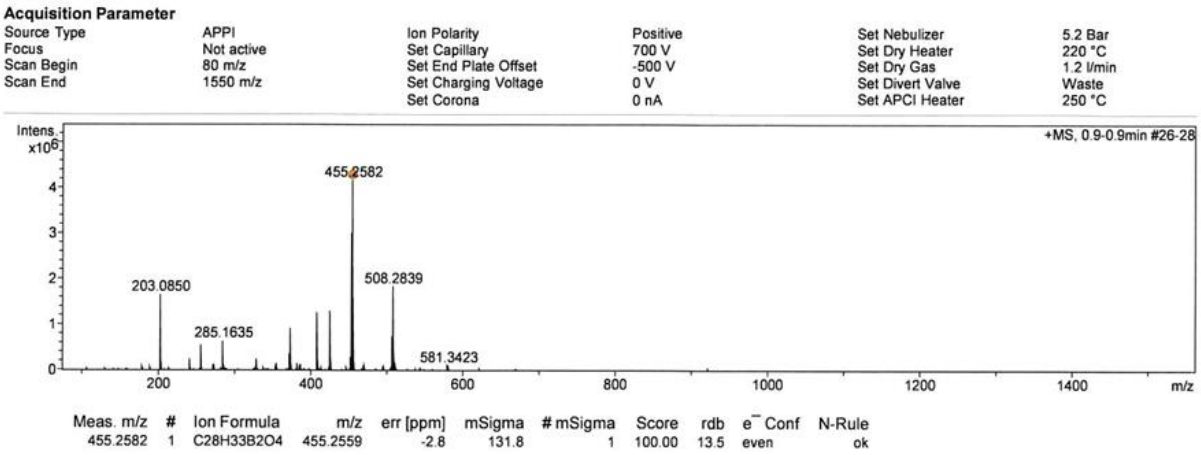
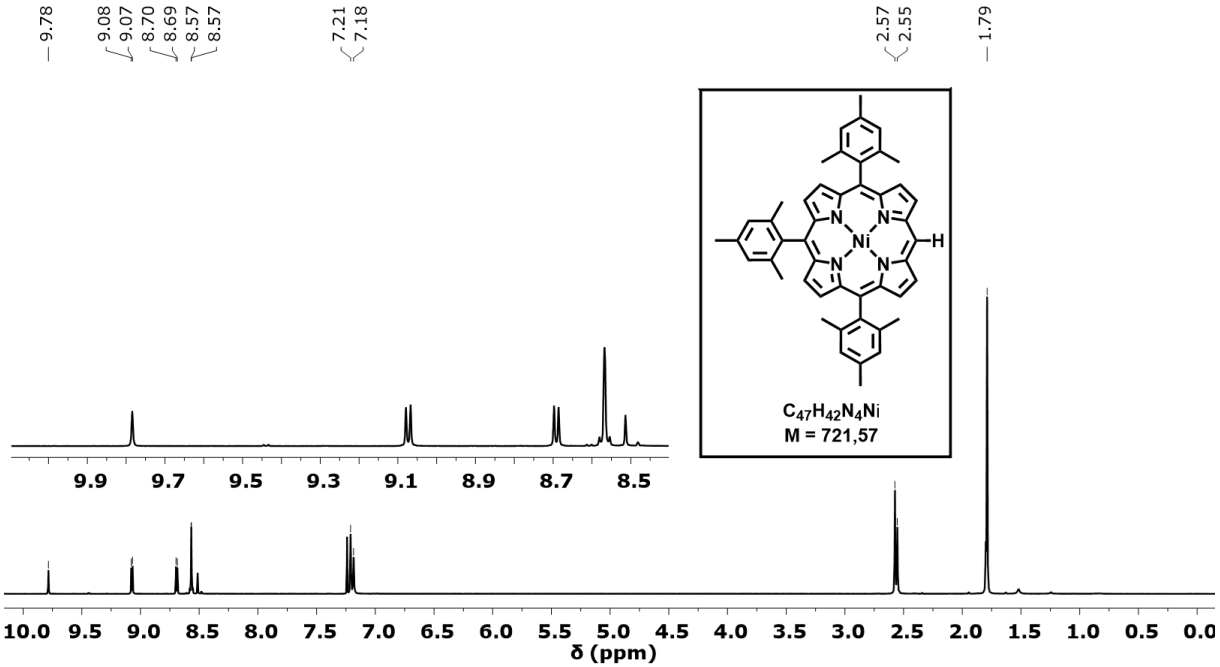


Figure S6. MS/HRMS (APPI) of **7**.

^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (101 MHz, $CDCl_3$, rt)

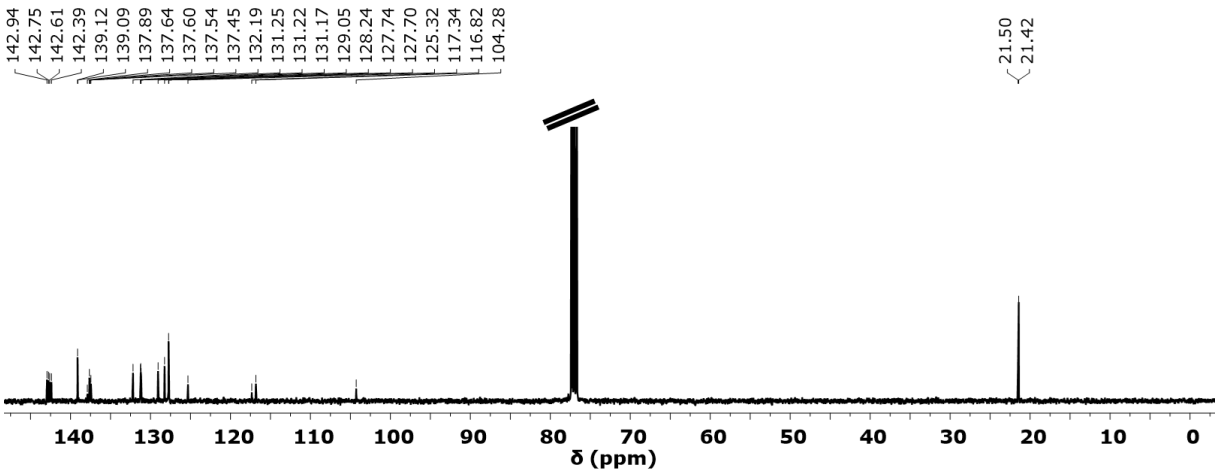
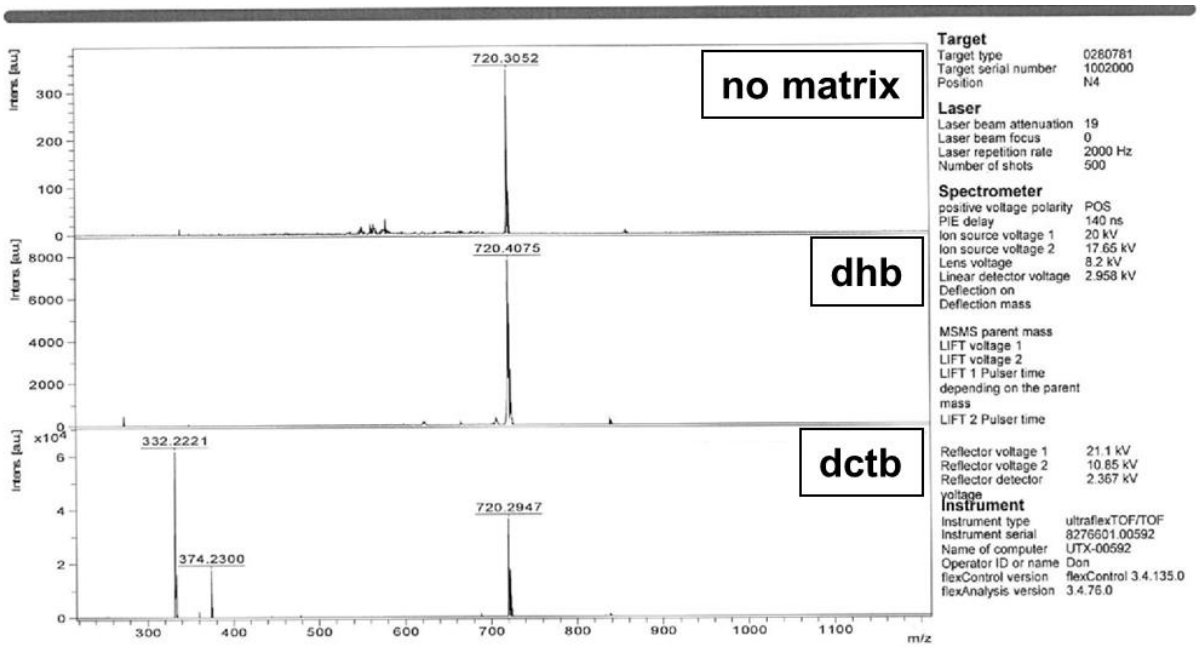
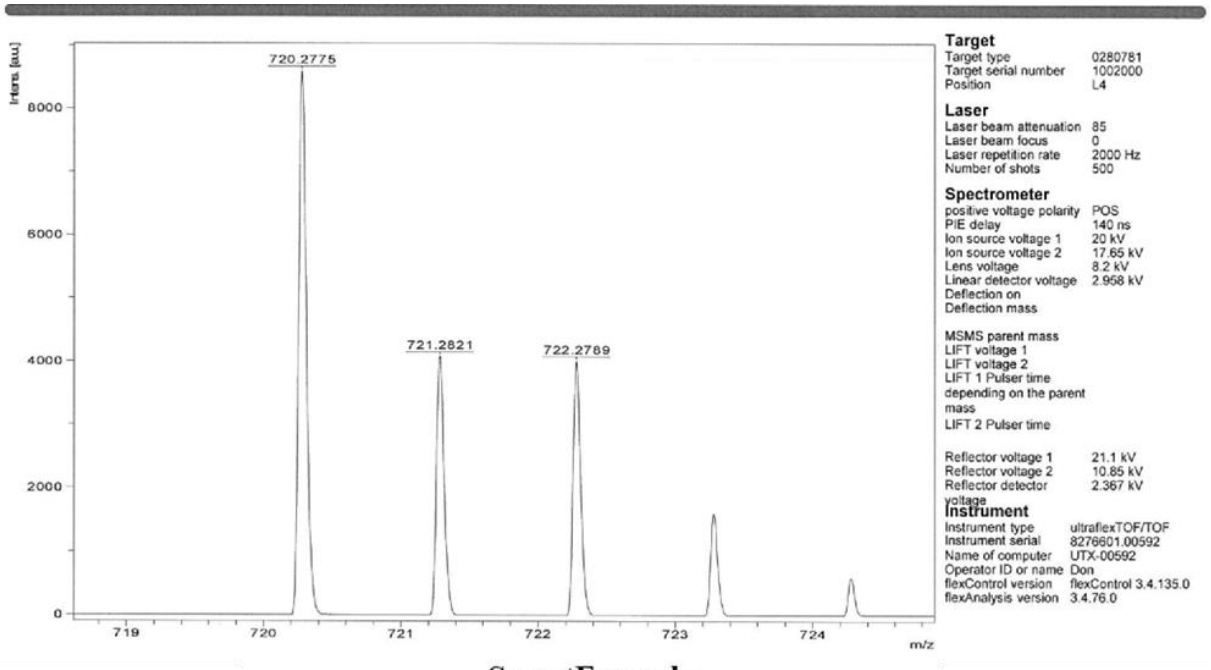


Figure S7. ^{1}H and ^{13}C NMR of **14**.

MS (MALDI)



HRMS (MALDI)

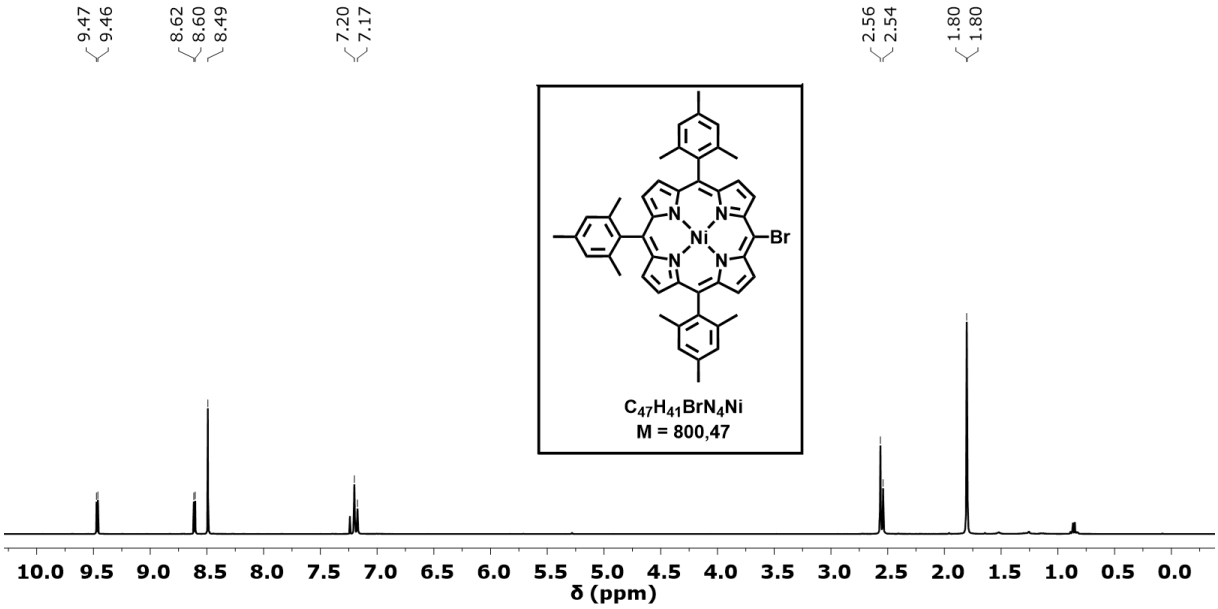


SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 47 H 42 N 4 Ni	720.2757	2.3975	100.6242	29.00	ok	odd

Figure S8. MS/HRMS (MALDI) of **14**.

^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (101 MHz, $CDCl_3$, rt)

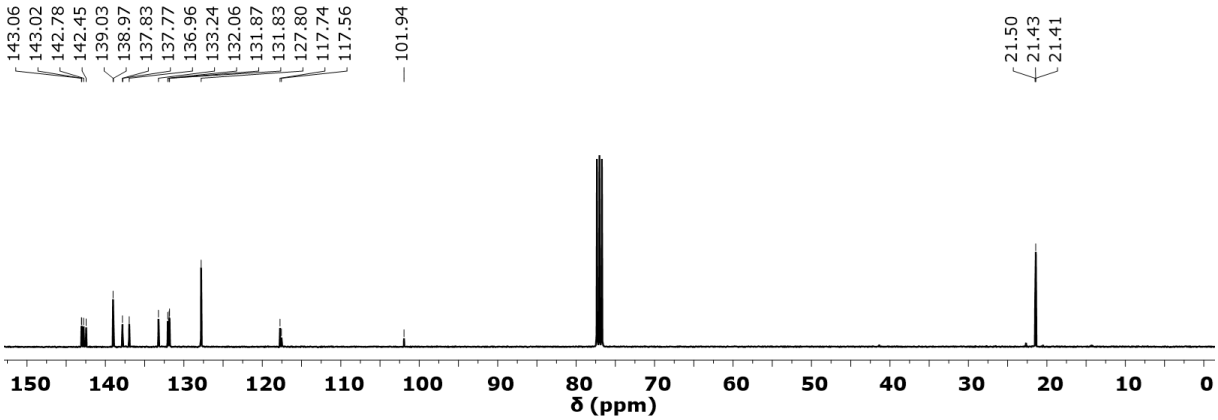
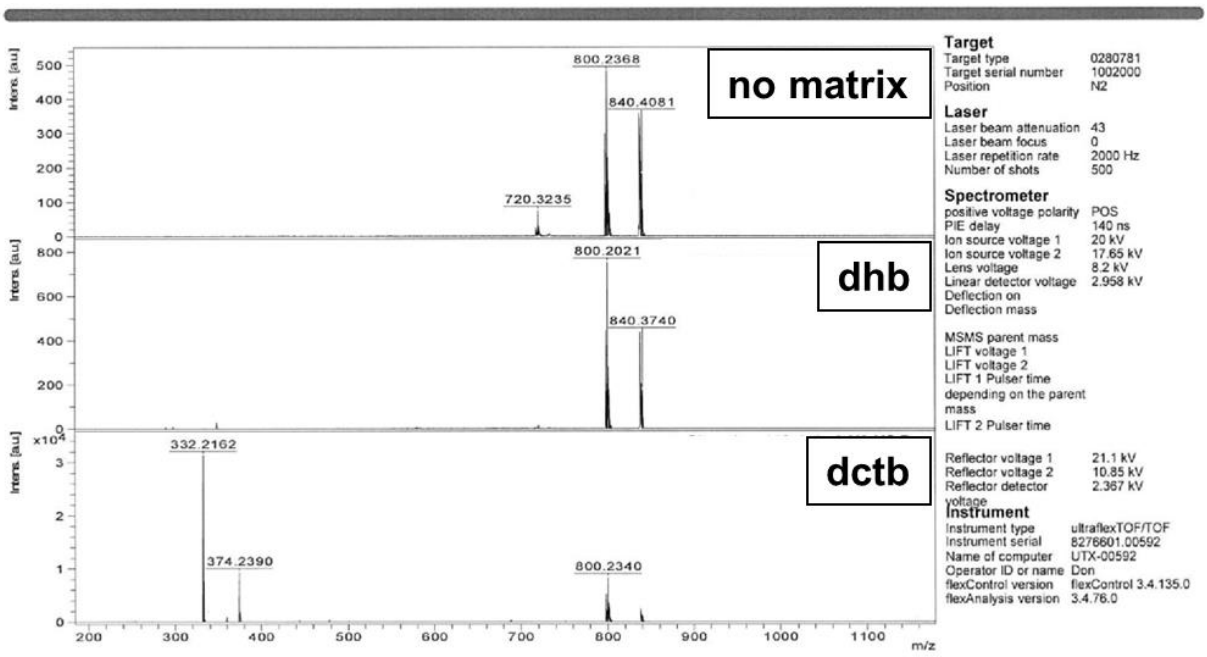
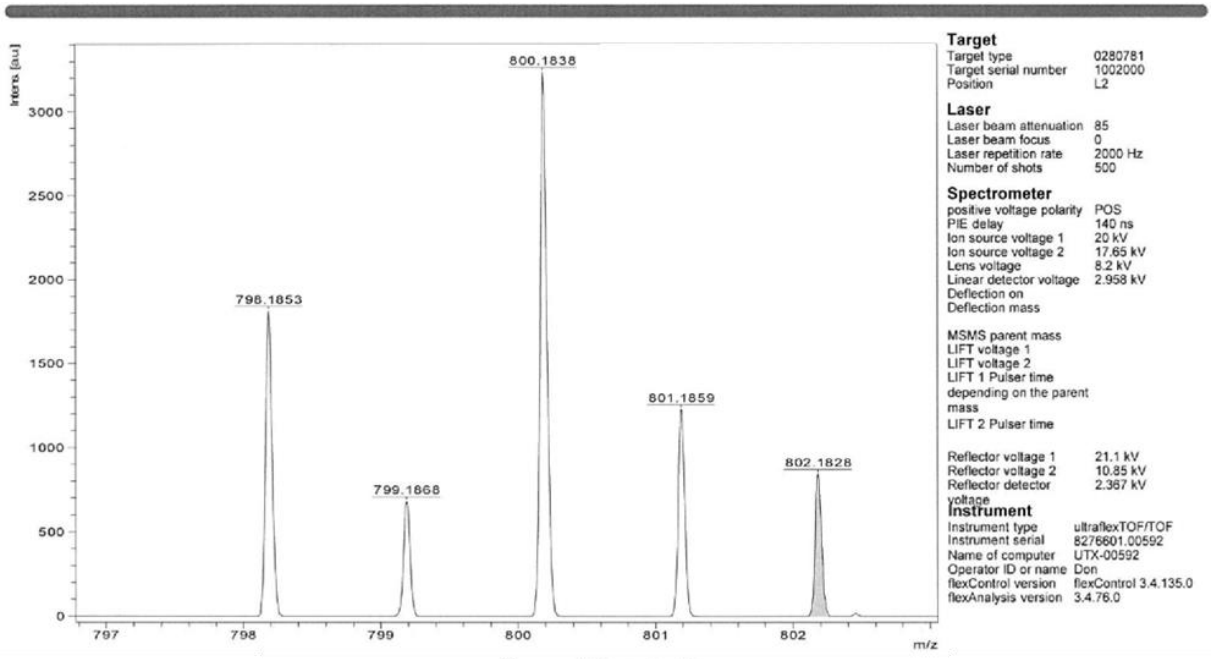


Figure S9. ^{1}H and ^{13}C NMR of **2**.

MS (MALDI)



HRMS (MALDI)

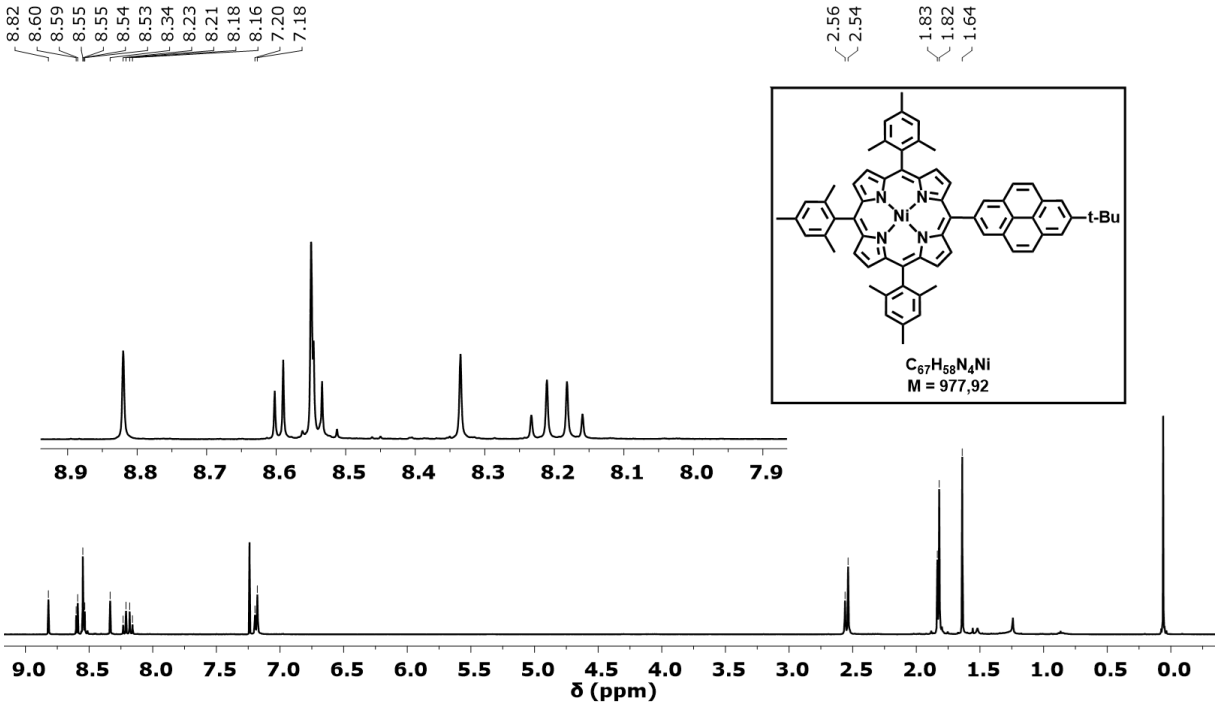


SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 47 H 41 Br N 4 Ni	798.1863	1.1747	247.2498	29.00	ok	odd

Figure S10. MS/HRMS (MALDI) of **2**.

^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (101 MHz, $CDCl_3$, rt)

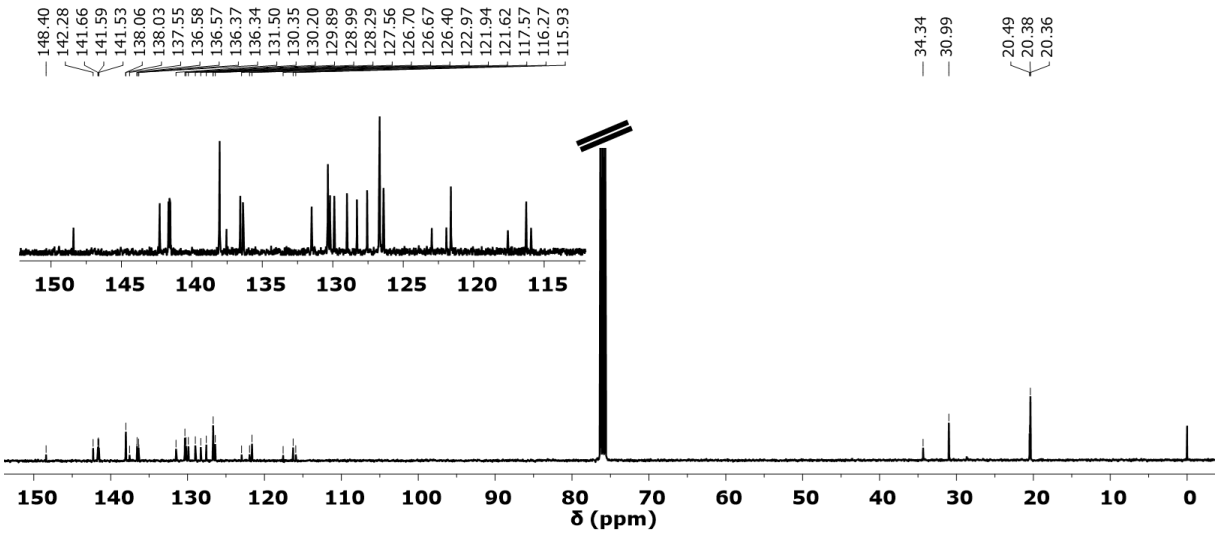
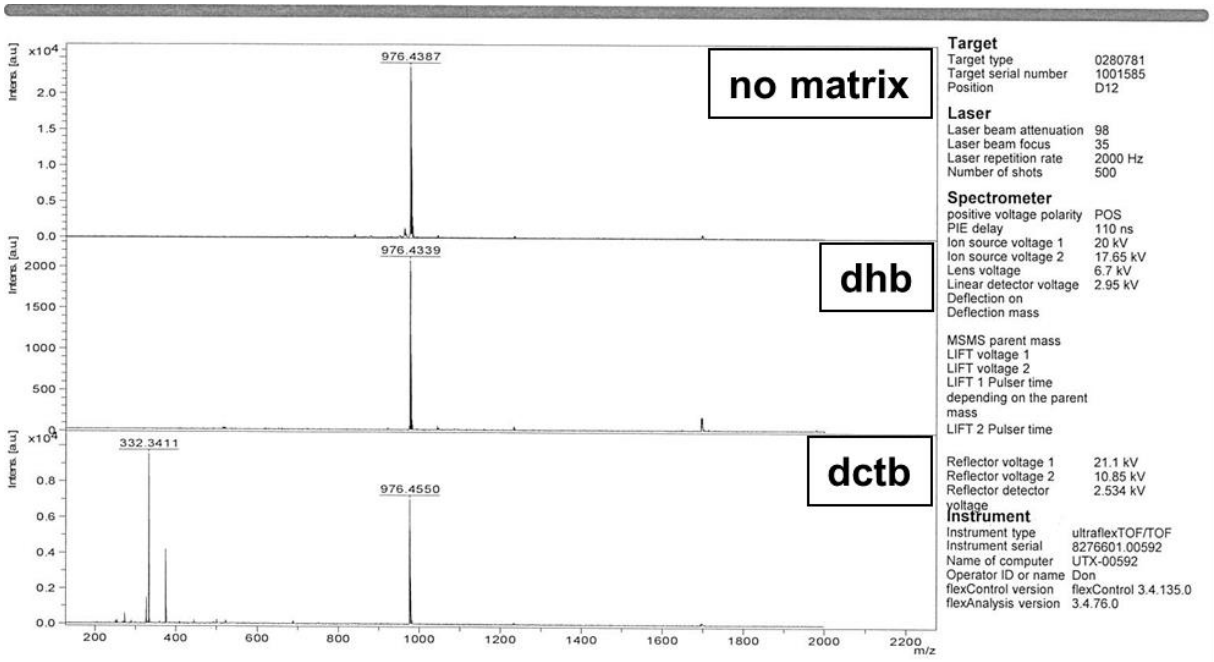
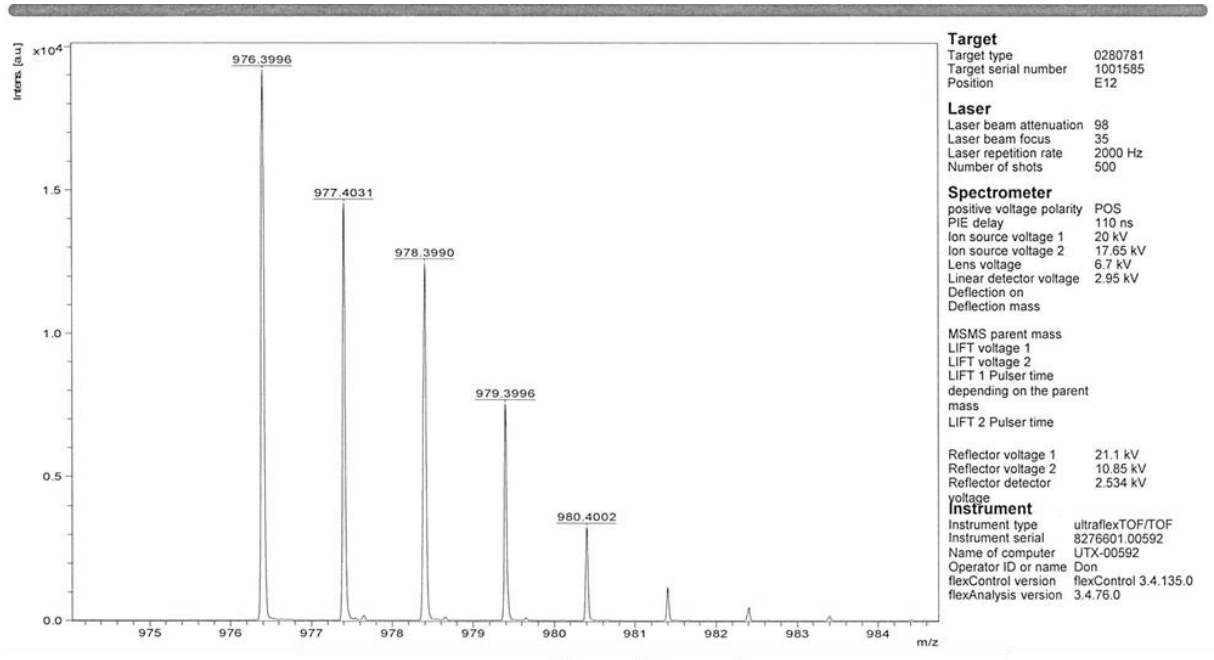


Figure S11. ^{1}H and ^{13}C NMR of **5**.

MS (MALDI)



HRMS (MALDI)



SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 67 H 58 N 4 Ni	976.4009	1.4163	28.8274	41.00	ok	odd

Figure S12. MS/HRMS (MALDI) of **5**.

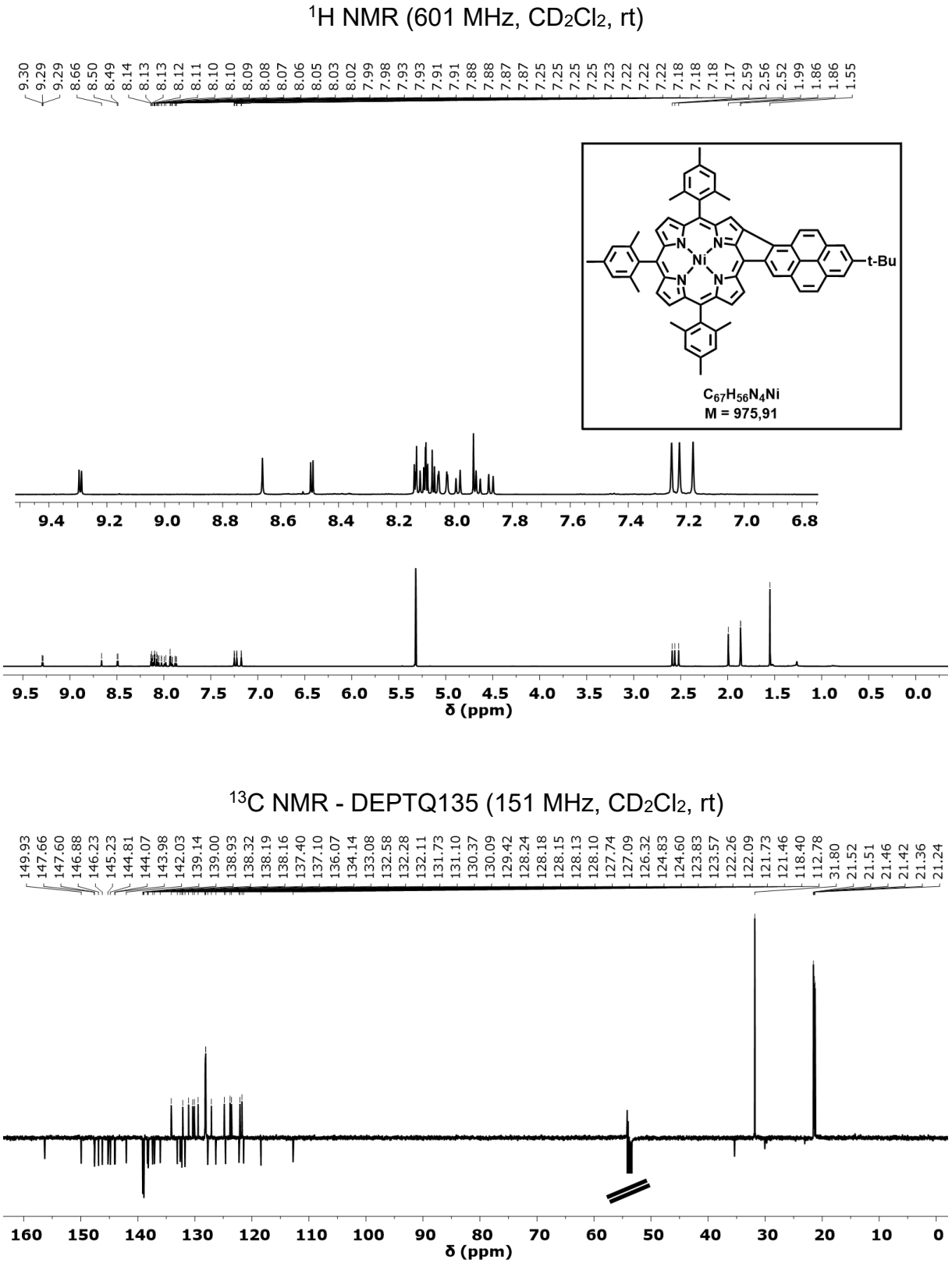


Figure S13. ^{1}H and ^{13}C NMR (DEPTQ135) of **PyrPor**.

^{1}H- ^{1}H COSY (601 MHz, CD_2Cl_2, rt)

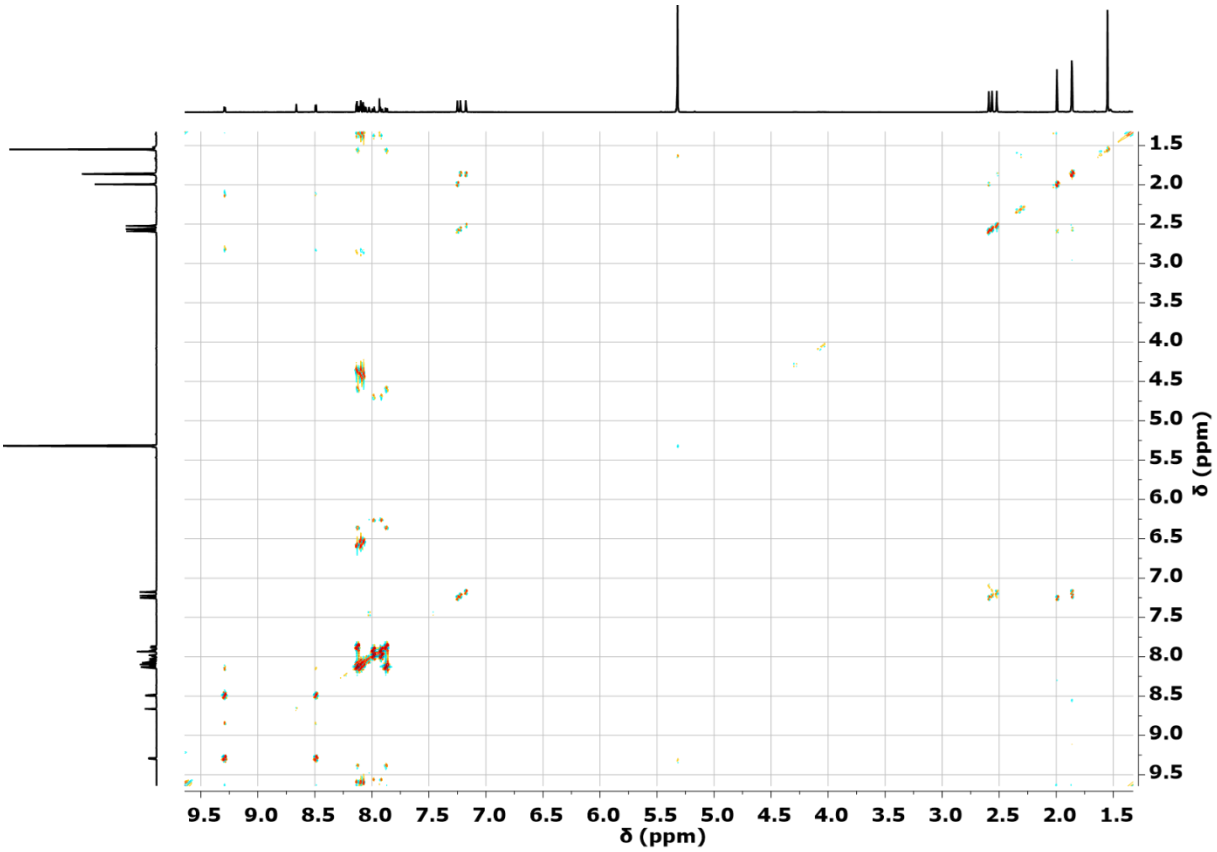


Figure S14. ^{1}H- ^{1}H COSY of **PyrPor**.

^{1}H- ^{13}C HSQC (601 MHz, CD_2Cl_2, rt)

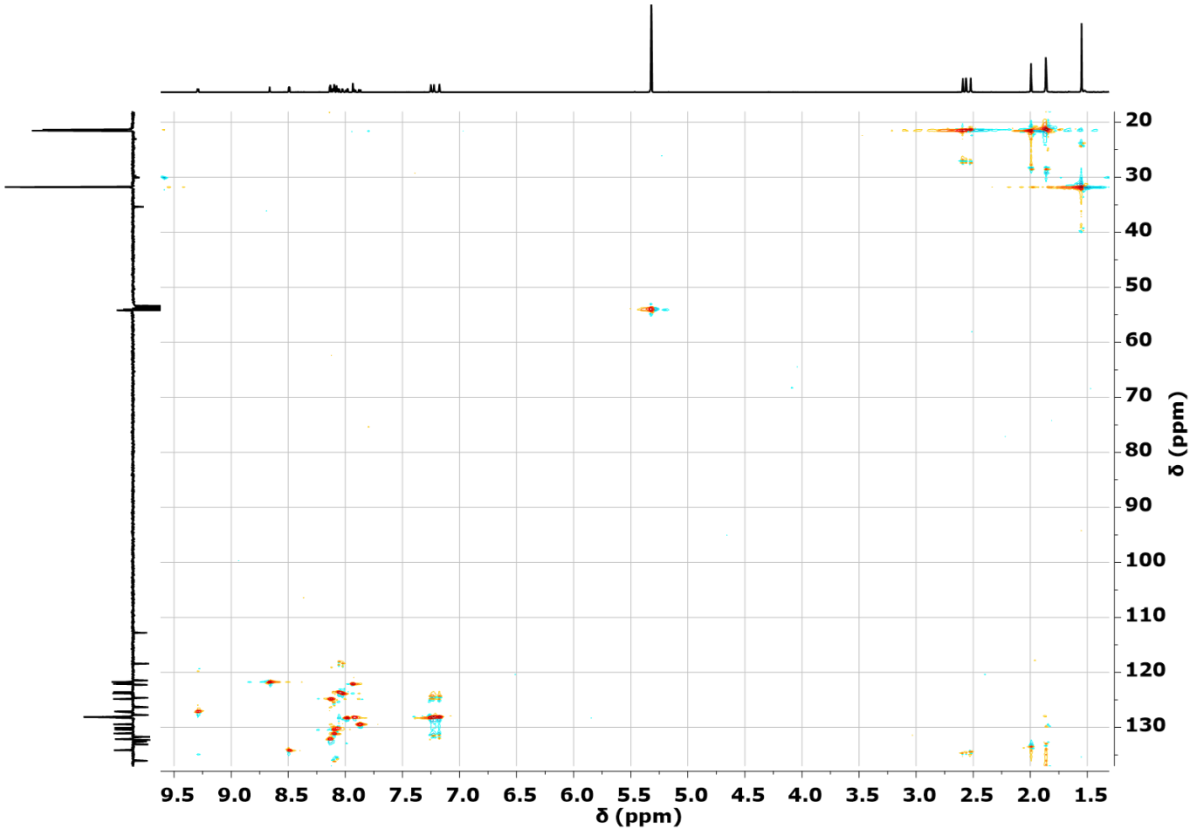


Figure S15. ^{1}H- ^{13}C HSQC of **PyrPor**.

^{1}H- ^{13}C HMBC (601 MHz, CD_2Cl_2, rt)

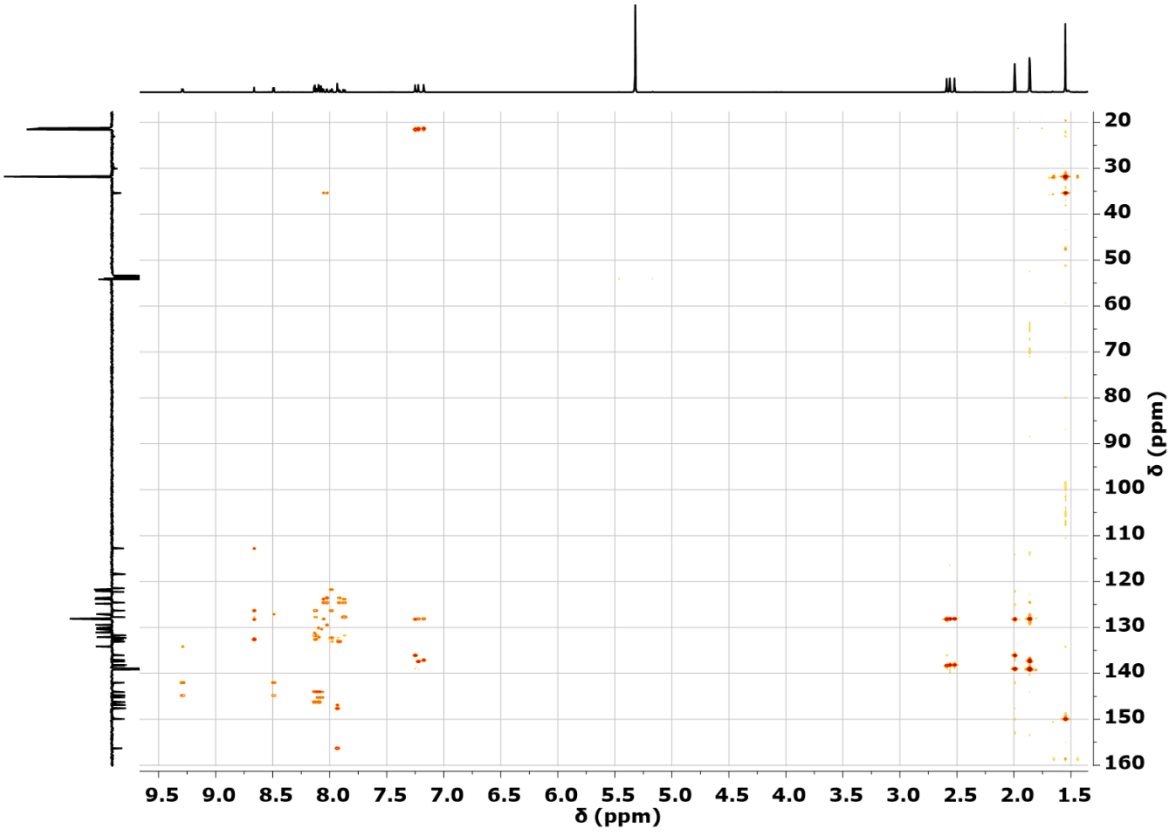
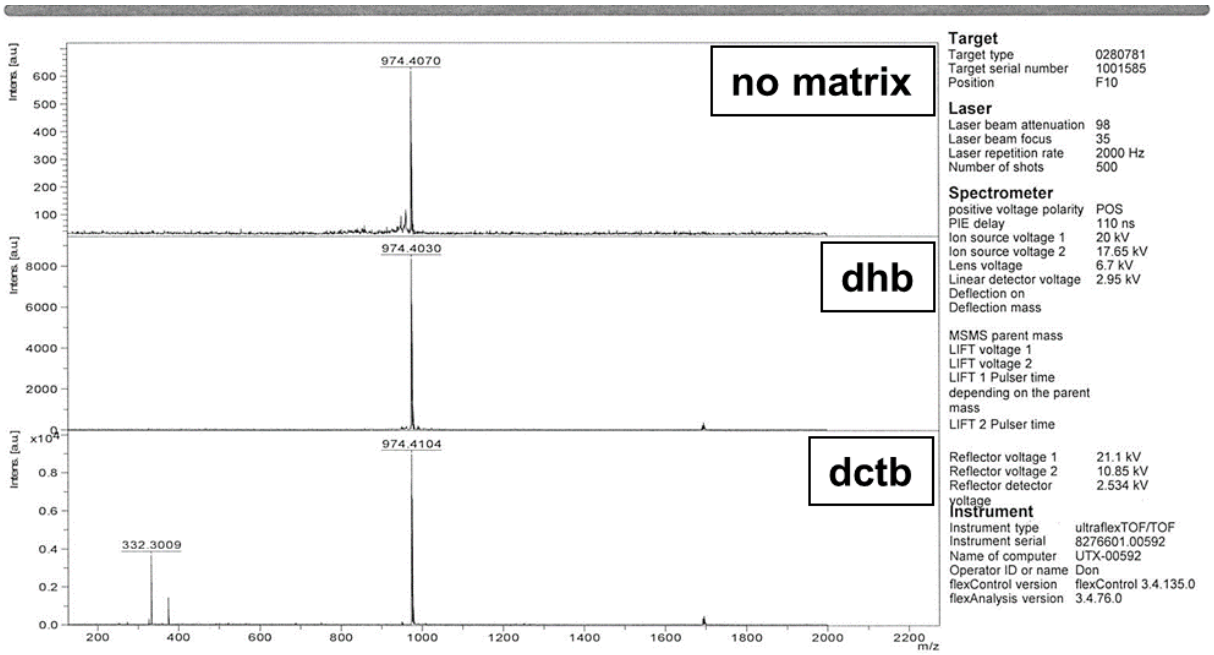
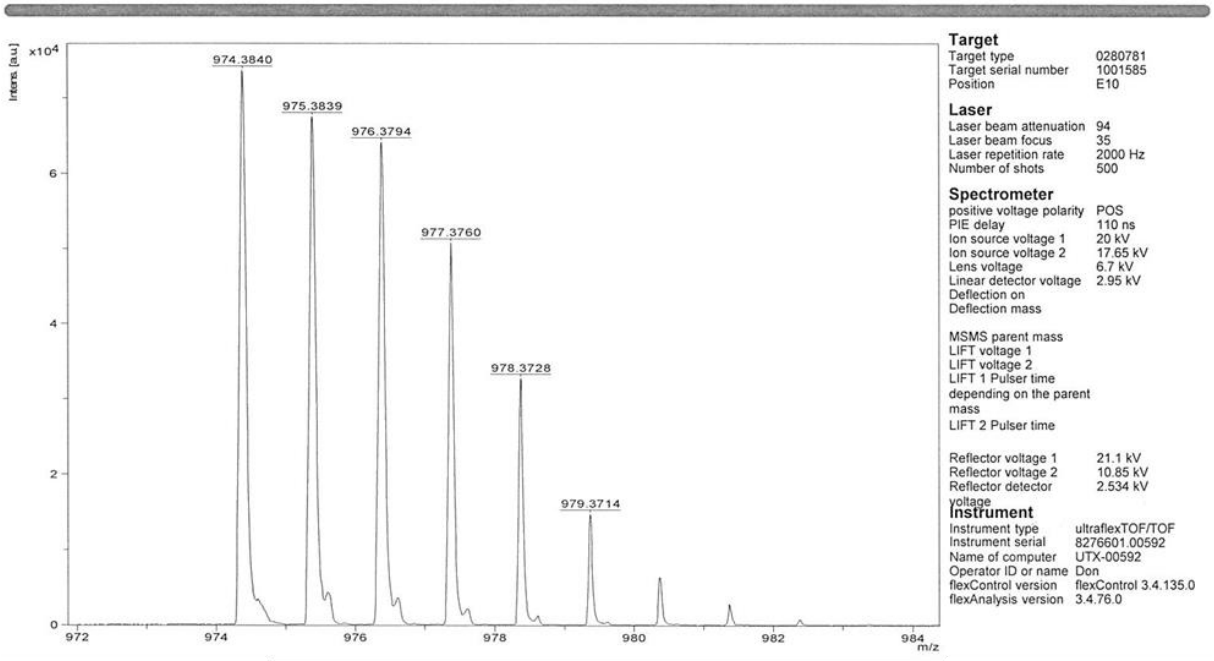


Figure S16. ^{1}H- ^{13}C HMBC of **PyrPor**.

MS (MALDI)



HRMS (MALDI)

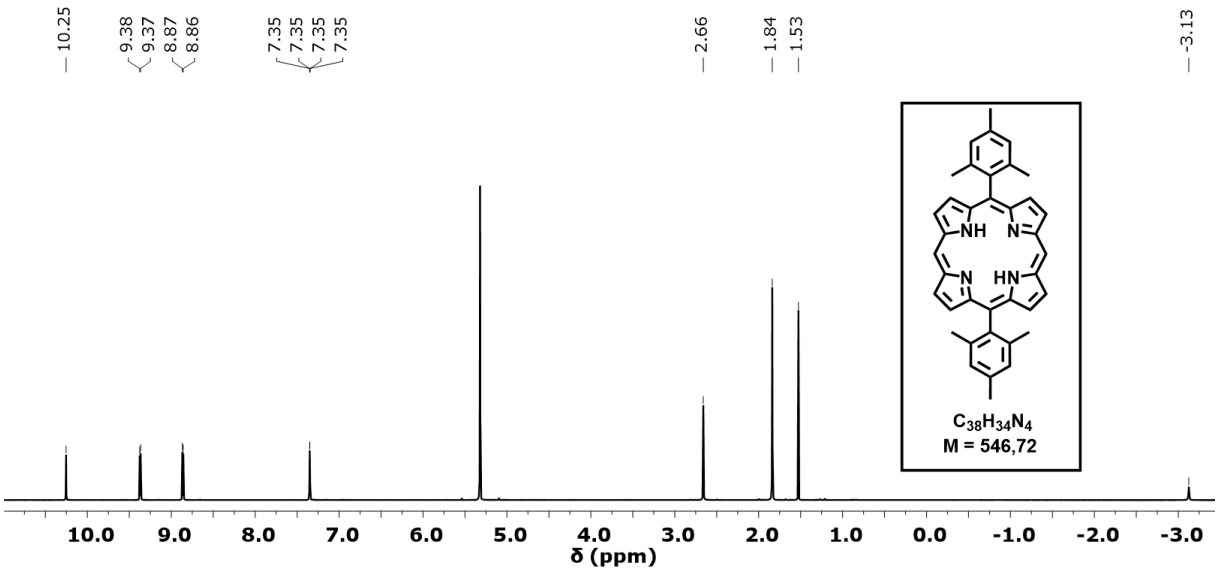


SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 67 H 56 N 4 Ni	974.3853	1.2898	170.4612	42.00	ok	odd

Figure S17. MS/HRMS (MALDI) of **PyrPor**.

^{1}H NMR (400 MHz, CD_2Cl_2, rt)



^{13}C NMR (101 MHz, CD_2Cl_2, rt)

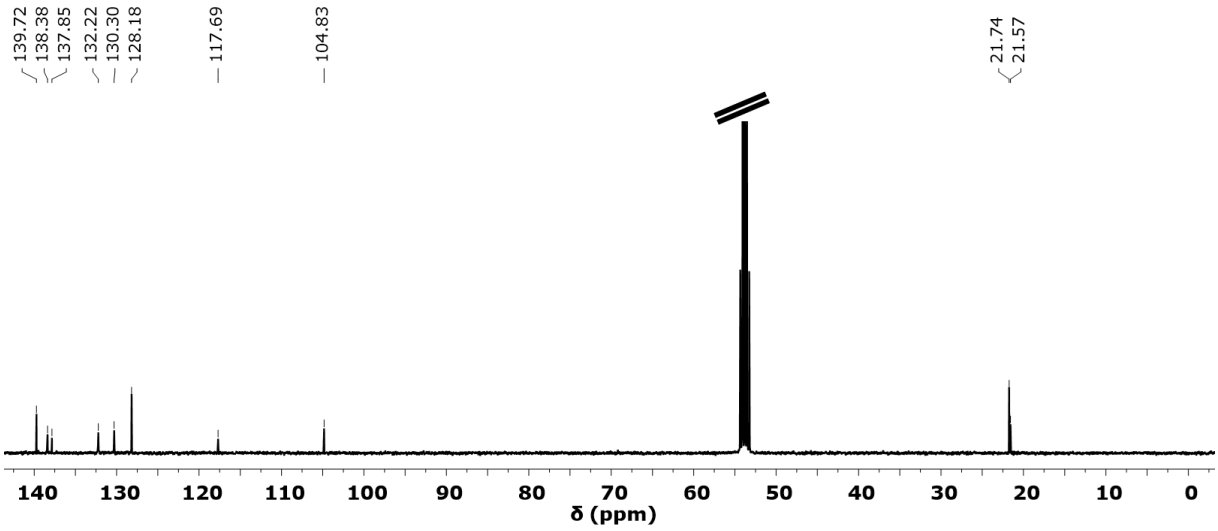
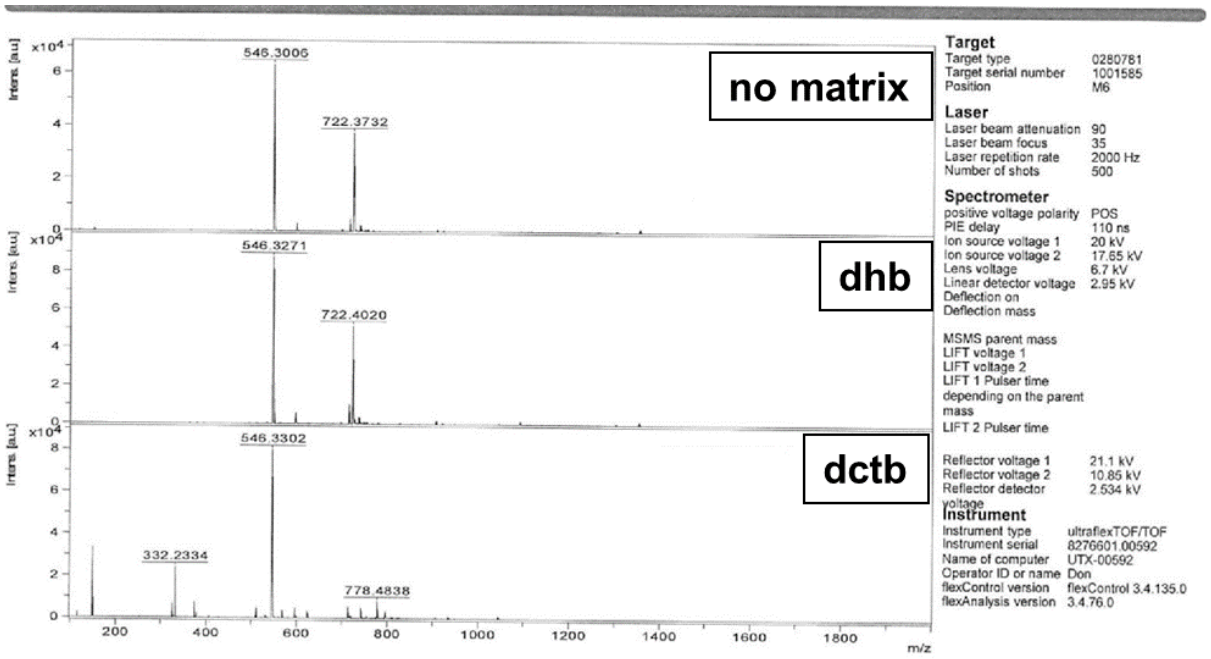
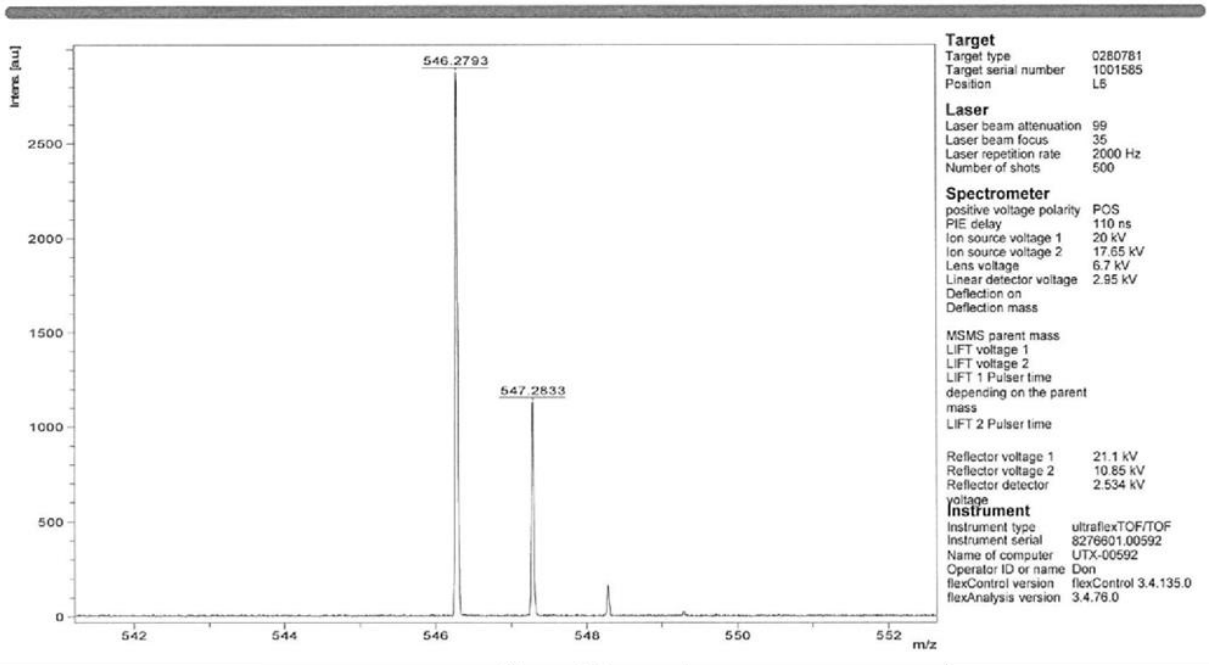


Figure S18. ^{1}H and ^{13}C NMR of **15**.

MS (MALDI)



HRMS (MALDI)

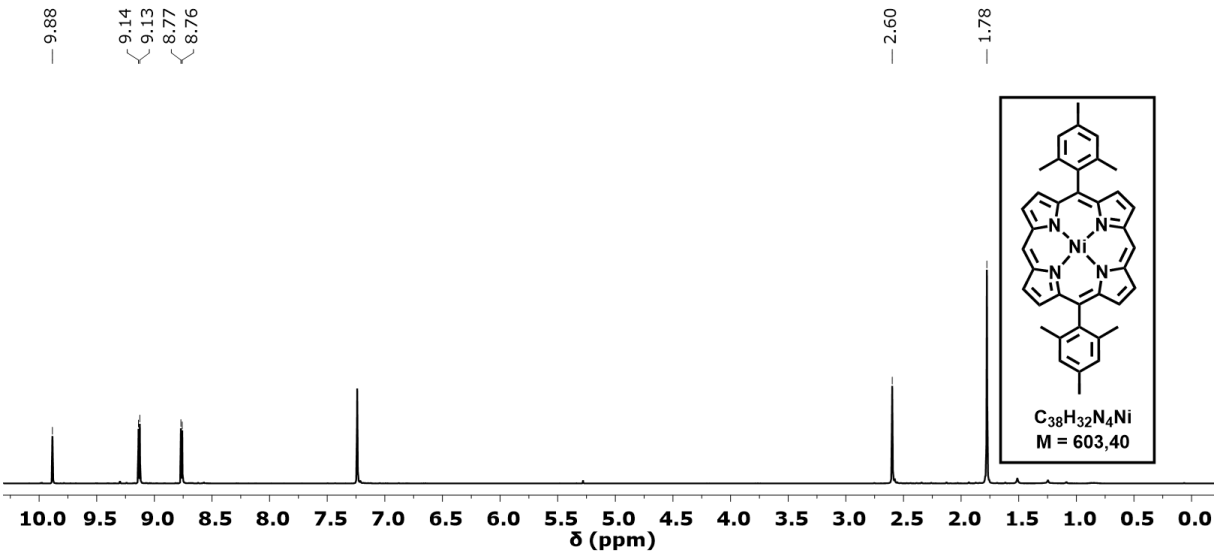


SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 38 H 34 N 4	546.2778	2.8010	48.8215	24.00	ok	odd

Figure S19. MS/HRMS (MALDI) of **15**.

^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (101 MHz, $CDCl_3$, rt)

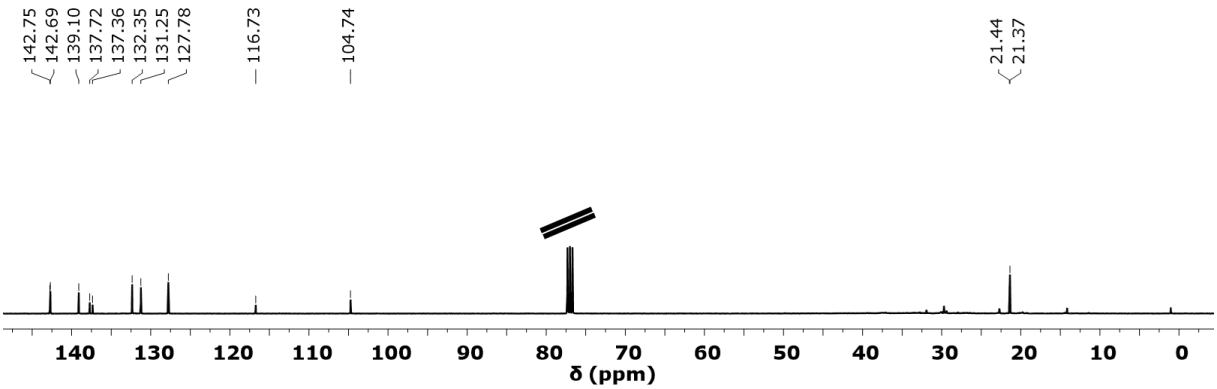
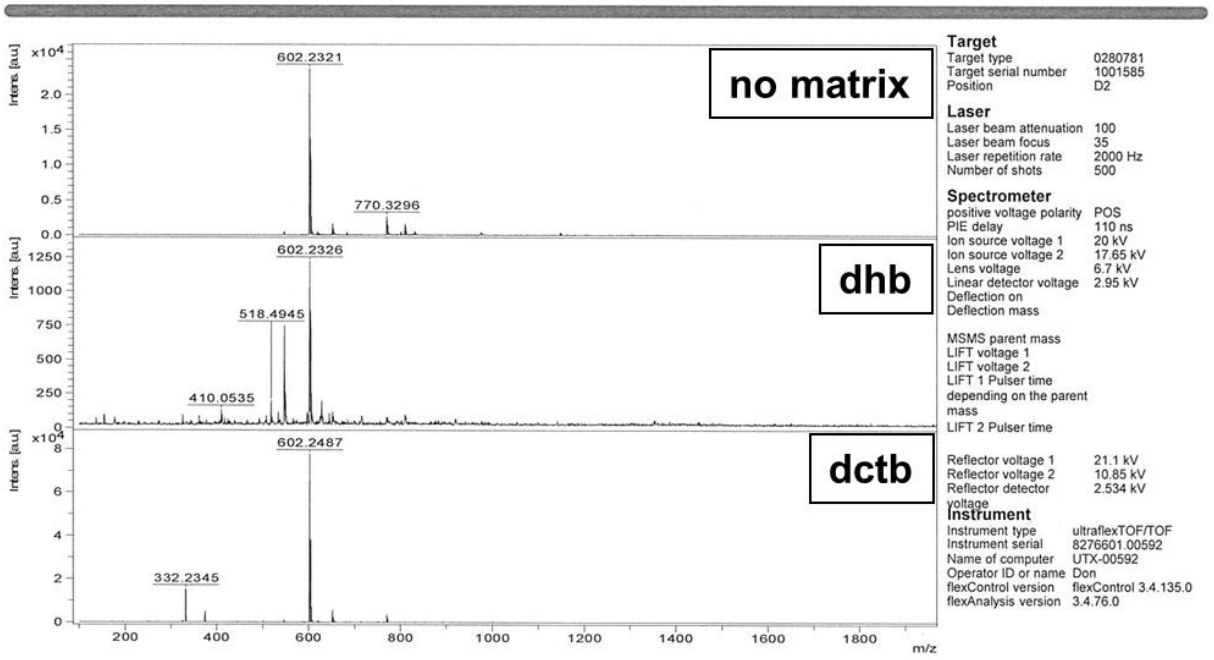
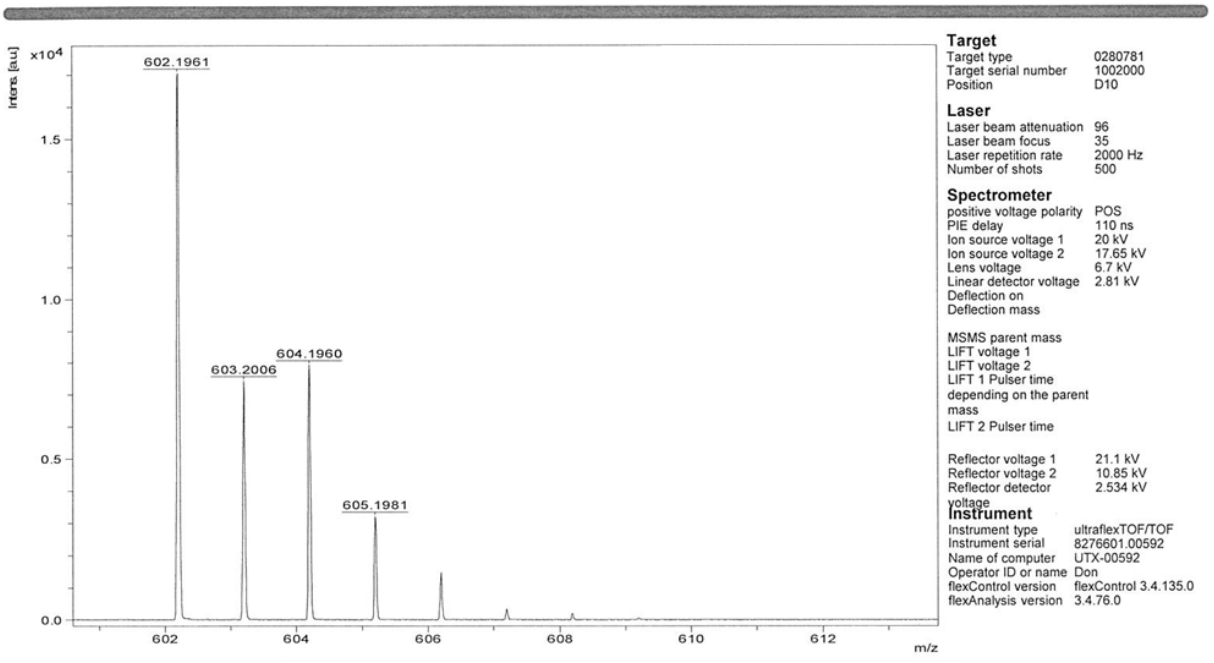


Figure S20. ^{1}H and ^{13}C NMR of **16**.

MS (MALDI)



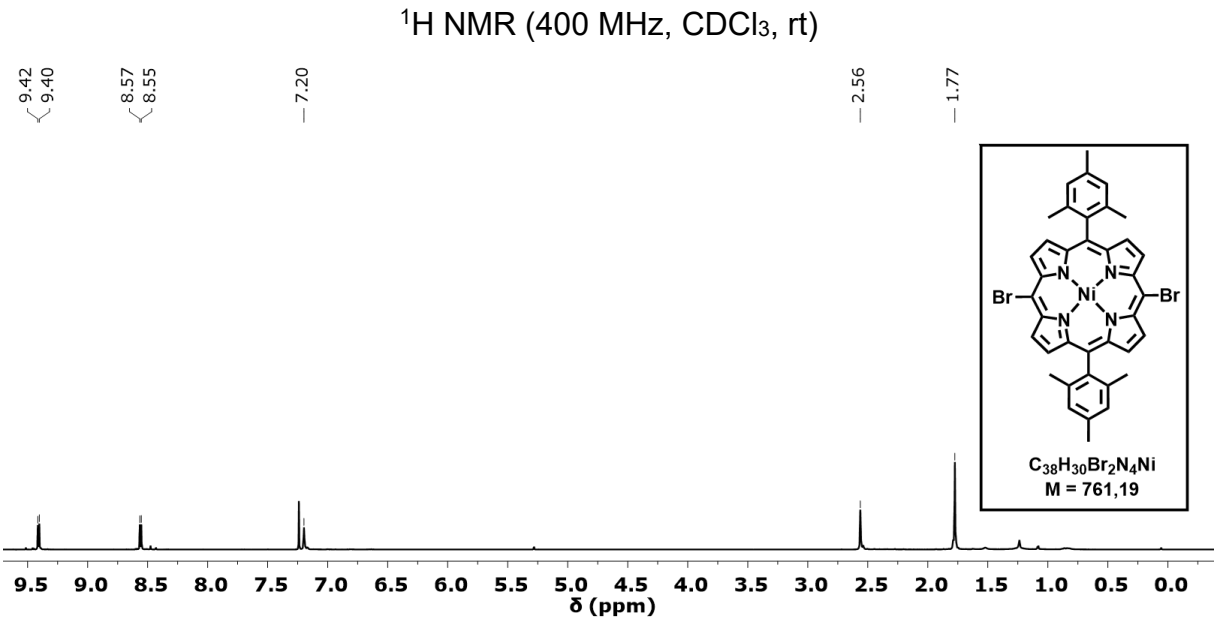
HRMS (MALDI)



SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 38 H 32 N 4 Ni	602.1975	2.3906	36.6292	25.00	ok	odd

Figure S21 MS/HRMS (MALDI) of **16**.



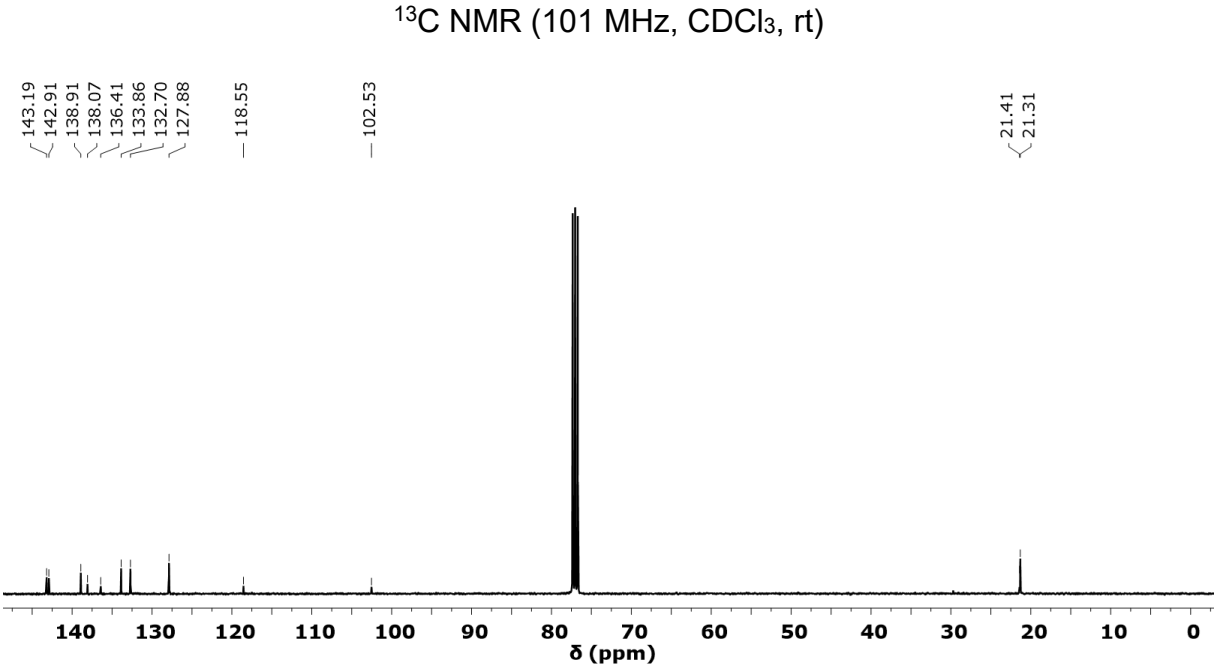
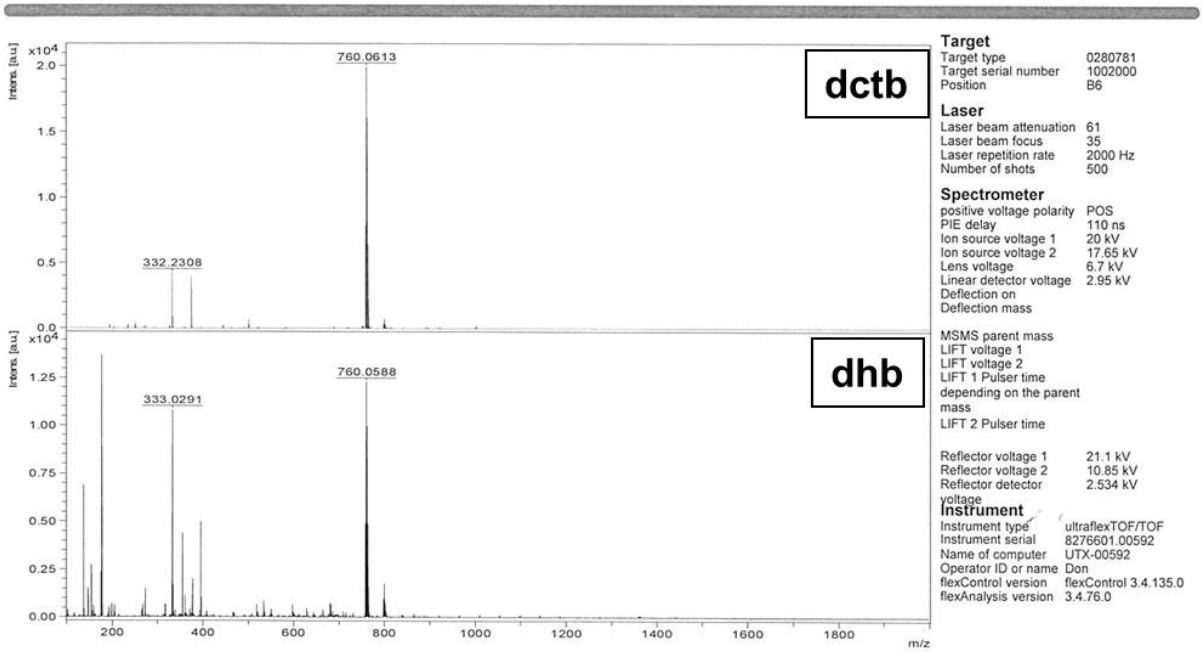
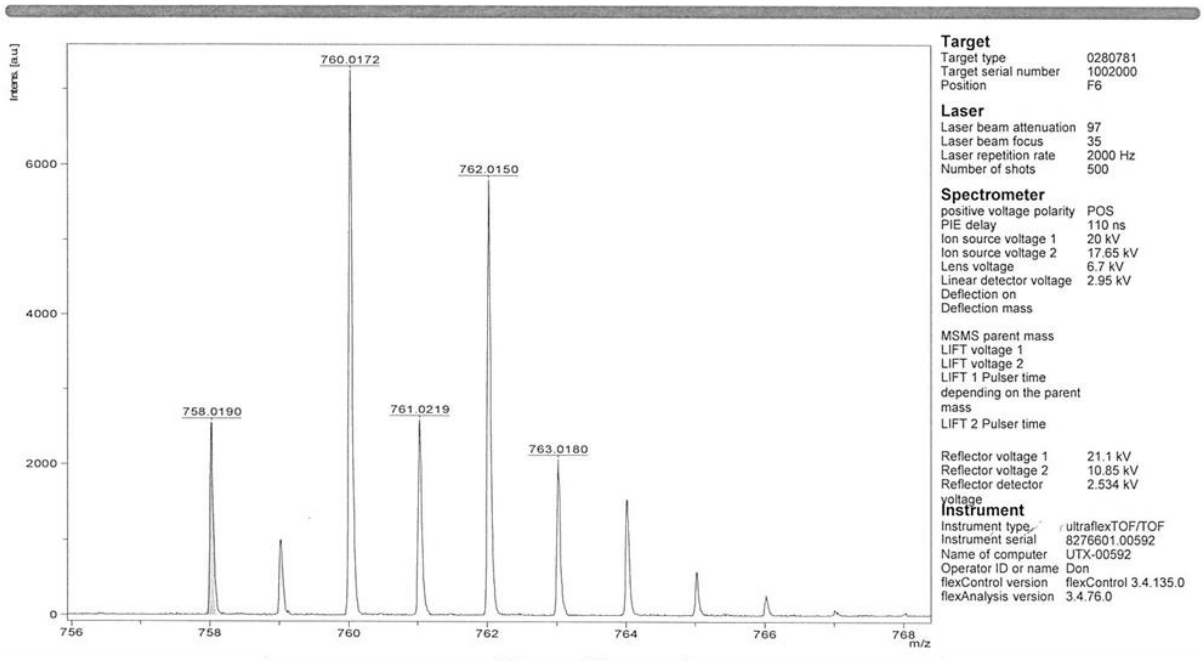


Figure S22. ^{1}H and ^{13}C NMR of **1**.

MS (MALDI)



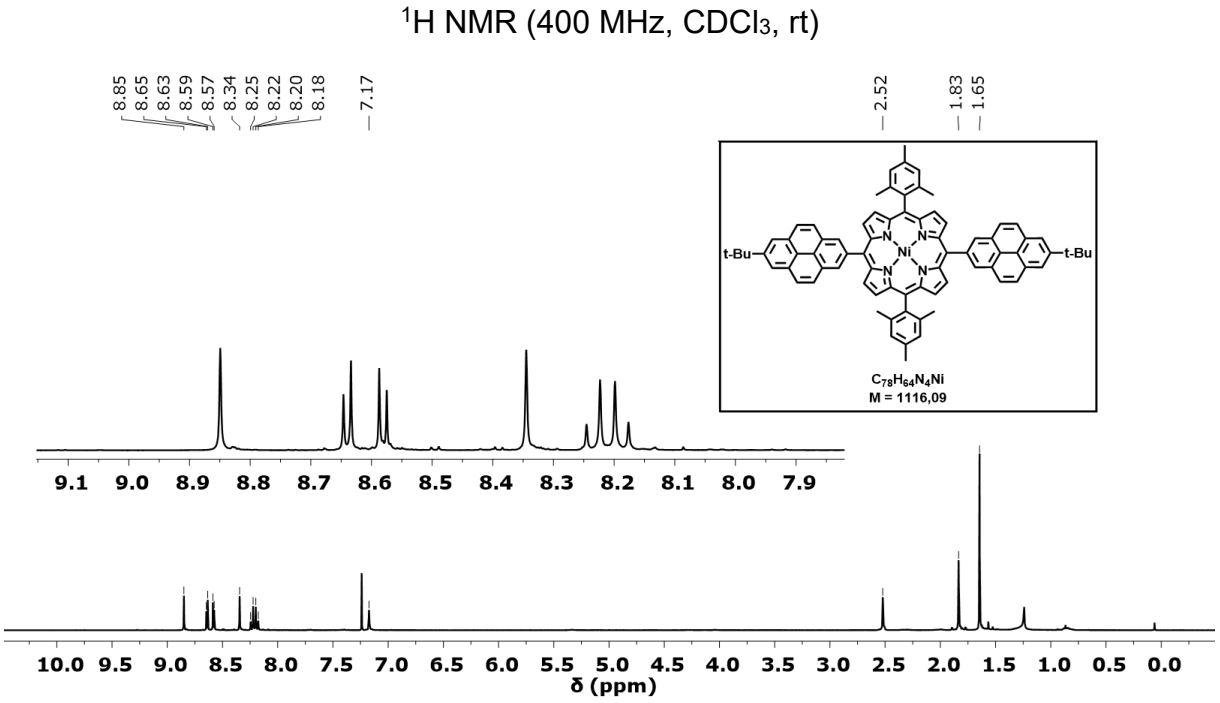
HRMS (MALDI)



SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 38 H 30 Br 2 N 4 Ni	758.0185	0.5873	108.3727	25.00	ok	odd

Figure S23. MS/HRMS (MALDI) of **1**.



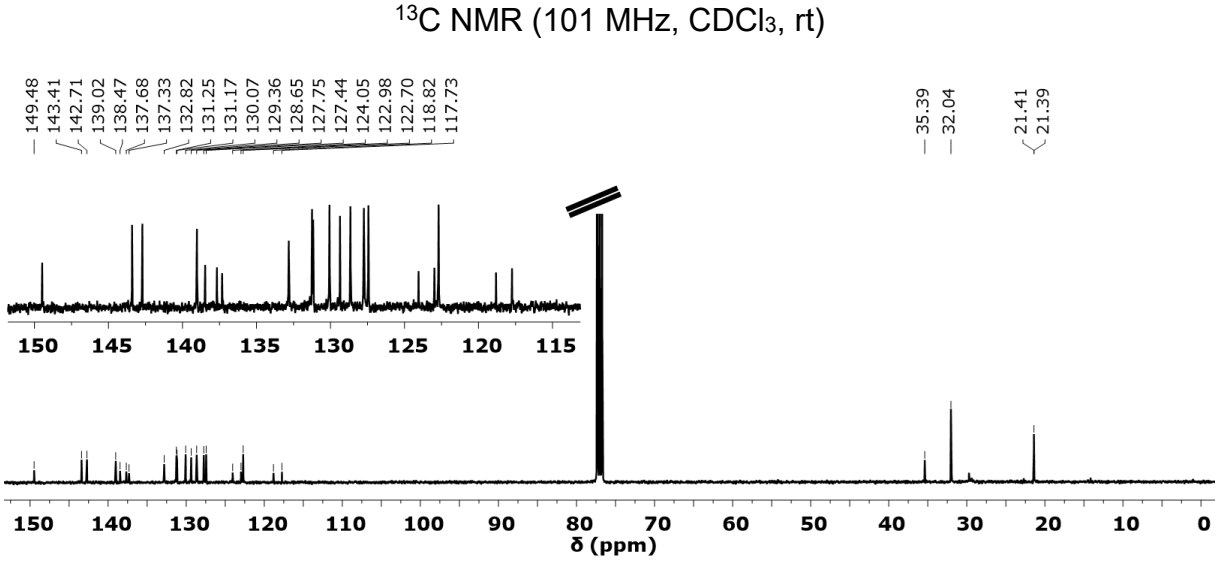
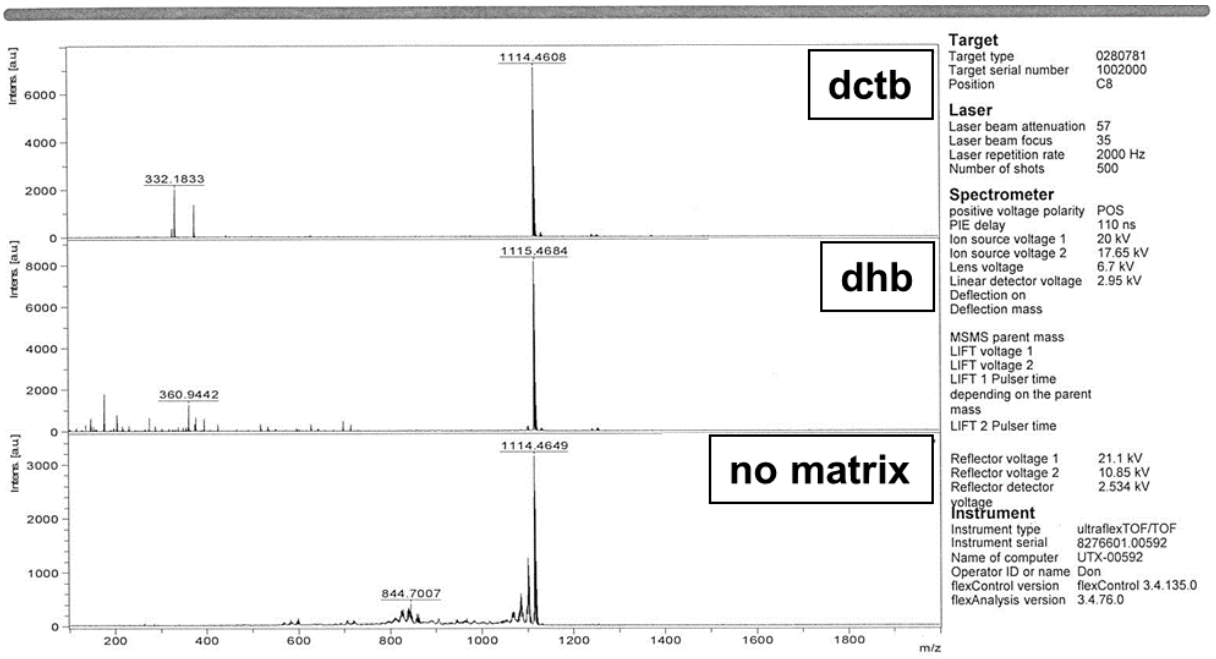
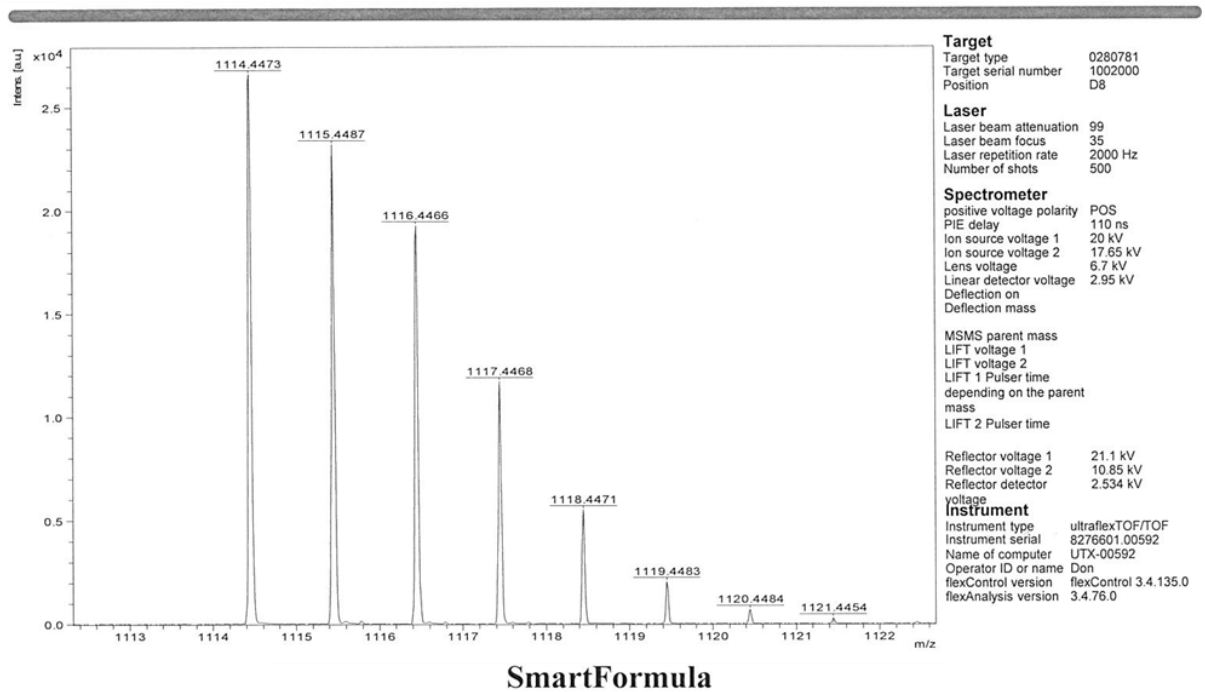


Figure S24. ^{1}H and ^{13}C NMR of **3**.

MS (MALDI)



HRMS (MALDI)

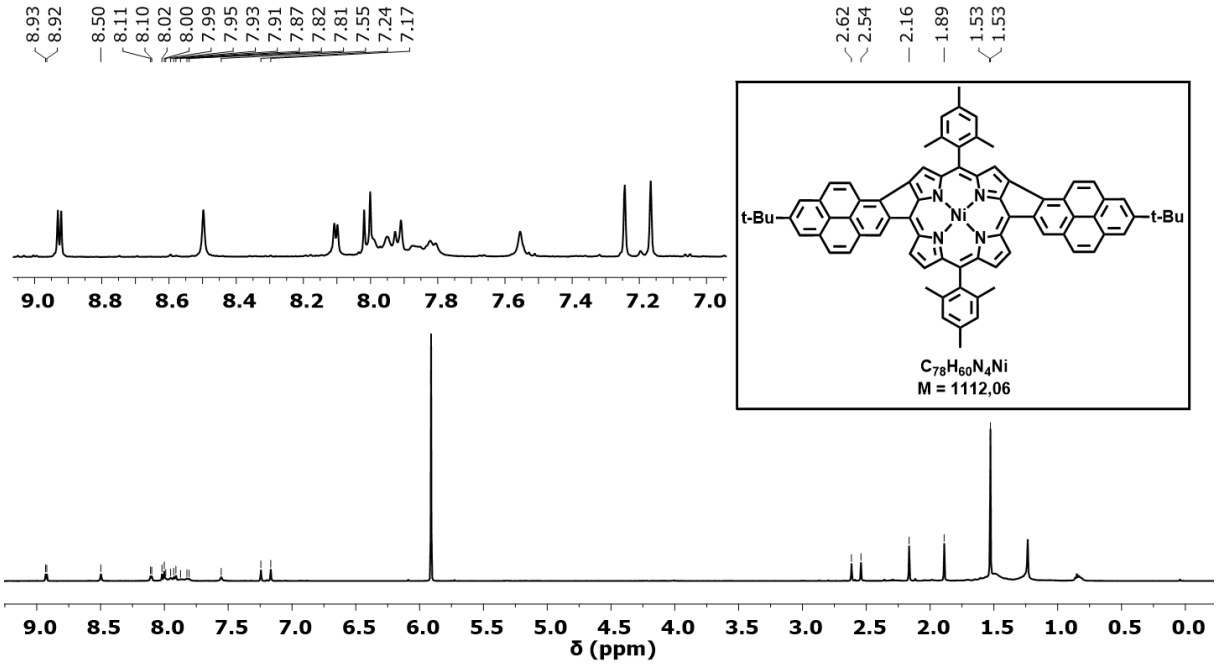


SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 78 H 64 N 4 Ni	1,114.4479	0.5233	16.9309	49.00	ok	odd

Figure S25. MS/HRMS (MALDI) of **3**.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 80°C)



^{13}C NMR - DEPTQ135 (126 MHz, $C_2D_2Cl_4$, 80°C)

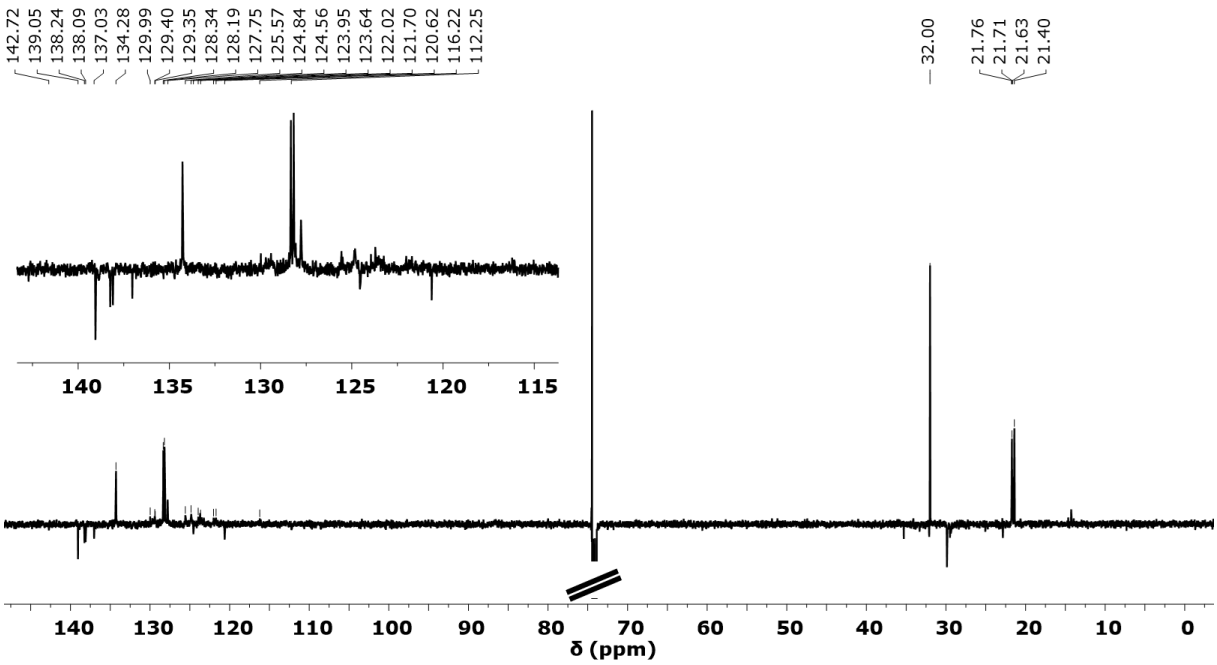


Figure S26. ^{1}H and ^{13}C NMR (DEPTQ135) of **PyrPorPyr**.

^{1}H- ^{1}H COSY (500 MHz, $C_2D_2Cl_4$, 80°C)

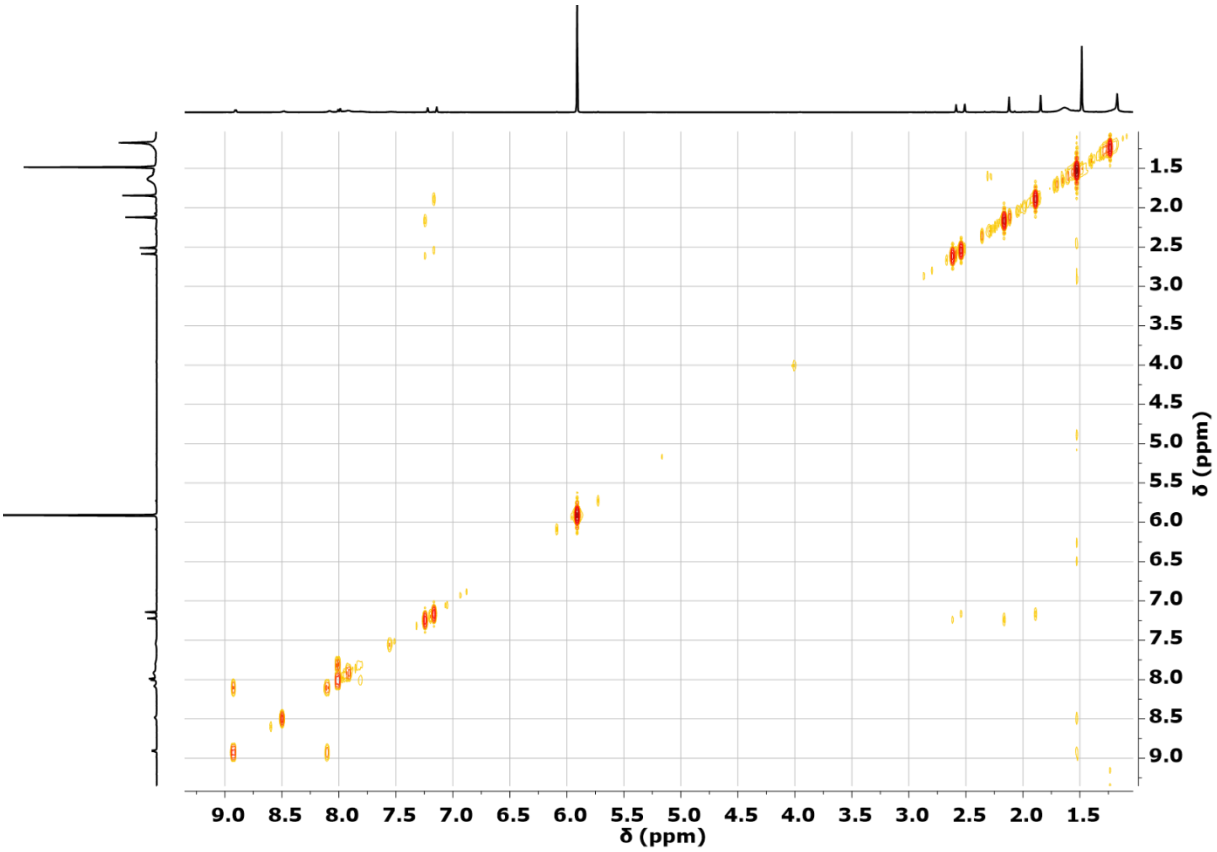


Figure S27. ^{1}H- ^{1}H COSY of **PyrPorPyr**.

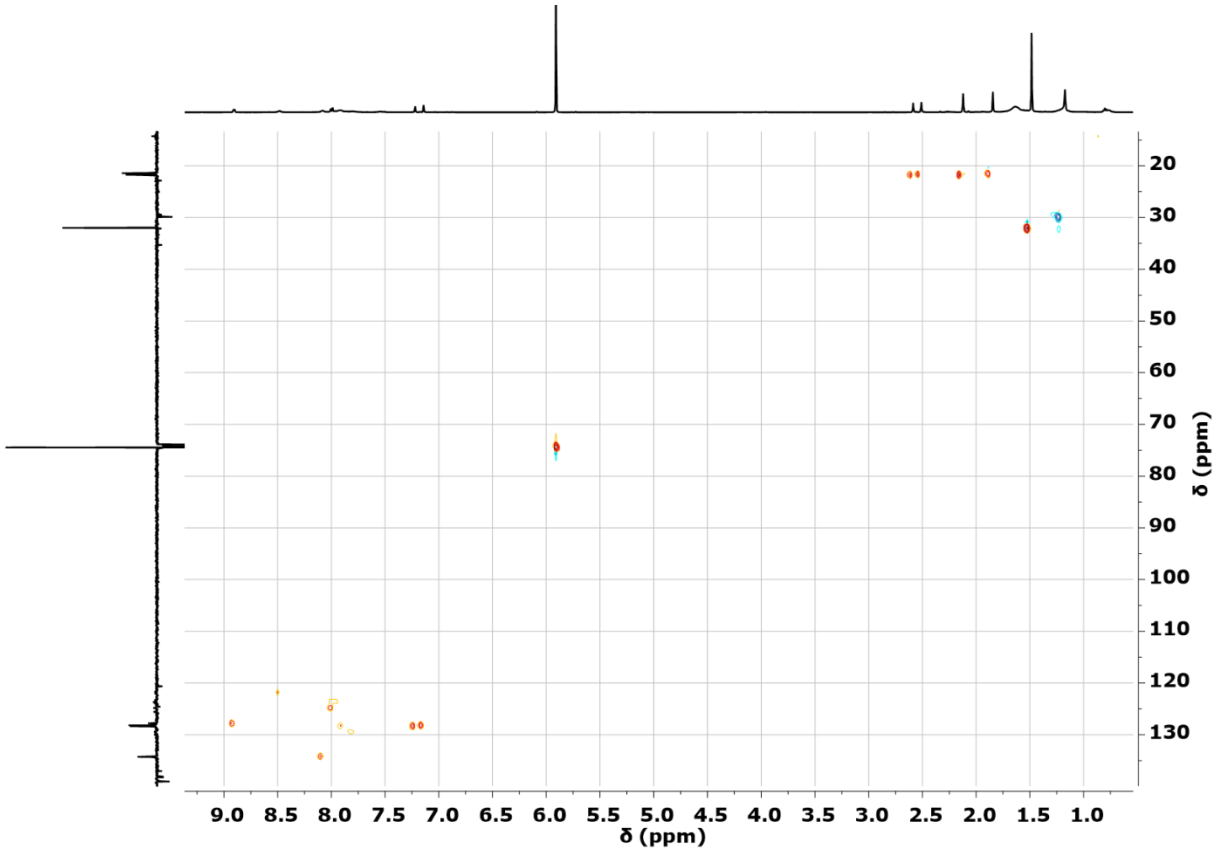


Figure S28. ^{1}H- ^{13}C HSQC of **PyrPorPyr**.

^{1}H- ^{13}C HMBC (500 MHz, $C_2D_2Cl_4$, 80°C)

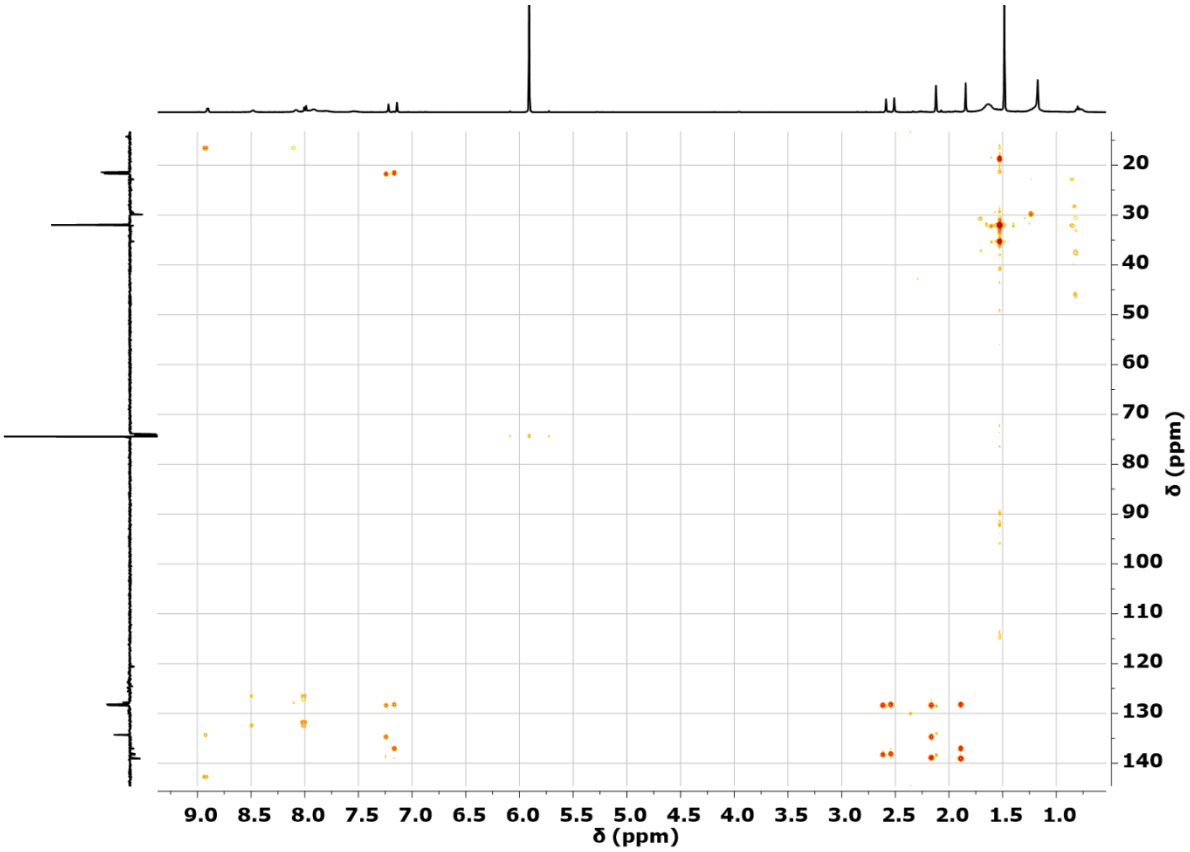
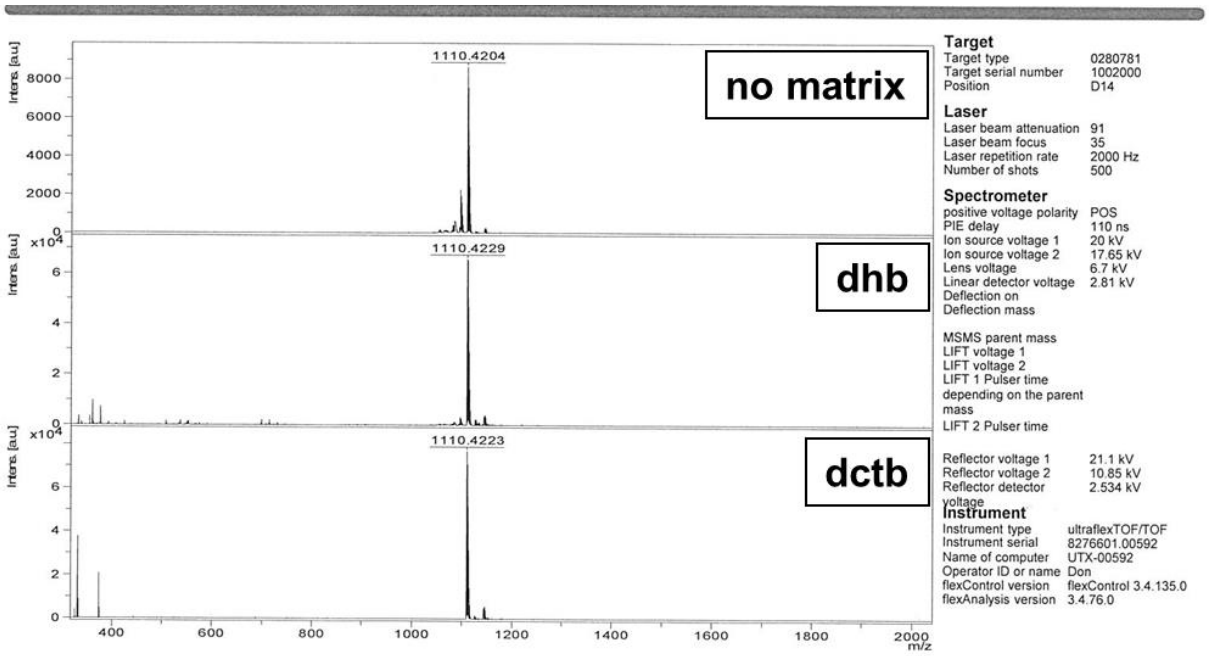
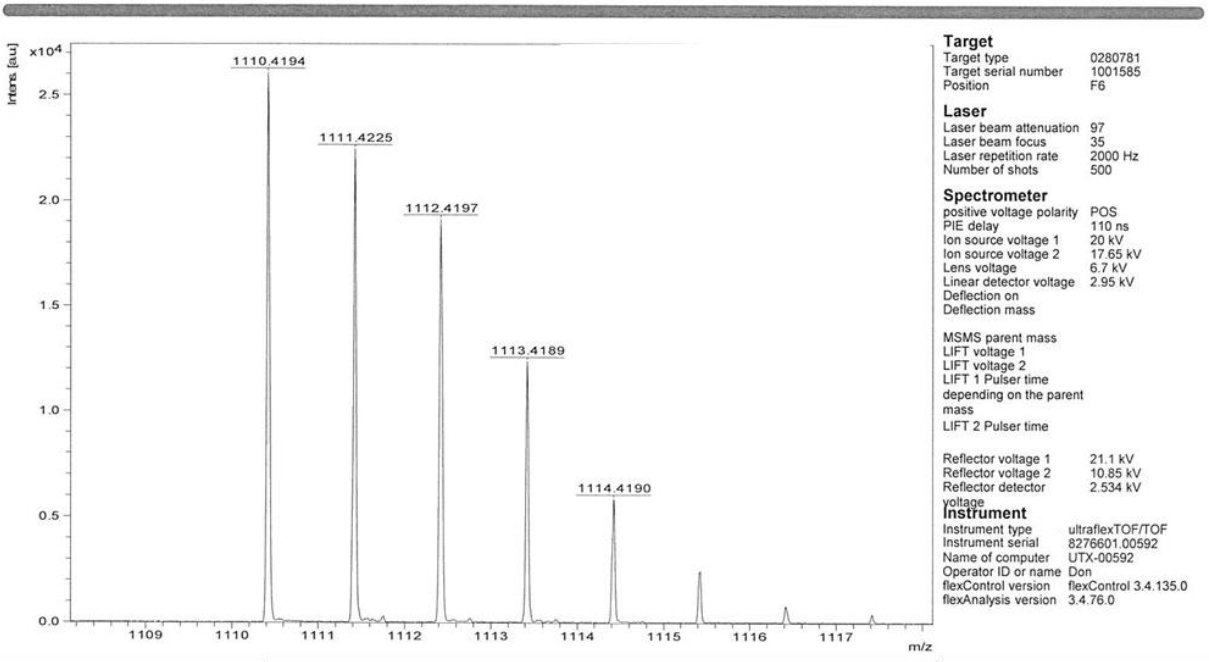


Figure S29. ^{1}H- ^{13}C HMBC of **PyrPorPyr**.

MS (MALDI)



HRMS (MALDI)

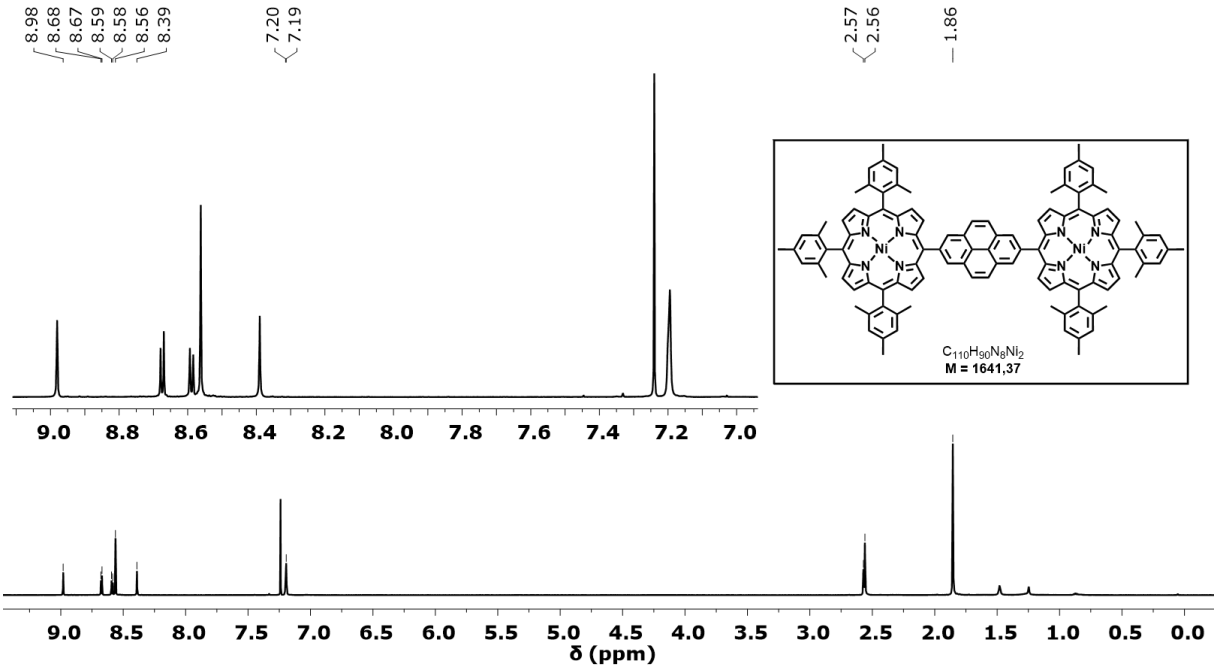


SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 78 H 60 N 4 Ni	1,110.4166	2.5010	37.2340	51.00	ok	odd

Figure S30. MS/HRMS (MALDI) of **PyrPorPyr**.

^{1}H NMR (500 MHz, $CDCl_3$, rt)



^{13}C NMR (126 MHz, $CDCl_3$, rt)

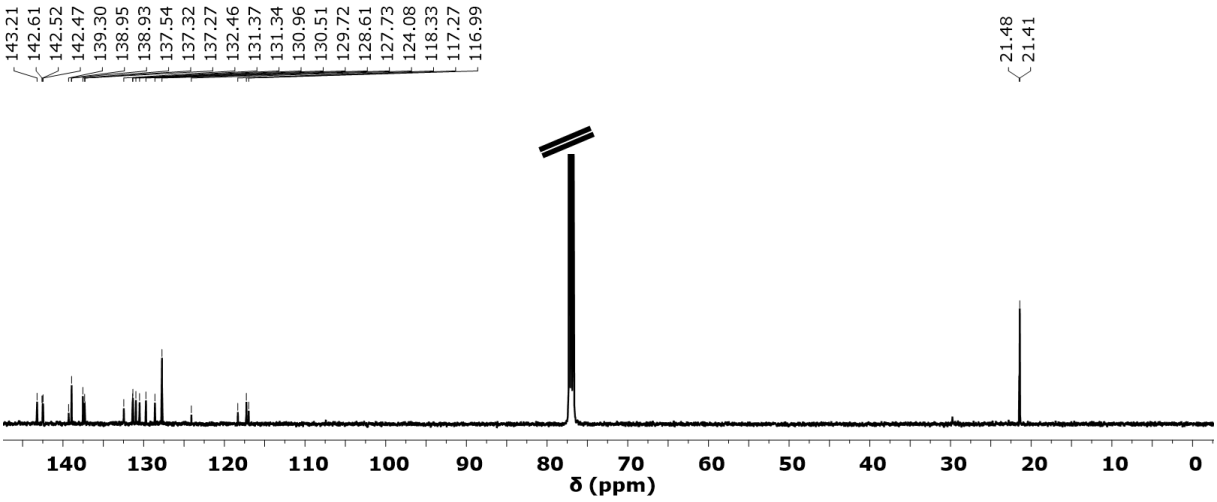
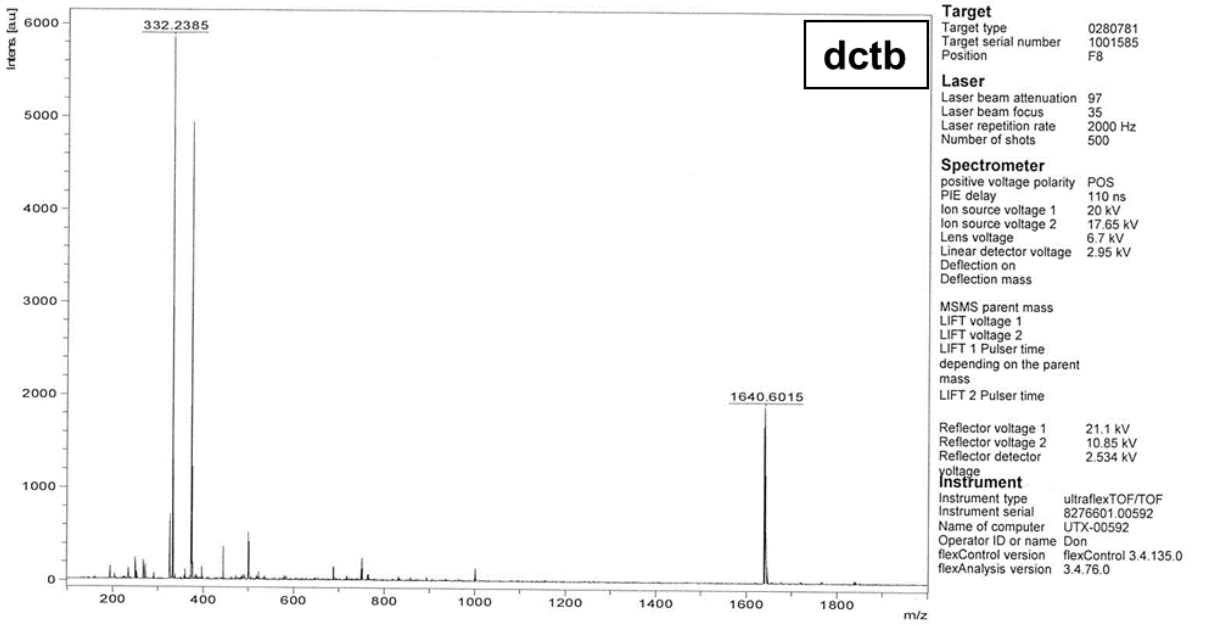
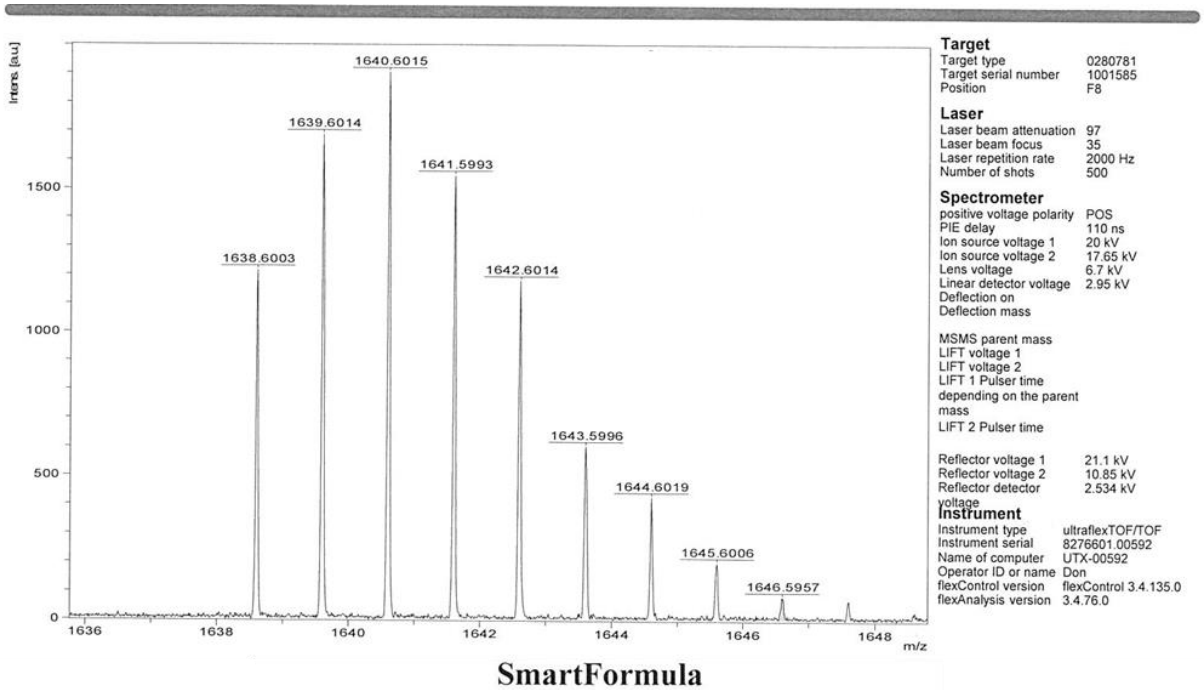


Figure S31. ^{1}H and ^{13}C NMR of **4**.

MS (MALDI)



HRMS (MALDI)

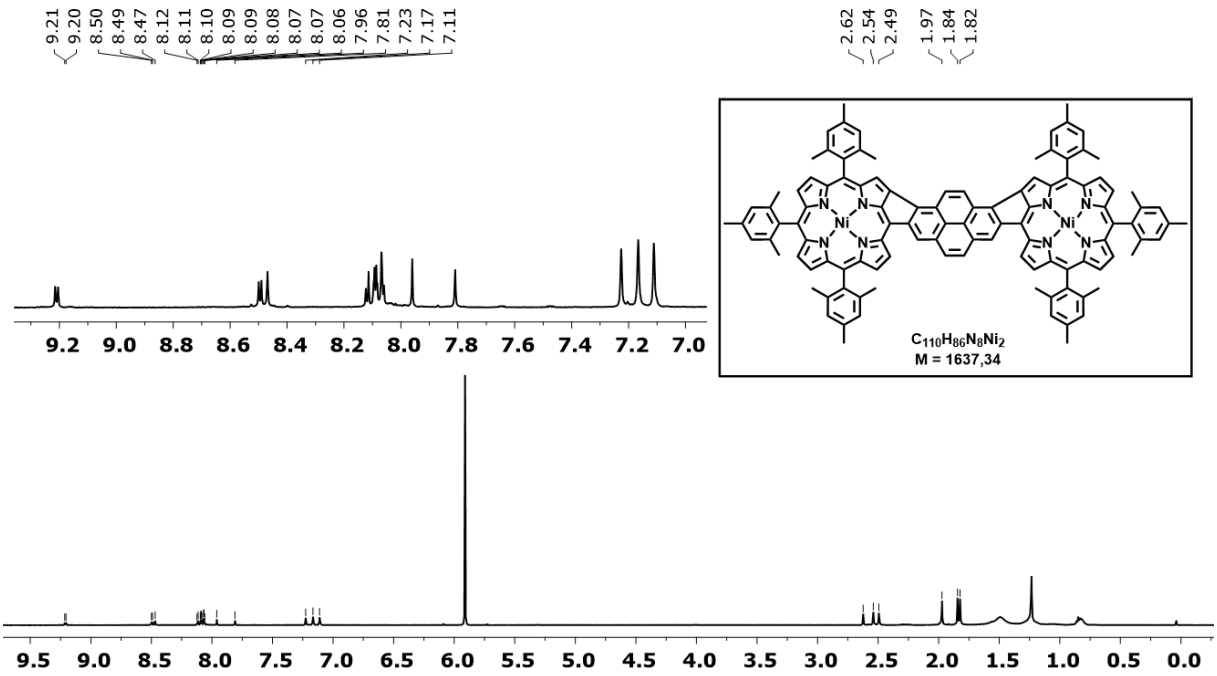


SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 110 H 90 N 8 Ni 2	1,638.5990	0.8148	87.3517	70.00	ok	odd

Figure S32. MS/HRMS (MALDI) of **4**.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 80°C)



^{13}C NMR - DEPTQ135 (126 MHz, $C_2D_2Cl_4$, 80°C)

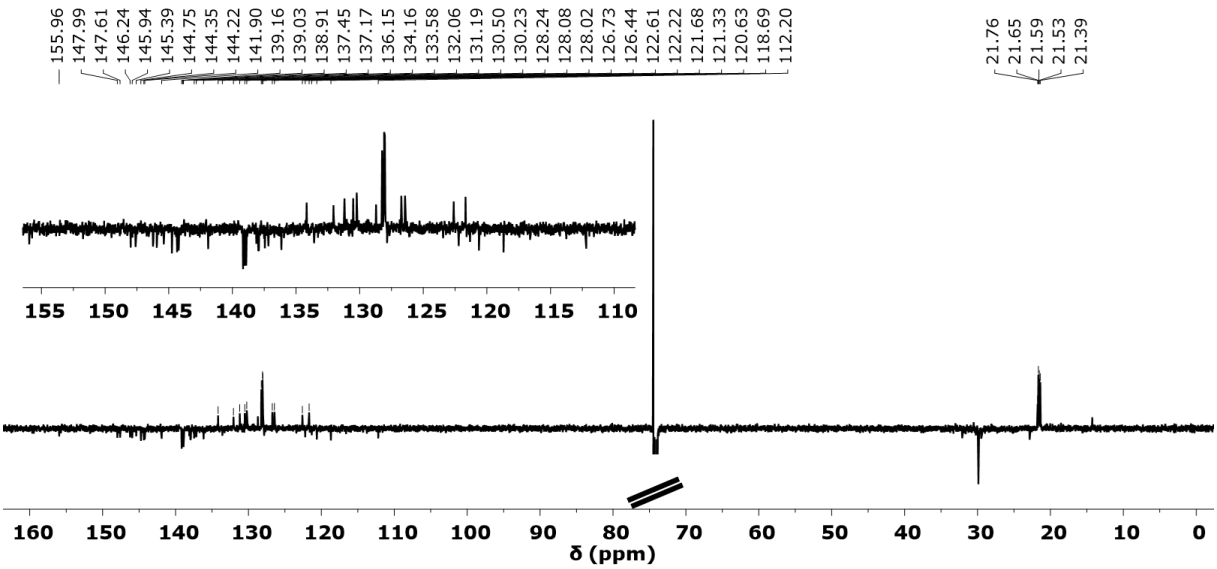


Figure S33. ^{1}H and ^{13}C NMR (DEPTQ135) of **PorPyrPor**.

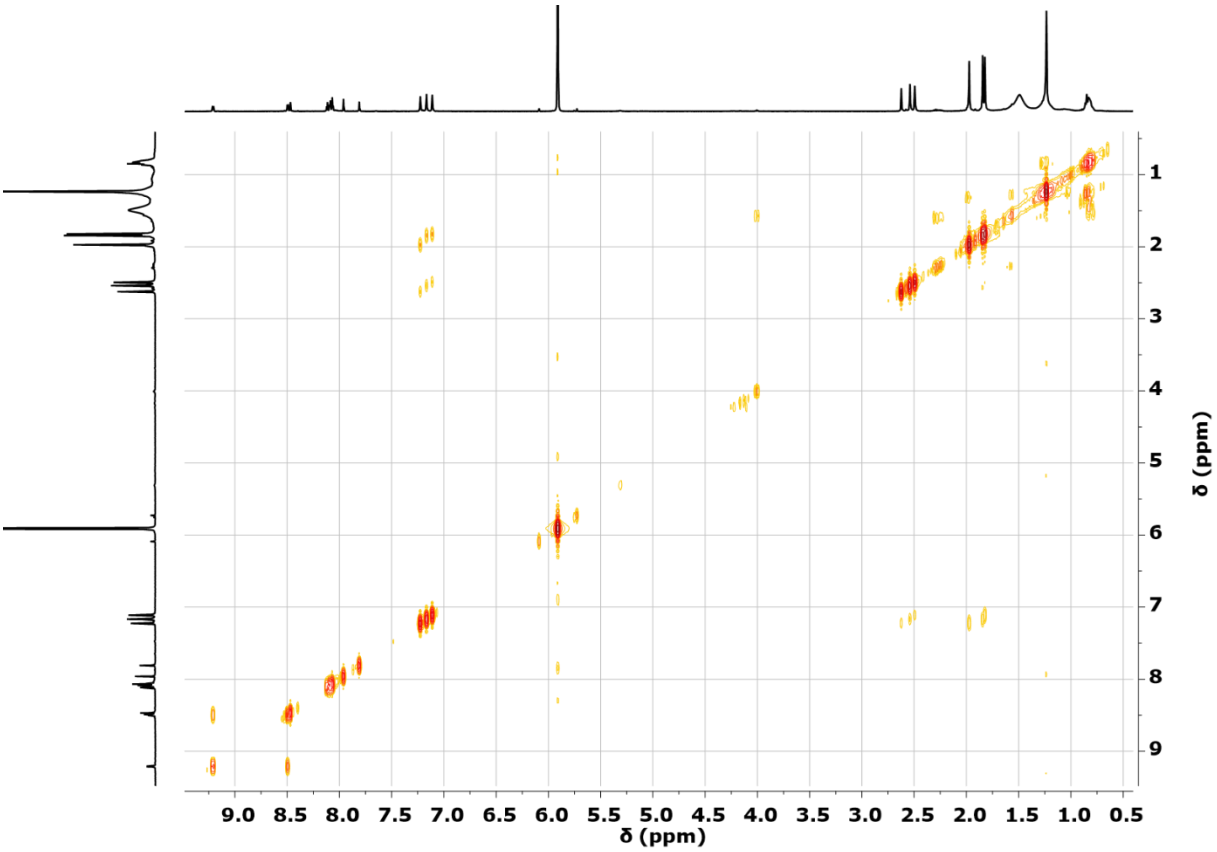


Figure S34. ^{1}H- ^{1}H COSY of **PorPyrPor**.

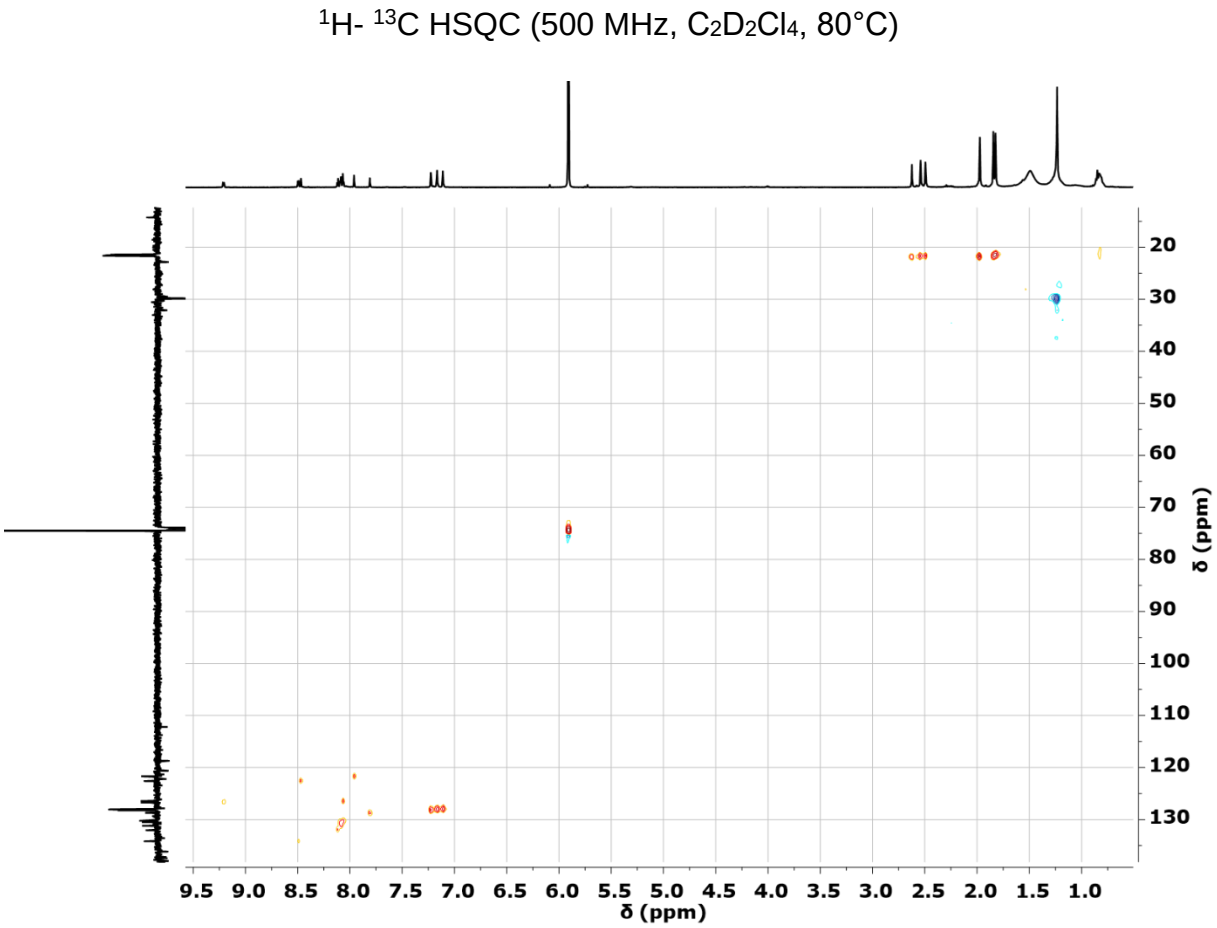


Figure S35. ^{1}H- ^{13}C HSQC of **PorPyrPor**.

^{1}H- ^{13}C HMBC (500 MHz, $C_2D_2Cl_4$, 80°C)

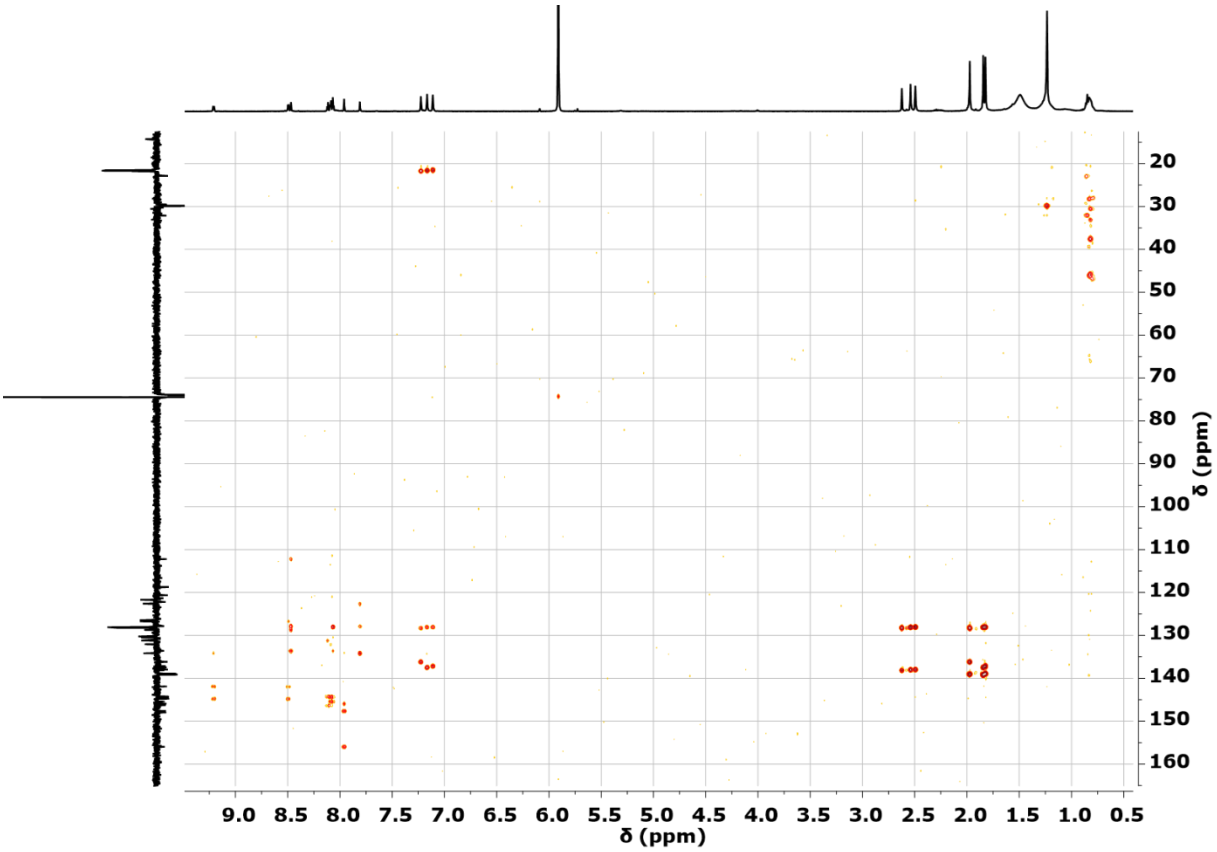
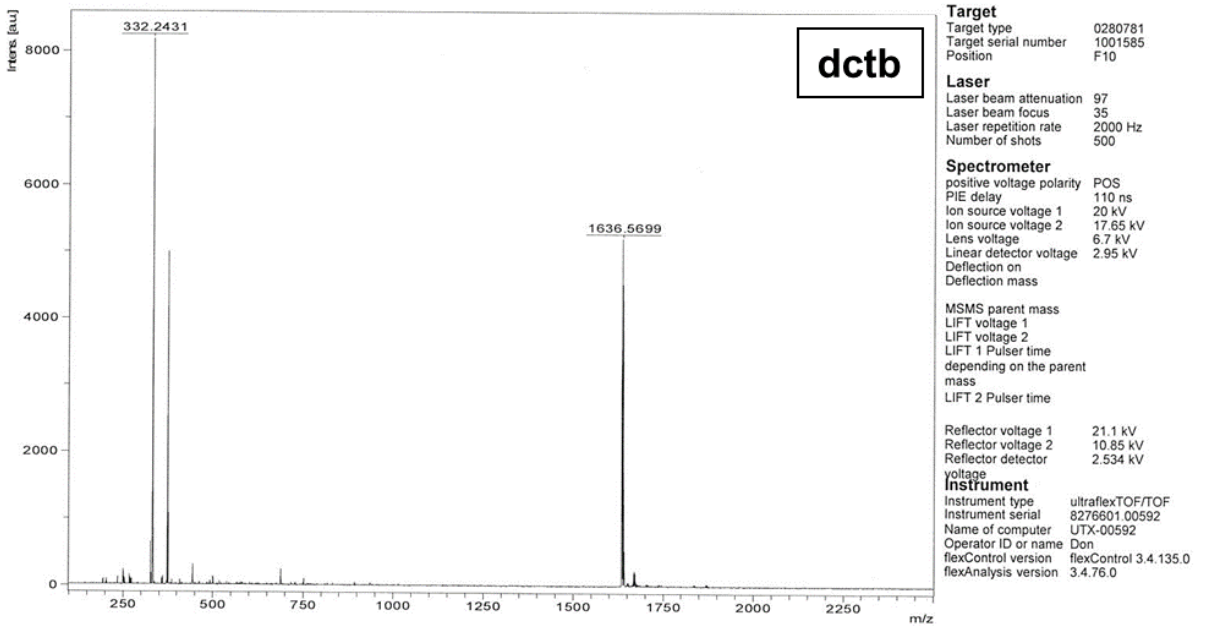
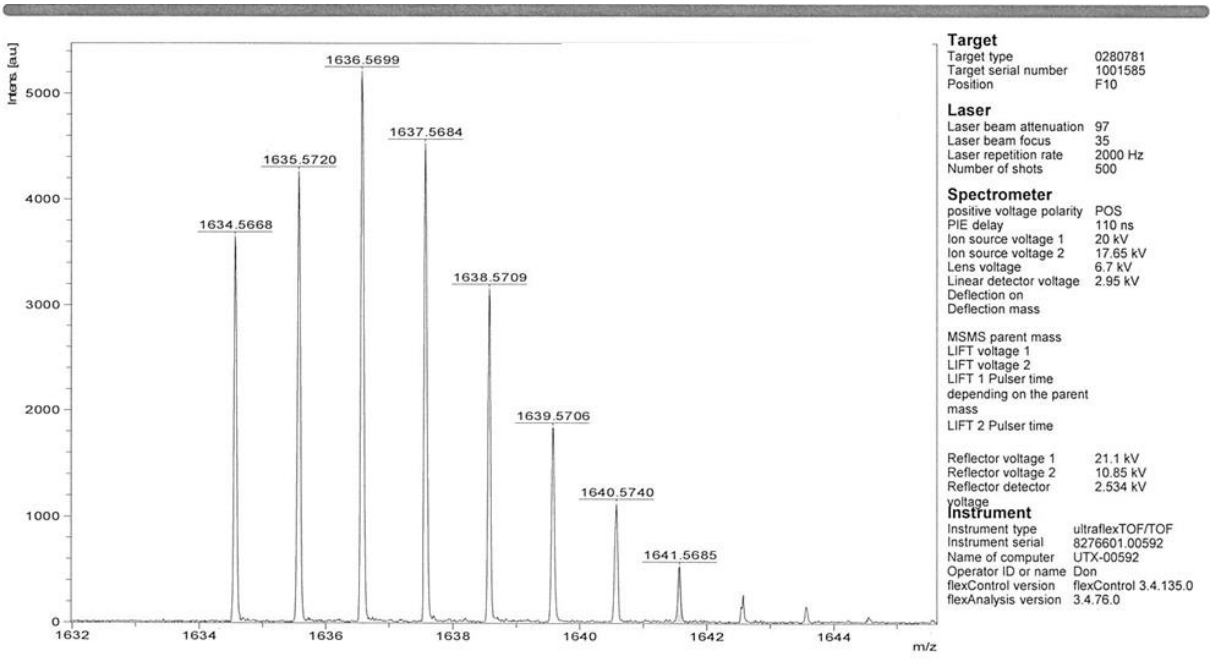


Figure S36. ^{1}H- ^{13}C HMBC of **PorPyrPor**.

MS (MALDI)



HRMS (MALDI)



SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 110 H 86 N 8 Ni 2	1,634.5677	0.5544	30.9748	72.00	ok	odd

Figure S37. MS/HRMS (MALDI) of **PorPyrPor**.

Assignment of Regiochemistry in the Double-Fused Conjugates

PyrPorPyr

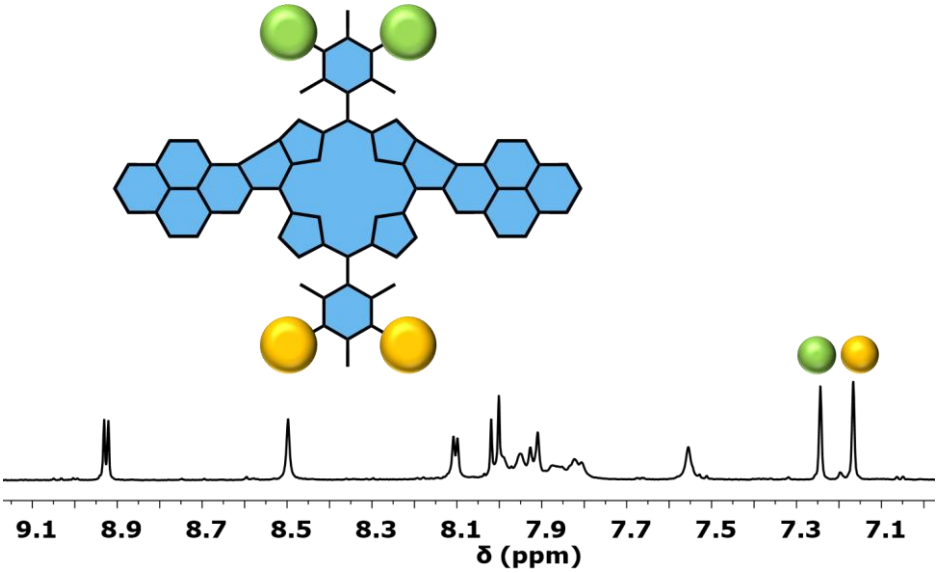


Figure S38. Aromatic region of the ^{1}H NMR spectrum of **PyrPorPyr** (500 MHz, $C_2D_2Cl_4$, 80 °C, Figure S26). Highlighted are the two signals associated with the mesitylene aromatic protons (*yellow*/*green*), which would appear as a single singlet in the case of the "*trans*"-isomer.

PorPyrPor

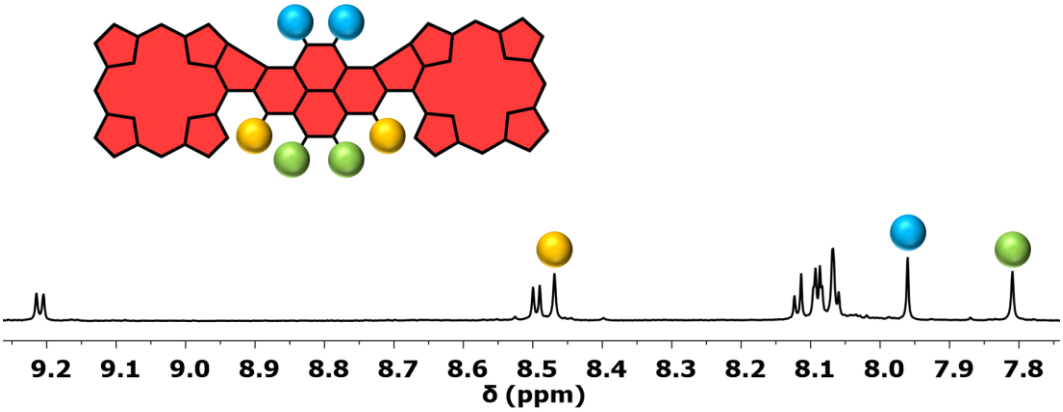


Figure S39. Aromatic region of the ^{1}H NMR spectrum of **PorPyrPor** (500 MHz, $C_2D_2Cl_4$, 80 °C, Figure S33). Highlighted are the three singlet signals associated with the pyrene protons (*yellow*/*green*/*blue*), which would appear as a mix of doublet and singlet signals in the case of the "*trans*"-isomer.

4 DFT Calculations

Geometries were relaxed using density-functional theory (DFT). The calculations were carried out with the plane-wave code PWScf of the Quantum Espresso software package,[4] utilizing the gradient-corrected Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,[5] Grimme D3 dispersion correction with Becke-Johnson damping,[6,7] Vanderbilt ultrasoft pseudopotentials,[8] and a plane-wave basis set with a kinetic energy cutoff of 30 Ry. Structures were assumed to be relaxed when a force convergence threshold of 5 meV/Å was reached.

Electronic properties were determined with the ORCA code,[9] using the B3LYP hybrid exchange-correlation functional,[10,11] the triple-zeta def2-TZVPP basis set,[12] and the RIJCOSX approximation with def2/J auxiliary basis functions.[13] Time-dependent density functional theory (TD-DFT) was used for the calculation of absorption spectra, utilizing the same settings but changing to the CAM-B3LYP long-range corrected hybrid exchange-correlation functional.[14] The lowest 150 vertical transitions were included in the TD-DFT calculations. In Figures S43-S45, the transitions were shifted by 80 nm to higher wavelengths to facilitate comparison. Solvation effects in DCM were taken into account by employing the implicit conductor-like continuum polarization model (C-PCM).

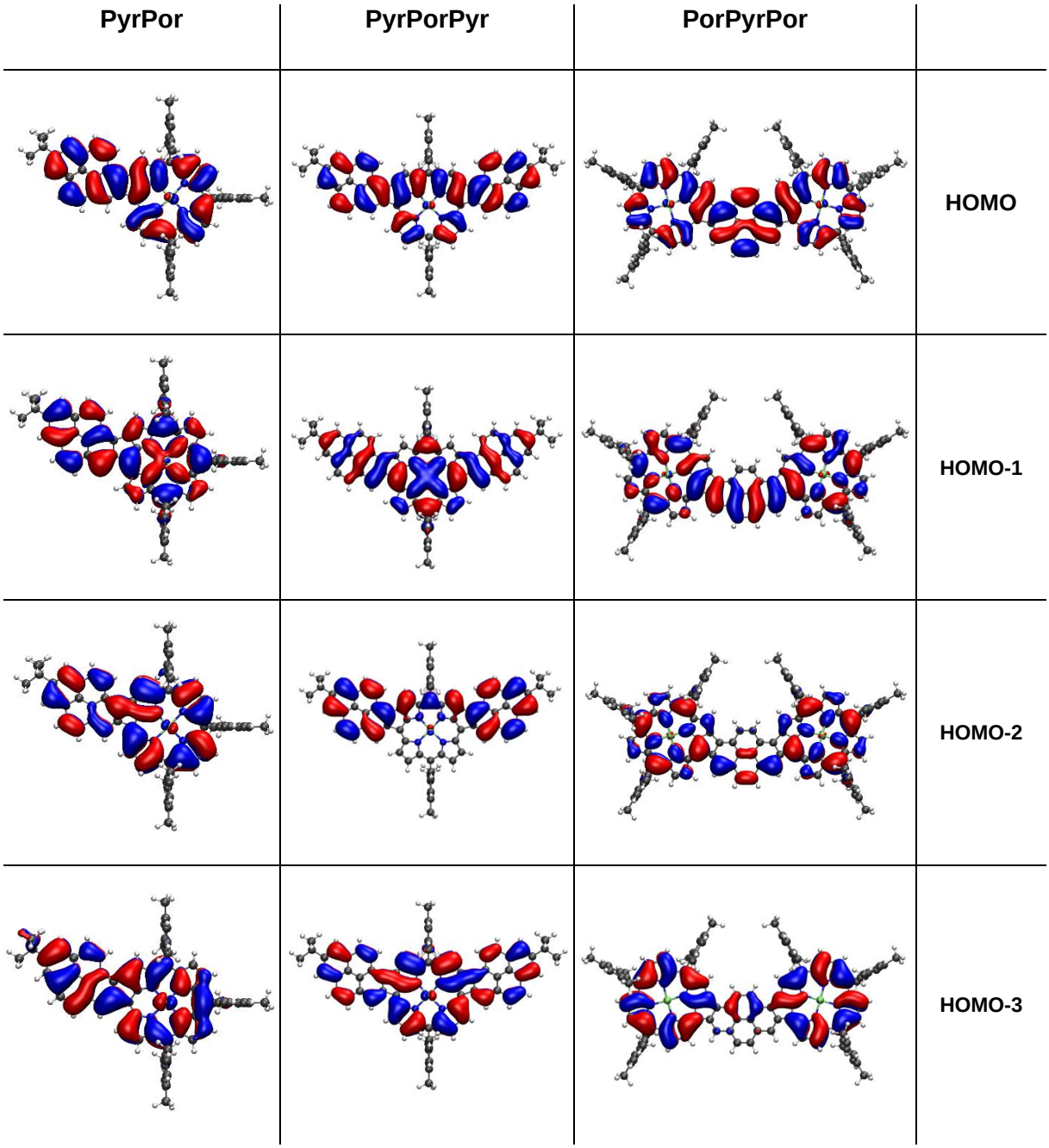


Figure S40. Optimized structures and orbitals of **PyrPor**, **PyrPorPyr** and **PorPyrPor**.

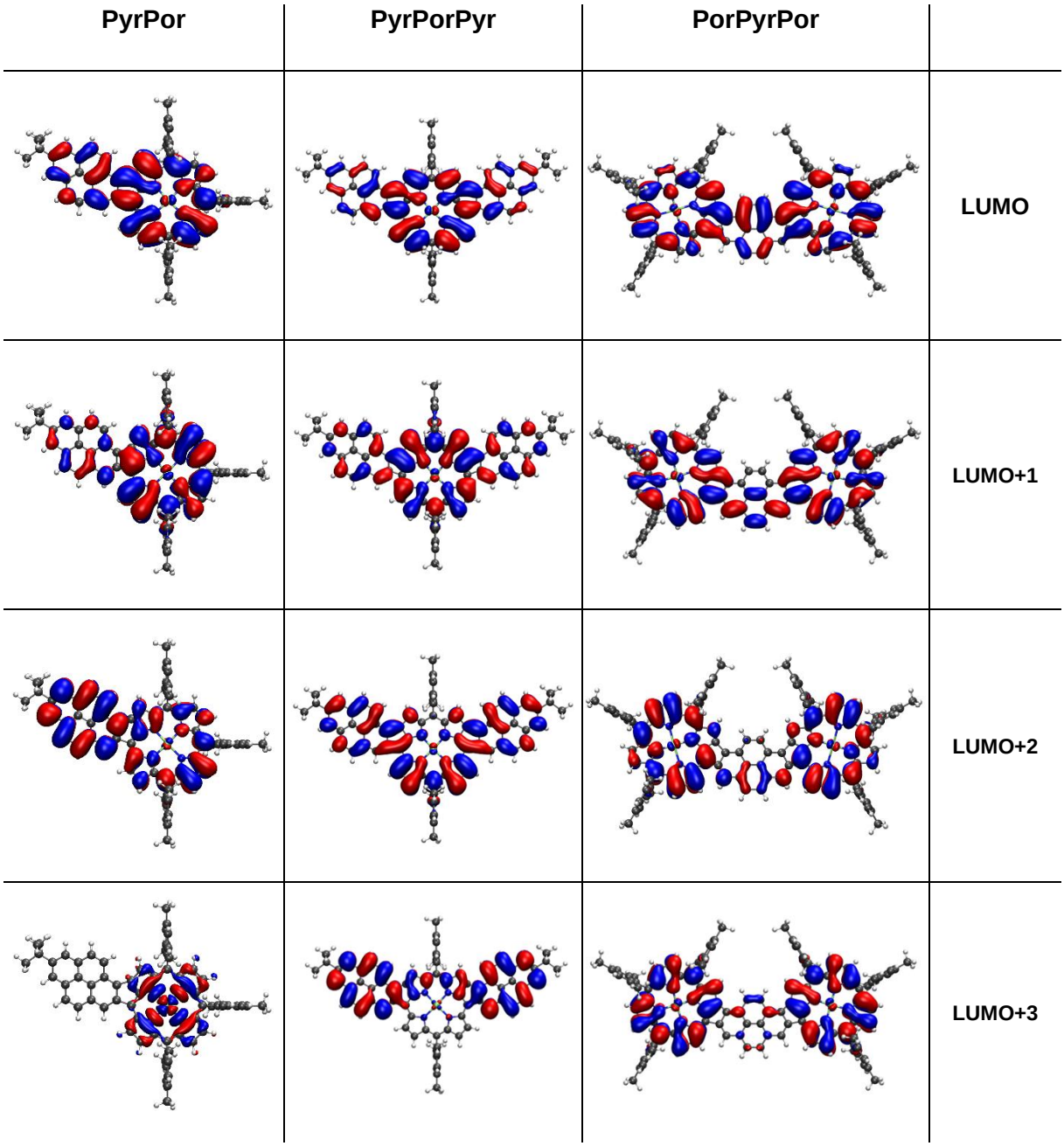


Figure S41. Geometry optimized structures and orbitals of **PyrPor**, **PyrPorPyr** and **PorPyrPor**.

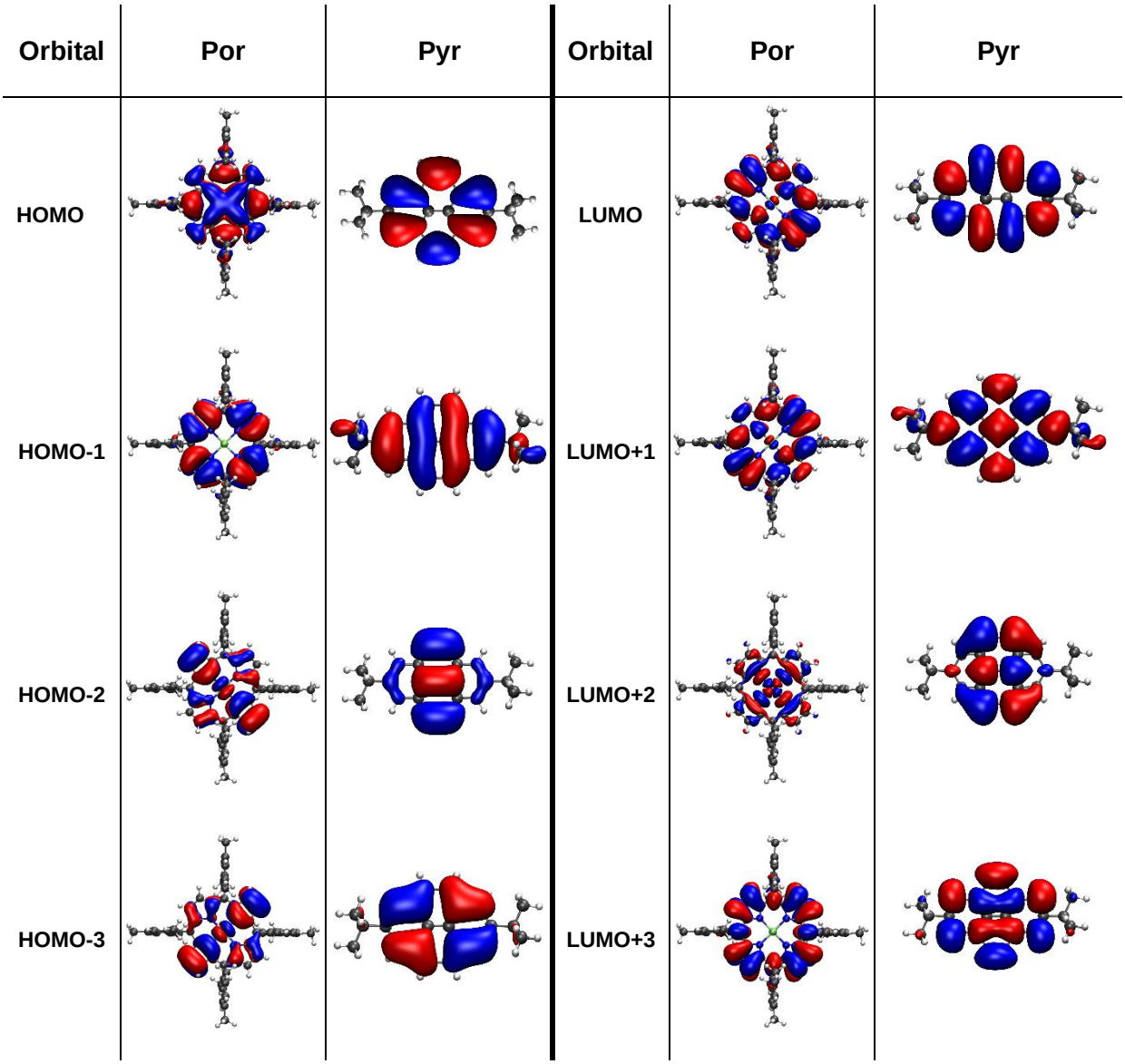


Figure S42. Geometry optimized structures and orbitals of **Por** and **Pyr**.

Table S1. Energy eigenvalues of selected orbitals of **PyrPor**, **PyrPorPyr**, **PorPyrPor**, **Por**, and **Pyr**.

	PyrPor	**PyrPorPyr**	**PorPyrPor**	**Por**	**Pyr**
Orbital	Energy (eV)	Energy (eV)	Energy (eV)	Energy (eV)	Energy (eV)
HOMO-3	-6.260	-5.884	-5.604	-6.273	-7.528
HOMO-2	-5.755	-5.440	-5.509	-6.272	-7.039
HOMO-1	-5.379	-5.331	-5.160	-5.478	-6.145
HOMO	-5.118	-4.997	-5.054	-5.411	-5.458
LUMO	-2.842	-3.082	-2.904	-2.441	-1.706
LUMO+1	-2.531	-2.665	-2.859	-2.439	-0.823
LUMO+2	-1.763	-1.985	-2.534	-1.503	-0.431
LUMO+3	-1.610	-1.739	-2.467	-0.945	0.164
GAP	2.276	1.916	2.150	2.970	3.752

Table S2. TD-DFT excitation energies and oscillator strengths of **PyrPor**.

Excited state	Energy (nm)	Energy (eV)	Oscillator strength *f*	Excited state	Energy (nm)	Energy (eV)	Oscillator strength *f*
1	621.1	1.996	0.0477	16	320.4	3.870	0.0031
2	579.0	2.141	0.0001	17	319.1	3.886	0.1737
3	557.1	2.226	0.0003	18	316.2	3.921	0.2592
4	555.1	2.233	0.0001	19	312.0	3.974	0.0003
5	551.5	2.248	0.0273	20	309.3	4.009	0.2016
6	470.0	2.638	0.0025	21	308.2	4.023	0.0226
7	453.6	2.734	0.6347	22	301.0	4.119	0.0219
8	412.9	3.002	2.8786	23	300.6	4.124	0.0566
9	389.3	3.185	0.2555	24	298.5	4.154	0.0003
10	363.9	3.407	0.0870	25	297.6	4.166	0.4073
11	362.7	3.419	0.6342	26	292.6	4.237	0.0633
12	355.4	3.488	0.2447	27	289.2	4.287	0.0023
13	341.1	3.635	0.2075	28	287.9	4.307	0.0002
14	337.1	3.678	0.5961	29	287.2	4.317	0.0045
15	336.1	3.689	0.0325	30	286.5	4.327	0.0930

Table S3. Orbital transitions and their relative contributions to optically active excitations with large oscillator strengths from the TD-DFT calculations of **PyrPor**. Only transitions with contributions exceeding 10% are listed.

State	Energy (eV)	Transition	Contribution (%)
1	1.996	HOMO → LUMO	79.5
5	2.248	HOMO-1 → LUMO	42.7
		HOMO → LUMO+1	38.7
7	2.734	HOMO-2 → LUMO	32.6
		HOMO-1 → LUMO	14.1
		HOMO-1 → LUMO+1	26.7
8	3.002	HOMO-1 → LUMO	27.2
		HOMO → LUMO+1	47.5
9	3.185	HOMO-2 → LUMO	21.3
		HOMO-2 → LUMO+1	21.3
		HOMO → LUMO+2	14.2
11	3.419	HOMO-10 → LUMO	14.7
		HOMO-2 → LUMO+1	16.0
		HOMO-1 → LUMO+1	20.7

Table S4. TD-DFT excitation energies and oscillator strengths of **PyrPorPyr**.

Excited state	Energy (nm)	Energy (eV)	Oscillator strength *f*	Excited state	Energy (nm)	Energy (eV)	Oscillator strength *f*
1	695.9	1.782	0.0787	16	356.8	3.475	0.0002
2	640.8	1.935	0.0106	17	349.0	3.552	0.3885
3	583.7	2.124	0.0027	18	341.7	3.628	0.214
4	560.9	2.210	0.0001	19	337.5	3.673	0.4016
5	558.7	2.219	0	20	333.9	3.713	0.0026
6	482.6	2.569	1.681	21	330.0	3.757	0.8072
7	481.9	2.573	0.0182	22	327.4	3.787	0.0317
8	467.2	2.654	0.3603	23	323.8	3.829	0.0214
9	459.8	2.696	2.7695	24	316.3	3.920	0.0008
10	410.8	3.018	0.1265	25	310.2	3.997	0.003
11	380.7	3.257	0.0144	26	309.2	4.010	0.0001
12	375.4	3.303	0.1977	27	306.1	4.050	0.0006
13	374.6	3.310	0.8134	28	301.6	4.111	0.0226
14	369.9	3.352	0.0467	29	300.8	4.121	0.1404
15	363.0	3.415	0.0001	30	298.8	4.150	0.0409

Table S5. Orbital transitions and their relative contributions to optically active excitations with large oscillator strengths from the TD-DFT calculations of **PyrPorPyr**. Only transitions with contributions exceeding 10% are listed.

State	Energy (eV)	Transition	Contribution (%)
1	1.782	HOMO → LUMO	86.5
2	1.935	HOMO-1 → LUMO	55.6
		HOMO → LUMO+1	32.0
6	2.569	HOMO-2 → LUMO	62.8
		HOMO-1 → LUMO	13.3
8	2.654	HOMO-26 → LUMO+5	56.8
9	2.696	HOMO-1 → LUMO	17.6
		HOMO → LUMO+1	46.2
10	3.018	HOMO-3 → LUMO	48.8
12	3.303	HOMO-10 → LUMO	55.9
13	3.310	HOMO-11 → LUMO	12.3
		HOMO-4 → LUMO	46.3
		HOMO-1 → LUMO+1	17.4

Table S6. TD-DFT excitation energies and oscillator strengths of **PorPyrPor**.

Excited state	Energy (nm)	Energy (eV)	Oscillator strength *f*	Excited state	Energy (nm)	Energy (eV)	Oscillator strength *f*
1	631.3	1.964	0.1619	16	427.5	2.900	0.2136
2	610.3	2.032	0.0545	17	385.3	3.218	0.2256
3	588.7	2.106	0.0002	18	381.9	3.247	0.2634
4	587.3	2.111	0.0001	19	375.8	3.299	0.2197
5	564.3	2.197	0.0012	20	370.2	3.349	0.1118
6	563.4	2.201	0.0005	21	368.4	3.365	0.0005
7	562.3	2.205	0.0004	22	367.0	3.378	0.0007
8	561.7	2.207	0.0001	23	360.1	3.443	0.023
9	560.7	2.211	0.0001	24	356.5	3.477	0.9216
10	548.2	2.261	0.2791	25	355.2	3.490	0.5999
11	483.4	2.565	4.1504	26	354.0	3.502	0.0281
12	471.3	2.631	0.0134	27	347.9	3.564	0.0039
13	470.6	2.634	0.0136	28	345.8	3.585	0.1231
14	460.2	2.694	0	29	339.7	3.649	0.0008
15	432.6	2.866	1.1423	30	339.6	3.650	0.0007

Table S7. Orbital transitions and their relative contributions to optically active excitations with large oscillator strengths from the TD-DFT calculations of **PorPyrPor**. Only transitions with contributions exceeding 10% are listed.

State	Energy (eV)	Transition	Contribution (%)
1	1.964	HOMO-1 → LUMO+1	33.5
		HOMO → LUMO	47.2
2	2.032	HOMO-2 → LUMO+1	11.3
		HOMO-1 → LUMO	35.2
		HOMO → LUMO+1	25.8
10	2.261	HOMO-3 → LUMO+1	23.5
		HOMO-2 → LUMO	20.7
		HOMO-1 → LUMO+3	18.2
		HOMO → LUMO+2	17.2
11	2.565	HOMO-2 → LUMO+2	11.1
		HOMO-1 → LUMO+1	21.6
		HOMO-1 → LUMO+3	11.1
		HOMO → LUMO	26.5
15	2.866	HOMO-5 → LUMO+1	12.1
		HOMO-4 → LUMO	16.0
		HOMO-3 → LUMO+3	16.0
		HOMO → LUMO+2	27.5
16	2.900	HOMO-3 → LUMO+2	15.0
		HOMO-1 → LUMO	23.9
		HOMO-1 → LUMO+4	11.6
		HOMO → LUMO+3	15.5

Calculated Absorption Spectra

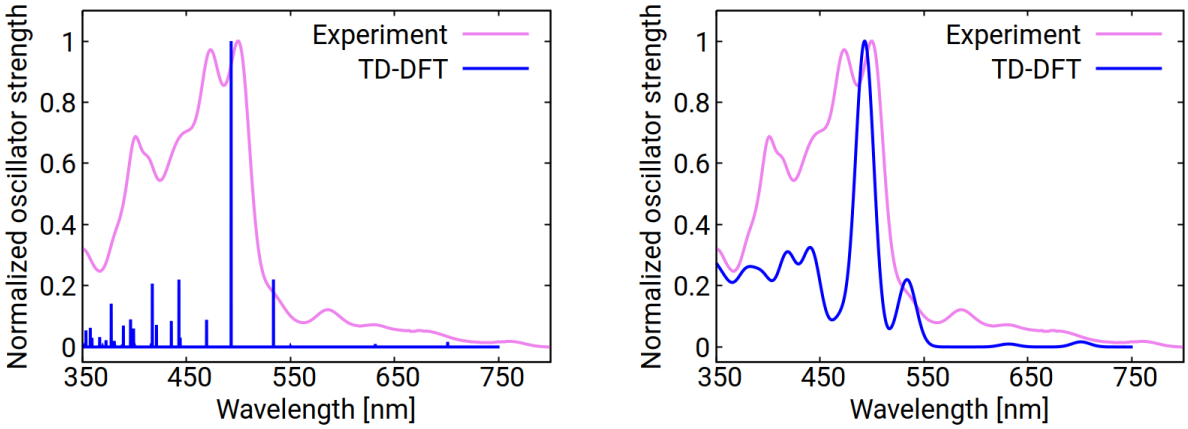


Figure S43. *Left*: Experimental UV/Vis spectrum overlaid with the TD-DFT calculated transitions for **PyrPor** (line spectrum). *Right:* The calculated transitions are broadened by a Gaussian function with a width of 10 nm.

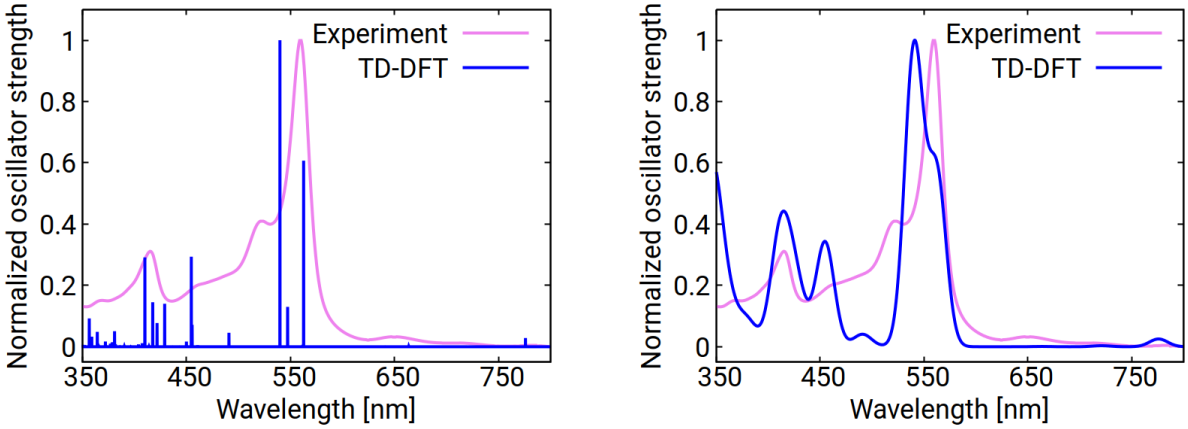


Figure S44. *Left*: Experimental UV/Vis spectrum overlaid with the TD-DFT calculated transitions for **PyrPorPyr** (line spectrum). *Right:* The calculated transitions are broadened by a Gaussian function with a width of 10 nm.

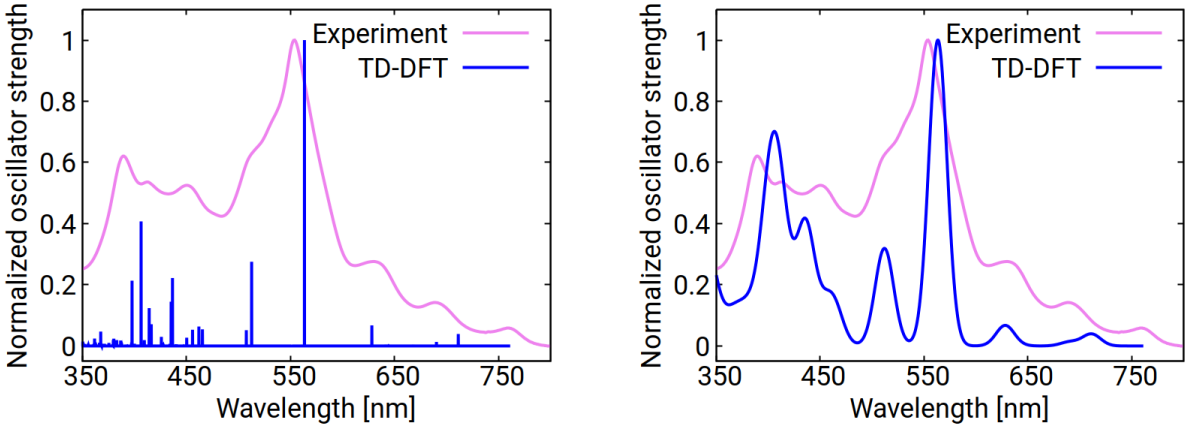


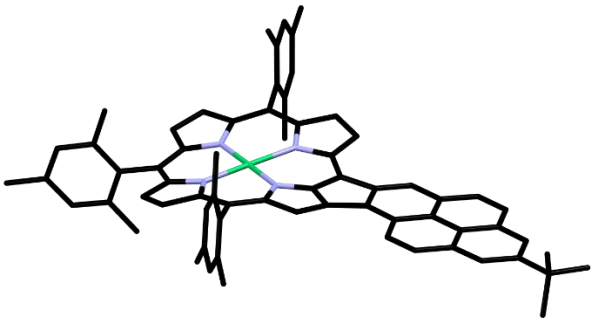
Figure S45. *Left*: Experimental UV/Vis spectrum overlaid with the TD-DFT calculated transitions for **PorPyrPor** (line spectrum). *Right:* The calculated transitions are broadened by a Gaussian function with a width of 10 nm.

Cartesian Coordinates of Calculated Structures

Fused Mono-Pyrene-Porphyrin PyrPor

Cartesian Coordinates (Angstroms)

	X	Y	Z
C	15.71756	26.38787	21.80199
C	15.64243	26.41442	23.24047
C	15.69400	27.62231	23.94544
C	15.82437	28.84123	23.19670
C	15.90287	28.80974	21.77067
C	15.85039	27.56793	21.09081
C	15.62792	27.69748	25.37589
C	15.68278	28.89700	26.02575
C	15.80903	30.13283	25.30647
C	15.88035	30.08612	23.87994
C	16.03524	30.04610	21.06694
C	16.08625	31.24543	21.72740
C	16.01091	31.30721	23.15356
C	16.06435	32.52778	23.85769
C	15.99637	32.58378	25.25120
C	15.86880	31.37295	25.95429
H	15.92603	27.57055	20.00287
H	16.09559	30.01733	19.97648
H	16.18719	32.17872	21.16878
H	15.53601	26.77026	25.94289
H	15.63409	28.93461	27.11657
H	16.16374	33.44357	23.27398
H	15.81479	31.38086	27.04543
C	16.06129	33.90354	26.03082
C	14.77517	34.06454	26.86785
H	13.88813	34.09303	26.21811
H	14.64554	33.23611	27.57825
H	14.81173	35.00180	27.44422
C	17.28526	33.87623	26.97036
H	18.21556	33.76387	26.39438
H	17.34545	34.81342	27.54502
C	16.19053	35.12288	25.10712
H	17.11103	35.08386	24.50602
H	15.33334	35.20916	24.42311
H	16.22688	36.03972	25.71356
H	17.22959	33.04382	27.68579
C	15.31333	22.83254	24.15584
N	15.45570	22.89336	22.76661
N	15.40112	22.95976	20.00546
C	15.11003	23.98782	17.93873
C	15.17395	22.74002	18.65647
C	15.09252	21.50290	18.02726
C	15.39074	20.41890	24.20752
Ni	15.48741	21.55250	21.42504
C	15.33550	24.16228	24.73771
H	17.48183	22.49914	16.70627
C	15.03564	21.67979	26.33954
C	13.55733	21.67184	28.25410
C	13.72961	21.61969	26.86698
C	12.53903	21.50148	25.95281
H	12.49956	22.33844	25.23901
C	15.57608	24.21482	22.51400
C	15.49882	24.35033	20.12468
C	15.33145	24.98086	18.84524
C	15.64082	24.97485	21.35460
C	15.52571	25.03585	23.69238
H	14.93028	24.06983	16.87088
H	15.22120	24.34753	25.80191
C	15.23083	21.64407	24.86095
H	12.54350	21.62411	28.66168
H	15.35509	26.05087	18.66936
C	16.14727	21.78401	27.19908
C	15.92956	21.83339	28.58134
C	14.64353	21.78436	29.12894
C	17.54605	21.84068	26.64424
H	17.76594	20.95905	26.02285
C	14.42771	21.87847	30.61629
H	15.31804	21.55640	31.17372
H	14.20906	22.91635	30.91612
H	13.57638	21.26193	30.93825
H	18.28796	21.88755	27.45197
H	16.79278	21.91154	29.24825
H	15.41734	19.06599	25.98489
H	17.68440	22.72114	25.99789
H	12.58672	20.58023	25.35194
H	11.60233	21.49112	26.52511
C	15.51438	19.17147	24.90835
C	15.79985	18.21509	23.97683
C	15.80780	18.86827	22.69715
C	15.79102	18.82482	20.26637
C	15.75315	18.12149	19.01109
C	15.42926	19.03549	18.05392
C	15.96784	18.19155	21.49008
C	16.27251	16.72965	21.51443
C	15.22690	15.78571	21.54702
C	15.54714	14.42309	21.56609
C	16.87189	13.97464	21.55592
C	17.89162	14.93183	21.51801
C	17.61586	16.30336	21.49774
H	15.93190	17.05584	18.90305
H	15.97656	17.15361	24.12218
C	17.19227	12.50432	21.61323
H	17.36520	12.17992	22.65237
H	16.36773	11.89780	21.21366
H	18.10206	12.26814	21.04341
C	13.78825	16.23023	21.55576
H	13.54873	16.82757	20.66250
H	13.11063	15.36701	21.58481
H	13.57236	16.86821	22.42653
C	18.73648	17.30813	21.45270
H	18.68250	17.92555	20.54272
H	18.68385	18.00323	22.30454
H	19.71423	16.80953	21.47330
H	18.93481	14.60390	21.50141
H	14.73449	13.69156	21.58692
N	15.55986	20.22616	22.83983
N	15.53165	20.17709	20.07554
C	15.31471	20.31134	18.71268
H	15.29244	18.88515	16.98720
C	14.82309	21.45176	16.55870
C	15.60524	21.44322	14.26948
C	15.89043	21.49306	15.63855
C	17.31482	21.58343	16.11844
H	17.56869	20.73895	16.77736
H	16.43486	21.47022	13.55731
H	18.01551	21.58426	15.27342
C	13.49391	21.35564	16.10176
C	13.25265	21.30965	14.72375
C	14.29324	21.35525	13.79069
C	14.00922	21.33463	12.31192
H	13.04482	20.85451	12.09564
H	13.96616	22.35791	11.90444
H	14.79331	20.79768	11.75939
C	12.34993	21.29745	17.07915
H	12.32252	22.19400	17.71730
H	11.38831	21.21750	16.55572
H	12.22027	21.23173	14.37142
H	12.44766	20.43509	17.75646



Double-Fused Bis-Pyrene-Porphyrin PyrPorPyr

Cartesian Coordinates (Angstroms)

	X	Y	Z
C	14.89585	30.16995	20.81667
C	13.46486	28.54817	20.69621
N	14.79423	28.77189	20.76167
N	14.66730	25.99345	20.79122
C	13.27549	26.15349	20.72903
C	12.61825	24.87815	20.79496
C	13.59234	23.93346	20.90786
C	14.85686	24.62625	20.89682
C	16.10301	30.86008	20.86024
C	12.67805	27.40174	20.65954
C	16.07595	23.95690	20.95774
H	11.54492	24.72638	20.77062
C	17.30425	30.15968	20.81719
C	18.62249	30.75809	20.79441
C	19.52053	29.71654	20.70860
C	18.72151	28.52609	20.69378
N	17.39409	28.76085	20.76016
N	17.49978	25.98091	20.78182
C	18.89217	26.12990	20.71098
C	19.53980	24.84898	20.76150
C	18.55909	23.91133	20.87558
C	17.30021	24.61482	20.88184
C	19.49904	27.37360	20.64915
H	18.65608	22.83199	20.94601
H	20.61168	24.68894	20.72557
H	18.78787	31.83082	20.83822
Ni	16.08868	27.37980	20.77205
C	12.67570	29.74549	20.70819
C	13.58267	30.77952	20.79307
H	13.48806	22.85556	20.98773
C	16.07002	22.46711	21.08135
C	16.09239	21.87009	22.35800
C	16.09086	20.47366	22.45198
C	16.06647	19.65727	21.31617
C	16.04814	20.27392	20.06094
C	16.04902	21.66653	19.92173
C	16.03592	18.15688	21.44147
H	16.57749	17.81697	22.33546
H	15.00036	17.78929	21.52766
H	16.48265	17.67209	20.56223
C	16.12267	22.71759	23.60242
H	15.24857	23.38476	23.65396
H	16.13191	22.09174	24.50435
H	17.01202	23.36606	23.62356
C	16.03382	22.29560	18.55379
H	15.15161	22.94021	18.41928
H	16.91541	22.93635	18.39852
H	16.02286	21.52852	17.76861
H	16.11265	20.01155	23.44297
H	16.03635	19.65351	19.16044
C	16.10894	32.34938	20.93481
C	16.10530	33.11445	19.75131
C	16.11492	34.51050	19.85051
C	16.12622	35.16371	21.08742
C	16.13381	34.38111	22.24717
C	16.12449	32.98269	22.19410
C	16.10451	36.66756	21.16739
H	16.57358	37.12320	20.28415
H	15.06987	37.04431	21.21934
H	16.62874	37.03094	22.06243
C	16.09582	32.44696	18.40175
H	15.20501	31.81275	18.27554
H	16.10435	33.19186	17.59551
H	16.96946	31.78970	18.27391
C	16.13530	32.16866	23.46064
H	15.25444	31.51114	23.51962
H	17.01859	31.51326	23.50651
H	16.14109	32.81717	24.34614
H	16.11628	35.10386	18.93174
H	16.14977	34.87116	23.22480
H	13.42638	31.85365	20.83702
C	11.27474	27.88225	20.61300
C	11.28490	29.32320	20.64868
C	10.09147	30.05503	20.62817
C	8.85149	29.33264	20.56808
C	8.84681	27.90465	20.52414
C	10.07338	27.19730	20.54584
C	10.05029	31.48779	20.66873
C	8.86393	32.16409	20.65508
C	7.60781	31.47148	20.59934
C	7.62057	30.04306	20.55419
C	7.59084	27.22616	20.46267
C	6.40552	27.91293	20.45041
C	6.37930	29.34161	20.49775
C	5.17303	30.07146	20.49160
C	5.14966	31.46691	20.53649
C	6.37994	32.14569	20.58869
H	10.03995	26.10828	20.50681
H	7.59359	26.13411	20.42675
H	5.45587	27.37492	20.40478
H	10.99268	32.03513	20.71287
H	8.85221	33.25608	20.68734
H	4.24123	29.50641	20.45043
H	6.39737	33.23755	20.62355
C	3.84351	32.27196	20.52617
C	3.76850	33.14069	21.79908
H	3.78334	32.51276	22.70188
H	4.61089	33.84346	21.86318
H	2.83749	33.72818	21.80283
C	3.82079	33.18388	19.28155
H	3.86760	32.58641	18.35935
H	2.89369	33.77726	19.26177
C	2.60173	31.37003	20.48616
H	2.57919	30.74614	19.58047
H	2.54957	30.70903	21.36397
H	1.69564	31.99341	20.48377
H	4.66947	33.88212	19.27407
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C	23.34041	29.27318	20.57330
C	23.33406	27.84547	20.52115
C	22.10197	27.14780	20.53601
C	22.15737	31.43724	20.68283
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C	24.59892	31.40245	20.62110
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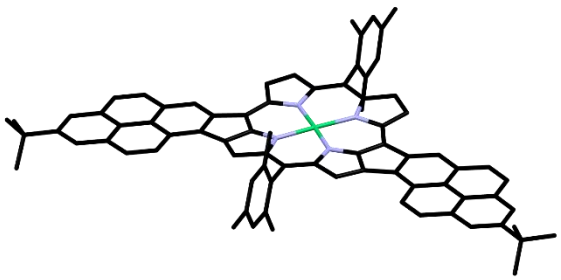
C	25.81262	29.26428	20.51170
C	27.02396	29.98566	20.51427
C	27.05643	31.38074	20.56674
C	25.83111	32.06777	20.61831
H	22.12656	26.05868	20.49223
H	24.57492	26.06633	20.41652
H	26.72130	27.29139	20.40968
H	21.21879	31.99088	20.72724
H	23.36826	33.19647	20.71510
H	27.95198	29.41442	20.47368
H	25.82110	33.15949	20.65889
C	28.36680	32.17819	20.56297
C	28.39994	33.08964	19.31838
H	28.35249	32.49308	18.39576
H	27.55550	33.79296	19.30824
H	29.33052	33.67752	19.30248
C	28.44099	33.04848	21.83467
H	28.41879	32.42285	22.73878
H	29.37504	33.63094	21.84079
C	29.60285	31.26864	20.52995
H	29.64439	30.60670	21.40759
H	29.62656	30.64482	19.62431
H	30.51316	31.88567	20.53366
H	27.60242	33.75620	21.89374
C	20.90753	29.28284	20.64740
C	20.90609	27.84229	20.60440



Double-Fused Bis-Porphyrin-Pyrene

Cartesian Coordinates (Angstroms)

	X	Y	Z
C	33.00576	19.68310	16.62899
C	32.24737	20.90930	16.56056
C	30.85144	20.89395	16.47773
C	30.18066	19.62215	16.45054
C	30.93915	18.41045	16.50818
C	32.35418	18.46512	16.59639
C	30.06444	22.08982	16.41863
C	28.70222	22.04004	16.34062
C	28.00325	20.78978	16.30745
C	28.76341	19.57028	16.36180
C	30.24467	17.16775	16.47489
C	28.87519	17.11766	16.38966
C	28.09361	18.30650	16.32940
C	26.67865	18.25765	16.23705
C	25.94150	19.42478	16.17711
C	26.61007	20.70327	16.22247
H	32.90435	17.52408	16.62614
H	30.82700	16.24452	16.51924
H	28.36060	16.15429	16.36537
H	30.57625	23.05274	16.43820
H	28.12274	22.96305	16.29949
H	26.19803	17.27897	16.22471
C	34.85455	23.54441	16.65800
N	35.51452	22.31093	16.67751
N	36.86545	19.91390	16.96796
C	37.02968	17.64104	17.44212
C	37.74037	18.88188	17.26828
C	39.12607	18.96805	17.32442
C	36.90612	24.81268	16.54466
Ni	37.35501	21.84032	16.72866
C	33.41636	23.36472	16.61538
H	38.82744	17.17889	15.06255
C	34.71983	26.02476	16.63310
C	33.64400	27.82357	17.84002
C	34.39852	26.64505	17.85679
C	34.86197	26.05320	19.16150
H	34.48632	25.02670	19.29084
C	34.50783	21.41175	16.63530
C	35.60703	19.30414	16.92701
C	35.71222	17.90132	17.21310
C	34.44487	20.02727	16.70818
C	33.20031	22.00641	16.58426
H	37.50261	16.69723	17.69609
H	32.71385	24.19305	16.60877
C	35.51336	24.76122	16.63222
H	33.39851	28.30561	18.79050
H	34.87805	17.20971	17.25807
C	34.28845	26.58652	15.41424
C	33.53587	27.76600	15.44321
C	33.19979	28.39859	16.64481
C	34.63355	25.93494	14.10136
H	35.72372	25.87305	13.96057
C	32.35999	29.64854	16.65211
H	32.52493	30.24858	15.74623
H	31.28640	29.40118	16.68955
H	32.58118	30.27599	17.52675
H	34.20927	26.49782	13.25984
H	33.20492	28.20315	14.49692
H	37.16575	27.02370	16.36377
H	34.25243	24.90347	14.05362
H	35.96028	25.99172	19.20457
H	34.51723	26.65590	20.01174
C	37.62893	26.04147	16.37097
C	38.94216	25.71263	16.20067
C	39.03028	24.28227	16.30288
C	40.30273	22.21869	16.47956
C	41.54510	21.49749	16.56387
C	41.23840	20.22154	16.92840
C	40.23276	23.58414	16.23792
C	41.49039	24.33619	15.95019
C	42.25226	24.87328	17.00647
C	43.42868	25.56990	16.70495
C	43.86557	25.74665	15.38841
C	43.09250	25.20081	14.35757
C	41.91018	24.49894	14.61440
H	42.52022	21.93890	16.38139
H	39.79250	26.36622	16.03158
C	45.11864	26.52414	15.08381
H	44.88032	27.56593	14.81441
H	45.79308	26.55451	15.95052
H	45.66583	26.08729	14.23623
C	41.81711	24.69693	18.43714
H	41.80023	23.63308	18.72077
H	42.49450	25.22377	19.12176
H	40.79757	25.07963	18.59609
C	41.10325	23.92043	13.48229
H	41.02683	22.82525	13.56527
H	40.07247	24.30634	13.48796
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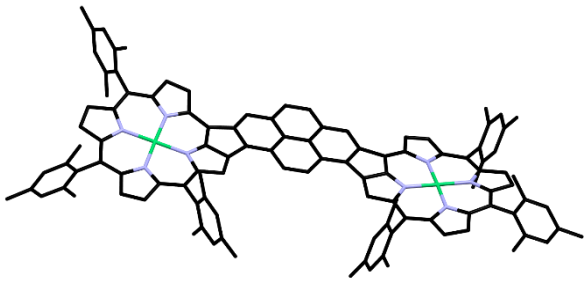

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H	21.26990	26.44175	16.44854
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