7 Experimental Part

7.1. General

All reactions involving air-sensitive compounds were carried out under nitrogen using standard Schlenk techniques and dry, oxygen-free solvents. Diethylether, toluene, THF, and triethylamine were distilled under nitrogen from sodium/benzophenone and dichloromethane was distilled from CaH_2. All reagents were purchased from Aldrich or Acros and used without further purification. BuLi was used as a 1.6 M solution in hexane.

7.1.1. Chromatographic Methods

Analytical TLC:

Reactions were monitored on silica gel alumina sheets (Merck ”Kieselgel 60”, with fluorescence indicator F254), or TLC-ready sheets by Macherey-Nagel (Polygram Alox N/UV_{254}, with 0.2 mm aluminium oxide with fluorescent indicator. For detection UV-light with wavelength λ = 254 or λ = 366 nm was used.

Column chromatography:

The chromatography was run with Merck flash silica gel (230-400 mesh ASTM, grain size 40-60 pm), or Fluka aluminium oxide neutral (Typ 507 C, 0.05-0.15 mm). For all chromatographed compounds the R_f value is given together with the eluting solvent in the TLC.

Analytical GPC:

Measurements were performed with a Waters Assoc. 150-c Alc/GPC chromatograph by using the column set Waters Styragel HR columns. THF was used as mobile phase. Detection was performed by a Waters 410 RI detector or a 484 UV/VIS detector against polystyrene as calibration standard.

Preparative GPC:

Separation was by using a Waters machine with UV detection; the mobile phase was THF. Separation columns were Waters Styragel HR columns. In some cases, the macrocycles were contaminated with THF oligomers after preparative GPC; then the compounds were dissolved in minimum amount of THF and precipitated with methanol.

7.1.2. Analysis

Melting point:

Büchi SMP 510, uncorrected values.

NMR spectroscopy:

Bruker WH 270, Bruker AB 250, Bruker AC 500. The signals of the non-deuterated solvents served as internal standard (^{1}H: $CDCl_3$ δ = 7.24 ppm, DMSO δ = 2.49 ppm, acetonitrile δ = 1.93 ppm, nitromethane δ = 4.29 ppm; ^{13}C: $CDCl_3$: δ = 77.00 ppm, DMSO: δ = 39.70 ppm, acetonitrile: δ = 117.79 ppm, nitromethane: δ = 62.80 ppm). The deuterated solvents were purchased from Merck and Deutero GmbH.

Mass spectrometry:

Perkin-Elmer Varian Type MAT 771 and CH6 (EI), Type CH5DF (FAB), or Bruker Reflex (MALDI-TOF) respectively. The high resolution mass spectra were obtained according to the peak match method (MAT 771).

MALDI-TOF mass spectrometry:

Spectra were recorded with a Kratos MALDI 3 from Shimadzu.

Elemental analysis:

It was done with a Perkin-Elmer EA 240.

Optical microscopy:

The optical microscope used was a “AXIOSKOP” 40 POL and the pictures were taken with a digital camera “Axio Cam” MRL.

7.2. Syntheses

The catalyst [$Pd(PPh_3)_4$] was synthesized according to literature[105] and stored in the dry-box. Compounds **63**,[57] **64**,[57] **65**,[57] **66**,[53] **67**,[53] **69**,[57] **70**,[57] **71**,[57] **73**, **74a**,**b**,[53] **75**,[17a] **76**,[17a] **77**,[63], [64] **78**,[65] **79**,[65] **87**,[30] **90**,[17a] **91**,[17a] **92**,[17a] **95**,[106] **96**,[107] [$Os(bpy)_2Cl_2$],[82] and [$Ru(bpy)Cl_3]_x$[84b] were prepared accordingly to literature procedure. Compounds **10**,[17a] **70**,[53] **72**,[57] **76**,[17a] **100a**,[57] and **100b**[57] are known, but were prepared by different procedures. Therefore their analytical and spectral data are not given. All other compounds are new. All polymers were not fully characterized by organic chemistry standards.

7.2.1. Compounds of chapter 4.2

General procedure for the coupling of terminal acetylene with aryl iodides or aryl bromides:

A heavy-walled flask was charged with the terminal acetylene, aryl iodide or aryl bromides, $[Pd(PPh_3)_4]$ (0.02 equiv. per coupling), CuI (0.02 equiv. per coupling), dry triethylamine, and dry toluene. The reaction mixture was evacuated, flushed with nitrogen, sealed with a Teflon screw cap, and stirred for 24 h at 60 °C for iodo compounds and at 80 °C for bromo ones, respectively. The reaction mixture was filtered and the solvent removed. The compounds were purified by column chromatography through silica gel.

General procedure for the deprotection of acetylenic trimethylsilyl groups:

A catalytic amount of 1M NaOH solution was added to the silyl compound in a mixture of THF/methanol (1:1) and stirred for 16 h at r. t. Then the reaction mixture was diluted with diethylether and brine, and the phases were separated. The aqueous phase was extracted with diethylether and the combined organic phases were dried over $MgSO_4$, the solvent was removed, and the compound purified by column chromatography through silica gel.

General procedure for the deprotection of acetylenic triisopropylsilyl groups:

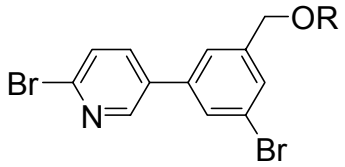
To a stirred solution of the silyl compound in THF, tetrabutylammonium fluoride trihydrate (1 equiv. per deprotection) was added and the reaction stirred for 24 h at r. t. The reaction mixture was diluted with diethylether and brine and the phases were separated. The aqueous phase was extracted with diethylether and the combined organic phases were dried over $MgSO_4$. The solvent was removed and the compound purified by column chromatography through silica gel.

General procedure for macrocycle synthesis:

A solution of **C** (0.98 mmol) and **D** (0.98 mmol) in a mixture of dry triethylamine (320 ml) and dry toluene (320 ml) was carefully degassed. After the addition of $[Pd(PPh_3)_4]$ (0.04 equiv) and CuI (0.04 equiv), the mixture was stirred under nitrogen at 60 °C for 4 d and then at 95 °C for 24 h. The solvent was removed, the residue dissolved in CH_2Cl_2 (300 ml), and the resulting mixture treated with a solution of KCN (265 mg) in

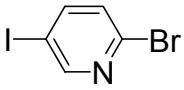
water (200 ml). The phases were separated, the aqueous one was extracted with CH_2Cl_2, and the combined organic phases were washed with water. It was then dried over $MgSO_4$ and the solvent removed. The macrocycles were purified by preparative GPC (Yields: 20-35%).

*General procedure for the synthesis of pyridines (**70a,b**):*



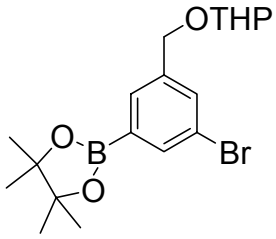
To a degassed mixture of boronic ester **73** (11.10 g, 27.95 mmol), 2-bromo-5-iodo-pyridine **72** (7.93 g, 27.95 mmol), Bu_4NBr (9.01 g, 27.95 mmol) in toluene (160 ml) and aq 2M Na_2CO_3 (80 ml), $[Pd(PPh_3)_4]$ (600 mg, 0.52 mmol) was added and the reaction degassed once more. After the mixture was refluxed for 4 d the layers were separated and the aqueous one extracted with toluene (2 × 50 ml). The combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by column chromatography through silica gel (hexane/ethyl acetate 25:1) to give **70** as a white solid (85-90%).

*2-Bromo-5-iodo-pyridine (**72**):*



To a stirred suspension of 2,5-dibromopyridine (**68**) (10 g, 42.2 mmol) in dry diethylether (280 ml) a solution of 1.6 M BuLi in hexane (28 ml, 44.8 mmol) was added drop wise at -78 °C. After 3 h diiodoethane was added in solid form (12.7 g, 45.1 mmol) to the resulting red suspension and the mixture was let to warm to r. t. Then water (100 ml) was added and the phases were separated. The aqueous phase was extracted with diethylether (2 × 100 ml) and the combined organic phases were washed with water. The organic phase was dried ($MgSO_4$), the solvent was removed, and the resulting solid was purified by column chromatography over silica gel (hexane/ethyl acetate 10:1) to give 9 g of **72** (75%) as a white solid.

*2-[3-Bromo-5-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-benzyloxy]-tetrahydropyran (**73b**):*



To a stirred solution of 2-(3,5-dibromo-benzyloxy)-tetrahydro-pyran (**67b**) (20 g, 57.1 mmol) in dry diethylether (200 ml) at -78 °C, a solution of 1.6 M BuLi in hexane (39.3 ml, 62.8 mmol) was added over a period of 15 min. After 3 h, triisopropylborate (13 g, 68.8 mmol) was added and the mixture let to warm to room temperature. The organic phase was washed with water and the aqueous one extracted with diethylether. The combined organic phases were dried over $MgSO_4$. The solvent was removed and the resulting oil used for the esterification without further purification. The crude boronic acid and 2.3-dimethylbutane-2.3-diol (5.91 g, 50.0 mmol) were dissolved in toluene (100 ml), and refluxed for 2 d. The formed water was removed from the reaction using a Dean-Stark trap. The solvent was removed and the oil was purified by column chromatography through silica gel (hexane/ethyl acetate 20:1) to give 4.65 g of **73b** (83%) as colorless oil.

R_f = 0.12 (hexane/ethyl acetate 20:1).

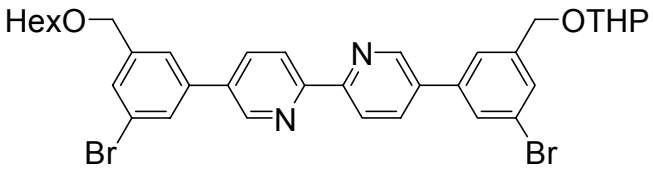
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.31 (s, 12 H, CH_3), 1.46-1.91 (m, 6 H, THP), 3.53 (m, 1 H, THP), 3.90 (m, 1 H, THP), 4.43 (d, 1 H, benzyl-CH_2), 4.66 (s, 1 H, THP), 4.72 (d, 1 H, benzyl-CH_2), 7.60 (s, 1 H, phenyl-H), 7.66 (s, 1 H, phenyl-H), 7.84 (s, 1 H, phenyl-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ =19.28, 24.83, 25.42, 30.48, 62.08, 68.01, 84.15, 97.92, 122.51, 132.45, 133.46, 136.57, 140.04.

MS (**EI**, 80 eV) *m/z* (%): 380.2 (1.20), 296.4 (60.67), 216.7 (21.90), 196.5 (14.75), 115.8 (12.68), 84.9 (100.00).

EA for $C_{18}H_{26}BBrO_4$ (397.11): calcd (%): C 54.44, H 6.60;
found (%): C 54.41, H 6.35.

*5'-(3-Bromo-5-hexyloxymethyl-phenyl)-5-[3-bromo-5-(tetrahydropyran-2-yloxymethyl)-phenyl]-[2,2']bipyridinyl (**74c**):*



To a stirred solution of **70a** (4.64 g, 10.86 mmol) in dry toluene (120 ml) a 1.6 N solution of BuLi in hexane (7.2 ml, 11.52 mmol) was added drop wise at -78 °C. After 2 h, to the resulting red solution Me_3SnCl (2.39 g, 12 mmol) was added in solid form. The mixture was let to warm to r. t. and then compound **70b** (4.64 g, 10.9 mmol) was added to the brownish solution of **71a**. The mixture was degassed, $[Pd(PPh_3)_4]$ (3 mol %) was added and the reaction mixture degassed again. After refluxing for 5 d the mixture was let to cool to r. t. An aq sat. KF solution (90 ml) was added to the organic phase followed by an aq 2N Na_2CO_3 solution (150 ml). The phases were separated, the aqueous one was extracted with toluene (2 × 100 ml). The combined organic phases were washed with water (100 ml) and dried ($MgSO_4$). The solvent was removed to give a brown oil which was purified by column chromatography trough silica gel (hexane/ethyl acetate 4:1) to give 2.5 g (30-35%) of **74c** as a white solid.

R_f = 0.38 (hexane/ethyl acetate 4:1).

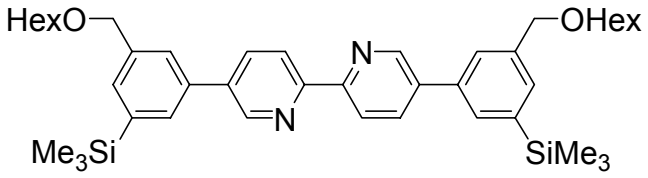
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.42 (t, 3 H, CH_3), 1.24-1.45 (m, 6 H, γ-, δ-, ε-CH_2-hexyl), 1.50-2.00 (m, 8 H, β-CH_2-hexyl, THP), 3.47 (t, 2 H, α-CH_2-hexyl), 3.60 (t, 1 H, THP), 3.91 (m, 1 H, THP), 4.56 (s, 2 H, benzyl-H), 4.56 (d, 1 H, benzyl-H), 4.76 (t, 1 H, THP), 4.85 (d, 1 H, benzyl-H), 7.53 (s, 2 H, phenyl-H), 7.59 (s, 2 H, phenyl-H), 7.71 (s, 2 H, phenyl-H), 8.00 (dd, ^3J = 8 Hz, 2 H, ^4J = 2 Hz, py-H,), 8.53 (d, ^3J = 8 Hz, 2 H, py-H), 8.88 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.00, 19.29, 22.58, 25.38, 25.84, 29.66, 30.48, 31.64, 62.22, 67.87, 71.04, 71.85, 98.10, 121.12, 123.22, 124.60, 124.82, 129.03, 130.06, 130.23, 135.16, 135.33, 139.55, 141.58, 141.58, 142.00, 147.52, 153.18, 154.82.

MS (**EI**, 80 eV): *m/z* (%): 694 (8.67), 612 (17.07), 594 (100).

EA: for $C_{35}H_{38}N_2Br_2O_3$ (694.50): calcd (%): C 60.53, H 5.52, N 4.03;
found (%): C 60.46, H 5.24, N 3.84.

*5,5'-Bis-(3-hexyloxymethyl-5-trimethylsilanyl-phenyl)-[2,2']bipyridinyl (**80**):*



First route: To a degassed mixture of **79** (15.32 g, 39.2 mmol) and 5,5-dibromo-2,2'-bipyridine (**77**) (5.60 g, 17.8 mmol) in toluene/aq 2M Na_2CO_3 2:1 (360 ml), [$Pd(PPh_3)_4$] (1.20 g, 1.04 mmol) was added and the mixture degassed once more. The reaction mixture was refluxed for 3 d and then the phases were separated. The aqueous one was extracted with toluene (2 × 100 ml) and the combined organic phases were dried over $MgSO_4$. The solvent was removed and the resulting oil purified by column chromatography through silica gel (hexane/ethyl acetate 4:1) to give 11 g of **80** (90%) as a white solid. R_f (hexane/ethyl acetate 9:1) = 0.35.

Second route: To a degassed solution of **81** (4.64 g, 11.04 mmol) in dry toluene (140 ml) of hexa-n-butyldistannane (3 ml, 50 mol%) and [$Pd(PPh_3)_4$] (290 mg, 0.25 mmol) were added and the reaction mixture was degassed again. After refluxing for 5 d the mixture was poured into aqueous EDTA (1M, 40 ml). After stirring for 15 min the phases were separated. The aqueous one was extracted with toluene and the combined organic phases were dried ($MgSO_4$). After evaporation of the solvent, the raw product was purified by column chromatography through silica gel (hexane/ethyl acetate 9:1) to give 3.23 g of **80** (85%) as a white solid.

R_f = 0.35 (hexane/ethyl acetate 9:1).

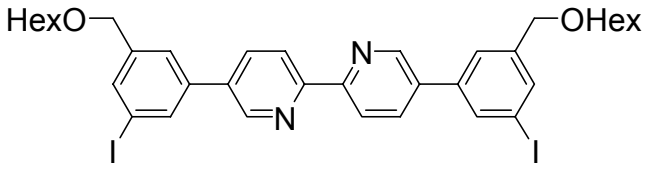
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.35 (s, 18 H, $Si(CH_3)_3$), 0.93 (t, 6 H, CH_3), 1.24-1.45 (m, 12 H, γ-, δ-, ε-CH_2), 1.68 (m, 4 H, β-CH_2), 3.58 (t, 4 H, α-CH_2), 4.64 (s, 4 H, benzyl-CH_2), 7.54 (s, 2 H, phenyl-H), 7.63 (s, 2 H, phenyl-H), 7.72 (s, 4 H, phenyl-H), 8.06 (d, ^3J = 8 Hz, 2 H, py-H), 8.55 (d, ^3J = 8 Hz, 2 H, py-H), 8.97 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = -1.10, 14.02, 22.62, 25.94, 29.76, 31.70, 70.83, 72.85, 120.91, 126.92, 131.17, 132.35, 135.36, 136.80, 137.12, 138.88, 141.80, 147.80, 154.59.

MS (**EI**): *m/z* (%): 680 (100), 580 (22.26), 375 (13.14).

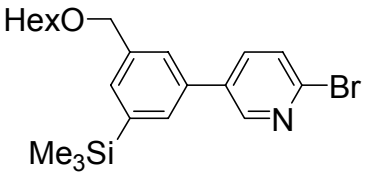
HRMS: ($C_{42}H_{60}O_2N_2Si_2$): calcd.: 680.41931;
Found: 680.41756.

*5,5'-Bis-(3-hexyloxymethyl-5-iodo-phenyl)-[2,2']bipyridinyl (**76**):*



Compound **80** (7.58 g, 11.02 mmol) was placed into a flask, which was evacuated and refilled with N_2. On the Schlenk line, dry CH_2Cl_2 (550 ml) and iodine monochloride (7.22 g, 44.47 mmol) were added under nitrogen. The mixture was heated to 45 °C for 48 h. Once it had cooled to room temperature, a solution of NaOH (2.22 g, 55 mmol) and $Na_2S_2O_3$ (6 g, 44.58 mmol) in water (140 ml) were added and the mixture stirred for 12 h. The phases were then separated, the aqueous one was extracted with CH_2Cl_2 (2 × 100 ml), and the combined organic phases were washed with 2N NH_4OH (140 ml) and then dried over $MgSO_4$. Removal of the solvent gave 8.00 g of **76** (98%) as a white solid.

*2-Bromo-5-(3-hexyloxymethyl-5-trimethylsilanyl-phenyl)-pyridine (**81**):*



To a degassed mixture of 2-bromo-5-iodopyridine **72** (5.17 g, 18.2 mmol) and **79** (7.11 g, 18.2 mmol) in toluene (110 ml) and aq 2M Na_2CO_3 (55 ml), $[Pd(PPh_3)_4]$ (410 mg, 0.35 mmol) was added. The mixture was degassed once more and refluxed for 3 d. Then the phases were separated, the aqueous one was extracted with toluene (2 × 100 ml) and the combined organic phases dried over $MgSO_4$. The solvent was removed under reduced pressure. The product was purified by column chromatography through silica gel (hexane/ethyl acetate 9:1) to give 6.88 g of **81** (90%) as a white solid.

R_f = 0.74 (hexane/ethyl acetate 6:1).

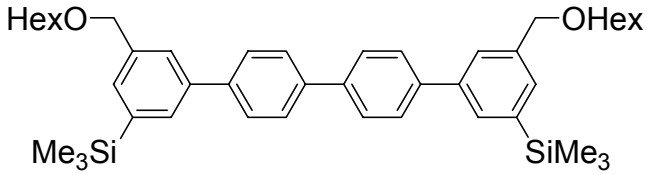
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.31 (s, 9 H, $Si(CH_3)_3$), 0.88 (t, 3 H, CH_3), 1.30-1.41 (m, 6 H, γ-, δ-, ε-CH_2), 1.63 (m, 2 H, β-CH_2), 3.52 (t, 2 H, α-CH_2), 4.57 (s, 2 H, benzyl-CH_2), 7.50-7.56 (m, 4 H, phenyl, py-H), 7.74 (dd, ^3J = 8 Hz, 1 H, py-H), 8.58 (s, 1 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = -1.15, 14.01, 22.60, 25.91, 29.72, 31.67, 33.10, 70.89, 72.69, 126.77, 127.91, 131.05, 132.59, 136.02, 136.35, 137.09, 139.01, 142.05, 148.61, 153.13.

MS (**EI**, 80 eV) *m/z* (%): 421.0 (44.13), 418.9 (42.34), 406.0 (66.00), 404.0 (61.49), 321 (100.00), 318.9 (95.72).

EA: for $C_{21}H_{30}BrNOSi$ (420.46): calcd.: C 59.99, H 7.19, N 3.33;
found: C 59.93, H 6.98, N 3.22.

*5,5'''-Bis-hexyloxymethyl-3,3'''-bis-trimethylsilanyl-[1,1';4',1'';4'',1''']-quaterphenyl (**82**):*



To a degassed mixture of **79** (3.62 g, 9.27 mmol) and 4,4'-diiododiphenyl **84** (1.79 g, 4.40 mmol) in toluene (60 ml) and aq. 1M Na_2CO_3 (60 ml), $Pd(PPh_3)_4$ (280 mg, 0.24 mmol) was added and the mixture refluxed for 72 h. The layers were separated and the aqueous one was extracted with toluene (3 × 50 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was removed. The yellow oil was purified by column chromatography through silica gel (hexane/ethyl acetate 30:1) to give 1.7 g (57%) of **82** as a white solid.

R_f = 0.29 (hexane/ethyl acetate 30:1).

M.p. 73.5-75 °C.

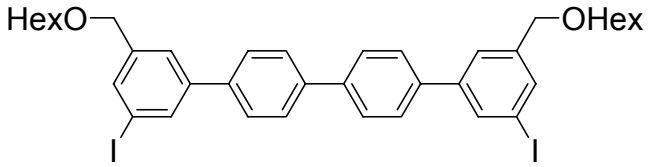
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.33 (s, 18 H, $Si(CH_3)_3$), 0.93 (t, 6 H, CH_3), 1.24-1.45 (m, 12 H, γ-, δ-, ε-CH_2) 1.65 (m, 4 H, β-CH_2), 3.53 (t, 4 H, α-CH_2), 4.60 (s, 4 H, benzyl-CH_2), 7.47 (s, 2 H, phenyl-H), 7.61 (s, 2 H, phenyl-H), 7.71 (s, 10 H, phenyl-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = -1.10, 14.02, 22.59, 25.91, 29.73, 31.66, 70.59, 72.92, 126.98, 127.25, 127.64, 131.16, 131.52, 138.40, 139.50, 140.08, 140.41, 141.08.

MS (**EI**): *m/z* (%) = 678 (100), 663 (5.47), 5.77 (6.00), 91 (27.32).

EA: for: $C_{44}H_{62}O_2Si_2$ (679.13): calcd.: C 77.82, H 9.20;
found: C 77.45, H 8.83.

*5,5'''Bis-hexyloxymethyl-3,3'-diiodo-[1,1';4',1'';4'',1''']quaterphenyl (**83**):*



To a stirred solution of **82** (1.52 g, 2.24 mmol) in dry CH_2Cl_2 (60 ml) a solution of ICl (1.10 g, 6.77 mmol) in CH_2Cl_2 (15 ml) was added dropwise over a period of 30 min at -15°C. The resulting mixture was stirred at this temperature for 30 min. Then a saturated solution of $Na_2S_2O_5$ (30 ml) was added. The layers were separated, the aqueous one was extracted with CH_2Cl_2 (2 × 30 ml). The combined organic phases were washed with water (20 ml), dried over $MgSO_4$, and the solvent removed to give 1.72 g (97%) of **83** as a pure colourless powder.

R_f = 0.32 (hexane/ethyl acetate 10:1).

M.p. 58-59 °C.

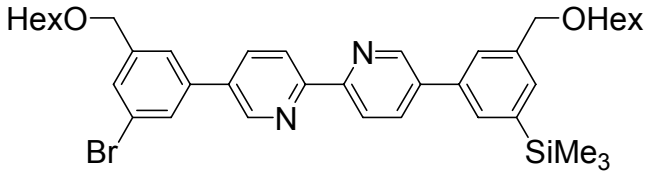
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.89 (t, 6 H, CH_3), 1.27-1.38 (m, 12 H, γ-, δ-, ε-CH_2) 1.62 (m, 4 H, β-CH_2), 3.50 (t, 4 H, α-CH_2), 4.50 (s, 4 H, benzyl-CH_2), 7.55 (s, 2 H, phenyl-H), 7.64 (d, 4 H, phenyl-H), 7.67 (d, 4 H, phenyl-H), 7.67 (s, 2 H, phenyl-H), 7.89 (s, 2 H, phenyl-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.04, 22.62, 25.87, 29.68, 31.66, 70.89, 71.90, 94.86, 125.41, 127.40, 127.52, 135.01, 135.25, 138.60, 139.90, 141.53, 142.74.

MS (**EI**): *m/z* (%) = 786 (100), 685 (7.5), 559 (9.73).

EA: for $C_{38}H_{44}O_2I_2$ (786.568): calcd.: C 58.03, H 5.64;
found: C 58.02, H 5.41.

*2-(5-(3-bromo-5-((hexyloxy)methyl)phenyl)pyridine-2-yl)-5-(3-((hexyloxy)methyl)-5-(trimethylsilyl)phenyl)pyridine (**84**):*



To a stirred solution of **70a** (3.03 g, 7.09 mmol) in dry toluene (50 ml) a 1.6 N solution of BuLi in hexane (4.7 ml, 7.52 mmol) was dropwise added at -78 °C. To the resulting red solution Me_3SnCl (1.53 g, 7.68 mmol) was added in solid form after 2 h. The mixture was let to warm to r.t (over night). Compound **81** (2.98 g, 7.09 mmol) was then added to the brownish solution of **71a**. The mixture was degassed and

[$Pd(PPh_3)_4$] (3 mol %) added. The reaction mixture was degassed once more and refluxed for 5 d. Then it was cooled to r. t. and an aq sat. KF solution (90 ml) added followed by an aq 2N Na_2CO_3 solution (150 ml). The phases were separated, the aqueous one was extracted with toluene (2 × 100 ml) and the combined organic phases washed with water (100 ml) and dried ($MgSO_4$). The solvent was removed and the crude brown oil purified by column chromatography through silica gel (hexane/ethyl acetate 9:1) to give 2.18 g of **84** (44%) as a white solid, together with the homocoupling products **74a** (0.64 g) and **80** (0.43 g).

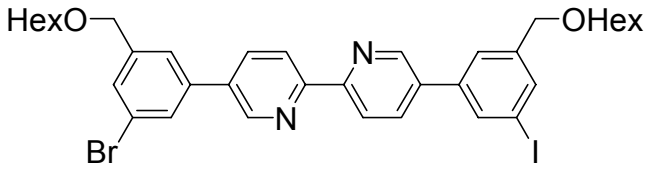
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.43 (s, 9 H, $Si(CH_3)_3$), 0.75-0.95 (m, 6 H, CH_3), 1.20-1.40 (m, 12 H, γ-, δ-, ε-CH_2), 1.60-1.75 (m, 4 H, β-CH_2), 3.45-3.55 (m, 4 H, α-CH_2), 4.53 (s, 2 H, benzyl-H), 4.59 (s, 2 H, benzyl-H), 7.53 (s, 3 H, phenyl-H), 7.61 (s, 1 H, phenyl-H), 7.68 (s, 2 H, phenyl-H), 7.98 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, py-H), 8.03 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 1 H, py-H), 8.52 (d, ^3J = 8 Hz, 2 H, py-H), 8.93 (s, 1 H, py-H), 8.93 (s, 1 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = -1.24, 13.60, 13.88, 22.22, 22.45, 25.71, 25.78, 29.52, 29.60, 31.27, 31.52, 31.79, 33.65, 70.62, 70.80, 71.62, 72.62, 120.72, 120.81, 123.04, 124.25, 126.65, 128.67, 129.69, 130.89, 132.15, 134.59, 134.86, 135.00, 136.63, 136.81, 138.74, 139.43, 141.49, 141.82, 147.30, 147.58, 154.09, 155.00.

MS (**EI**) *m/z* (%) = 688 (100), 586 (35).

HRMS: for $C_{39}H_{51}N_2O_2SiBr$: calcd.: 686.290319,
found: 686.29333.

*2-(5-(3-bromo-5-((hexyloxy)methyl)phenyl)pyridin-2-yl)-5-(3-((hexyloxy)methyl)-5-iodophenyl)pyridine (**85**):*



To a solution of **84** (4.79 g, 6.96 mmol) in dry dichloromethane (350 ml), ICl (3.39 g, 20.8 mmol) was added under nitrogen. The reaction mixture was refluxed for 2 d. After it was cooled to r. t., a solution of NaOH (1 g) and $Na_2S_2O_3$ (2.8 g) in water (30 ml) was added and stirring continued for 2 h. The organic phase was separated, washed with 2N NH_4OH (65 ml) and dried over $MgSO_4$. The solvent was removed and the mixture purified by column chromatography through silica gel (hexane/ethyl acetate 9:1) to give 1.86 g of **85** (79%) as a white solid.

R_f = 0.59 (hexane/ethyl acetate 4:1).

M.p. 87 °C.

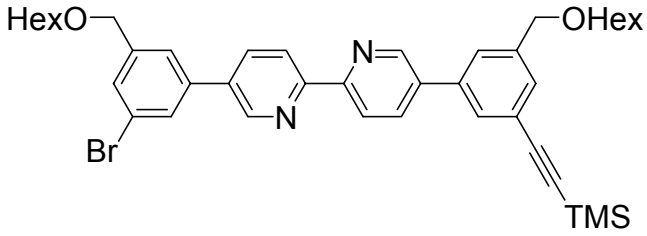
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.87 (t, 6 H, CH_3), 1.10-1.40 (m, 12 H, γ-, δ-, ε-CH_2), 1.75-1.60 (m, 4 H, β-CH_2), 3.50 (t, 4 H, α-CH_2), 4.50 (s, 2 H, benzyl-H), 4.53 (s, 2 H, benzyl-H), 7.52 (s, 2 H, phenyl-H), 7.55 (s, 1 H, phenyl-H), 7.67 (s, 1 H, phenyl-H), 7.72 (s, 1 H, phenyl-H), 7.87 (s, 1 H, phenyl-H), 7.97 (m, ^3J = 8 Hz, 2 H, py-H), 8.48 (d, ^3J = 8 Hz, 2 H, py-H) 8.86 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = 14.03, 22.60, 25.85, 29.66, 31.64, 71.02, 71.72, 71.84, 95.01, 121.03, 123.20, 124.61, 125.34, 128.99, 130.03, 134.94, 134.98, 135.23, 136.00, 139.61, 139.68, 141.89, 141.95, 147.57, 154.98.

MS (**FAB**) *m/z* (%): 741 (9.78) $[M]^+$.

EA: for $C_{36}H_{42}BrIN_2O_2$ (741.54): calcd.: C 58.31, H 5.71, N 3.78;
Found: C 58.22, H 5.52, N 3.56.

*2-(5-(3-bromo-5((hexyloxy)methyl)phenyl)pyridin-2-yl)-5-(3-((hexyloxy)metyl)-5-(2-(trimethylsilyl)ethynyl)phenyl)pyridine (**86a**):*



85 (3.83 g, 5.14 mmol), trimethylsilylethyne (0.53 g, 5.32 mmol), trietylamine (70 ml), toluene (40 ml), reaction time: 24 h at 60 °C. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate 10:1) to give 3.21 g (88%) of **86a** as colourless oil.

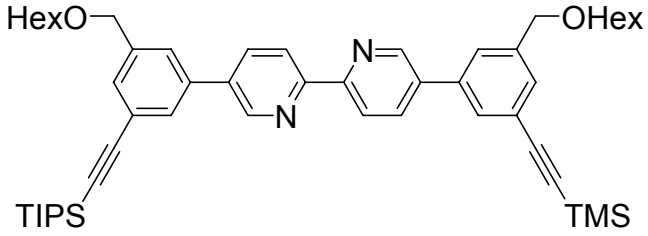
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.25 (s, 9 H, $Si(CH_3)_3$), 0.75-0.98 (t, 6 H, CH_3), 1.20-1.45 (m, 12 H, γ-, δ-, ε-CH_2), 1.55-1.75 (m, 4 H, β-CH_2), 3.42 (t, 4 H, α-CH_2), 4.41 (s, 2 H, benzyl-H), 4.44 (s, 2 H, benzyl-H), 7.42 (s, 3 H, phenyl-H), 7.47 (s, 1 h, phenyl-H), 7.56 (s, 1 H, phenyl-H), 7.59 (s, 1 H, phenyl-H), 7.81-7.89 (m, 2 H, py-H), 8.39 (d, ^3J = 8 Hz, 2 H, py-H), 8.75 (s, 1 H, py-H), 8.80 (s, 1 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = 0.24, 13.87, 22.40, 25.66, 29.47, 31.44, 70.60, 70.71, 71.52, 71.86, 94.65, 104.44, 120.63, 122.93, 123.80, 124.12, 125.76, 128.54, 129.15, 129.60, 130.29, 134.47, 134.72, 135.14, 137.42, 139.25, 139.76, 141.68, 147.20, 147.25, 154.35, 154.71.

MS (**EI**, 80 EV) *m/z* (%): 712.2 (21),$[M]^+$, 611.9 (100), $[M\text{-}OHex]^+$.

HRMS: for $C_{41}H_{51}O_2N_2Si^{79}Br$: calcd.: 710.29034;
Found: 710.29211.

*2-(5-3-((hexyloxy)methyl)-5-(2-(triisopropylsilyl)ethynyl)phenyl)pyridin-2-yl)-5-(3-((hexyloxy)methyl)-5-(2-(trimetylsilyl)ethynyl)phenyl)pyridine (**86b**):*



86a (1.68 g, 2.36 mmol), triisopropylsilylethyne (0.54 g, 3.07 mmol), triethylamine (50 ml), toluene (35 ml), 24 h, at 80 °C. The compound was purified by column chromatography through silica gel (hexane/ethyl acetate 4:1) to give 1.44 g of **86b** (75%) as colourless oil.

R_f = 0.53 (hexane/ethyl acetate 4:1).

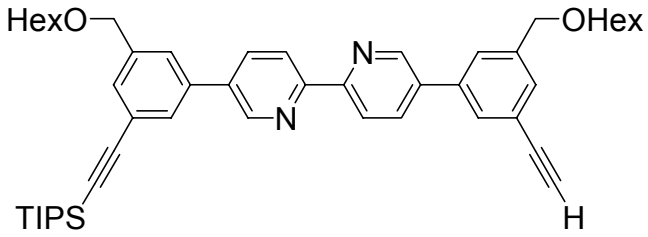
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.23 (s, 9 H, $Si(CH_3)_3$), 0.83 (t, 6 H, CH_3), 1.10 (s, 21 H, $Si(C_3H_7)_3$), 1.20-1.40 (m, 12 H, γ-, δ-, ε-CH_2), 1.50-1.60 (m, 4 H, β-CH_2), 3.40 (t, 4 H, α-CH_2), 4.41 (s, 2 H, benzyl-H), 4.43 (s, 2 H, benzyl-H), 7.30-7.45 (m, 4 H, phenyl-H), 7.58 (s, 2 H, phenyl-H), 7.87 (m, 2 H, py-H), 8.44 (d, ^3J = 8 Hz, 2 H, py-H) 8.81 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = -0.31, 11.06, 13.81, 18.43, 22.39, 25.66, 29.45, 31.42, 70.53, 71.79, 90.84, 94.45, 104.46, 106.44, 120.54, 123.78, 124.14, 125.63, 129.08, 129.19, 130.16, 130.23, 134.63, 135.01, 135.10, 137.46, 137.51, 139.74, 147.21, 154.47.

MS (**EI**) *m/z* (%): 812.5 (5), $[M]^+$, 769.4 (25), $[M\text{-}C_3H_7]^+$.

HRMS: for $C_{52}H_{72}O_2N_2Si_2$: calcd.: 812.51324,
Found: 812.51533.

*5-(3-ethynyl-5-((hexyloxy)methyl)phenyl)-2-(5-(3-((hexyloxy)methyl)-5-(2-(triisopropylsilyl)ethynyl)phenyl)pyridin-2-yl)pyridine (**86c**):*



86b (1.28 g, 1.57 mmol), THF (20 ml), methanol (10 ml), catalytical amount of 1M NaOH solution, 24 h. The compound was purified by column chromatography through silica gel (hexane/ethyl acetate 4:1) to give 1.14 g of **86c** (89%) as colourless oil.

$\mathbf{R_f}$ = 0.61 (hexane/ethyl acetate 4:1).

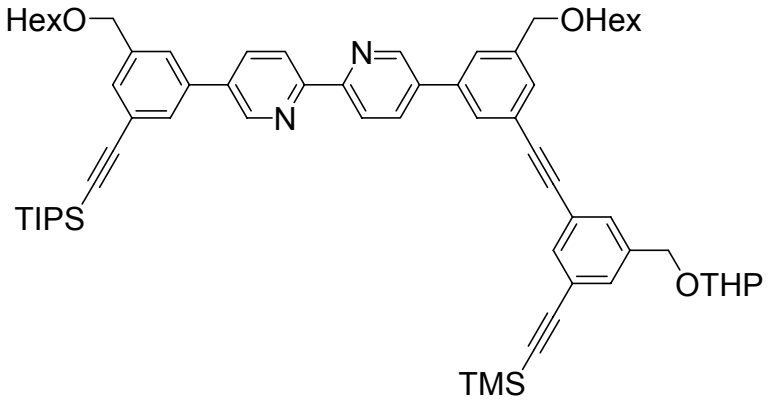
^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.86 (t, 6 H, CH_3), 1.13 (s, 21 H, $Si(C_3H_7)_3$), 1.20-1.40 (m, 12 H, γ-, δ-, ε-CH_2), 1.61 (quintet, 4 H, β-CH_2), 3.13 (s, 1 H, ethynyl-H), 3.42-3.55 (m, 4 H, α-CH_2), 4.50 (s, 2 H, benzyl-H), 4.51 (s, 2 H, benzyl-H), 7.47 (s, 2 H, phenyl-H), 7.54 (s, 1 H, phenyl-H), 7.57 (s, 1 H, phenyl-H), 7.65 (s, 2 H, phenyl-H), 7.90-8.05 (m, 2 H, py-H), 8.48 (d, ^3J = 8 Hz, 2 H, py-H) 8.87 (s, 1 H, py-H), 8.89 (s, 1 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = 11.12, 13.85, 18.49, 22.42, 25.69, 29.50, 31.48, 70.64, 71.79, 71.90, 77.75, 83.07, 90.98, 106.47, 120.63, 122.84, 124.21, 125.68, 125.99, 129.31, 130.34, 134.71, 134.74, 134.99, 135.21, 137.57, 137.62, 139.77, 139.92, 147.25, 154.49, 154.58.

MS (**EI**) *m/z* (%): 740.4 (14), $[M]^+$, 697.6 (100), $[M\text{-}C_3H_7]^+$, 655.6 (23), [M-Hex].

HRMS: for $C_{49}H_{64}O_2N_2Si$): calcd.: 740.47369;
Found: 740.47522.

*5-(3-((hexyloxy)methyl)-5-(2-(3-(2-(trimethylsilyl)ethynyl)-5-((tetrahydro-2H-pyran-2-yloxy)methyl)phenyl)ethynyl)phenyl)-2-(5-(3-((hexyloxy)methyl)-5-(2-(triisopropylsilyl)ethynyl)phenyl)pyridin-2-yl)pyridine (**86d**):*



86c (1.14 g, 1.54 mmol), (2-(3-bromo-5-((tetrahydro-*2H*-pyran-2-yloxy)methyl)phenyl)ethynyl)trimethylsilane (0.68 g, 1.85 mmol), triethylamine (30 ml), toluene (40 ml), at 80 °C for 24 h. The compound was purified by column chromatography through silica gel (hexane/ethylacetate 6:1) to give 1.12 g of **86d** (71%) as colourless oil.

R_f = 0.48 (hexane/ethyl acetate 4:1).

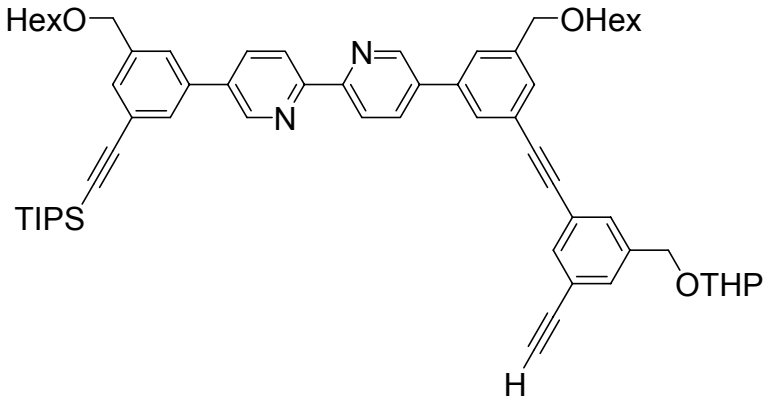
^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.24 (s, 9 H, $Si(CH_3)_3$), 0.75-0.95 (m, 6 H, CH_3), 1.12 (s, 21 H, $Si(C_3H_7)_3$), 1.20-1.90 (m, 22 H, β-, γ-, δ-, ε-CH_2, THP-H), 3.40-3.58 (m, 5 H, α-CH_2, 1 THP-H), 3.80-3.89 (m, 1 H, THP-H), 4.43 (d, ^2J = 12 Hz, 1 H, benzyl-H), 4.52 (s, 2 H, benzyl-H), 4.53 (s, 2 H, benzyl-H), 4.68 (s, 1 H, THP-H), 4.71 (d, ^2J = 12 Hz, 1 H, benzyl-H), 7.41 (s, 1 H, phenyl-H), 7.47-7.57 (m, 6 H, phenyl-H), 7.64 (s, 1 H, phenyl-H), 7.69 (s, 1 H, phenyl-H), 7.99 (d, ^3J = 8 Hz, 2 H, py-H), 8.50 (d, ^3J = 8 Hz, 2 H, py-H) 8.90 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = -0.20, 11.22, 13.96, 18.56, 19.13, 22.55, 25.33, 25.82, 29.61, 29.65, 30.36, 31.60, 61.89, 67.67, 70.78, 70.34, 72.08, 89.02, 89.42, 91.20, 94.88, 97.67, 103.99, 106.49, 120.85, 123.20, 123.49, 123.87, 124.37, 125.92, 129.06, 129.51, 130.11, 130.57, 130.82, 134.02, 135.05, 135.42, 135.53, 137.76, 137.89, 138.91, 139.90, 140.10, 147.52, 154.73, 154.80.

MS (**EI**) *m/z* (%): 1014.8 (10.82), 983.5 (27.09), 870.3 (8.88).

HRMS: for $C_{63}H_{79}N_2O_4Si_2$ $[M-C_3H_7]^+$: calcd.: 983.55784;
Found: 983.55705.

*5-(3-(2-(3-ethynyl-5-((tetrahydro-2H-pyran-2-yloxy)methyl)phenyl)ethynyl)-5-((hexyloxy)methyl)phenyl)-2-(5-(3-((hexyloxy)methyl)-5-(2-(triisopropylsilyl)ethynyl)phenyl)pyridin-2-yl)pyridine (**86e**):*



86d (1 g, 0.97 mmol), THF (20 ml), methanol (15 ml). Purification by column chromatography through silica gel (hexane/ethyl acetate 6:1) gave 0.88 g of **86e** (95%) as colourless oil.

R_f = 0.38 (hexane/ethyl acetate 6:1).

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.84 (t, 6 H, CH_3), 1.11 (s, 21 H, $Si(C_3H_7)_3$), 1.20-1.50 (m, 12 H, γ-, δ-, ε-CH_2), 1.50-1.95 (m, 10 H, THP, β-CH_2), 3.09 (s, 1 H, acetylene-H), 3.40-3.52 (m, 5 H, α-CH_2, 1 THP-H), 3.78-3.89 (m, 1 H, THP-H), 4.45

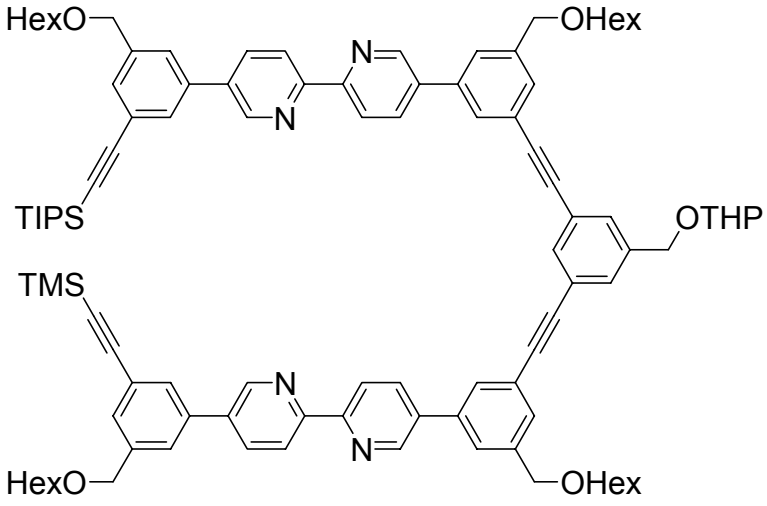
(d, ^2J = 12 Hz, 1 H, benzyl-H), 4.48 (s, 2 H, benzyl-H), 4.49 (s, 2 H, benzyl-H), 4.66 (t, 1 H, THP-H), 4.69 (d, ^2J = 12 Hz, 1 H, benzyl-H), 7.40 (s, 1 H, phenyl-H), 7.45 (s, 1 H, phenyl-H), 7.51 (s, 2 H, phenyl-H), 7.52 (s, 1 H, phenyl-H), 7.55 (s, 1 H, phenyl-H), 7.62 (s, 1 H, phenyl-H), 7.66 (s, 1 H, phenyl-H), 7.96 (d, ^3J = 8 Hz, 2 H, py-H), 8.48 (d, ^3J = 8 Hz, 2 H, py-H) 8.87 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = 11.10, 13.87, 18.49, 19.01, 22.44, 25.21, 25.71, 29.50, 30.20, 31.48, 61.74, 67.48, 70.67, 71.91, 77.83, 82.54, 88.75, 89.45, 91.05, 97.63, 106.30, 120.76, 122.40, 123.17, 123.62, 124.23, 125.79, 128.92, 129.35, 129.98, 130.45, 130.75, 133.90, 134.90, 135.28, 137.64, 138.98, 139.76, 139.97, 147.36, 154.55.

MS (**FAB+**) *m/z* (%): 955.4 (5.24), 884.9 (2.10).

HRMS: for $C_{60}H_{73}N_2O_4Si$: calcd.: 913.53396;
Found: 913.53219.

*5-(3-((hexyloxy)methyl)-5-(2-(3-(2-(3((hexyloxy)methyl)-5-(6-(5-(3-((hexyloxy)methyl)-5-(2-(trimethylsilyl)ethynyl)phenyl)pyridin-2-yl)pyridin-3-yl)phenyl)ethynyl)-5-((tetrahydro-2H-pyran-2-yloxy)methyl)phenyl)ethynyl)phenyl)-2-(5-(3-((hexyloxy)methyl)-5-(2-(triisopropylsilyl)ethynyl)phenyl)pyridin-2-yl)pyridine (**88a**):*



86a (0.39 g, 0.55 mmol), **86e** (0.47 g, 0.49 mmol), toluene 35 ml, triethylamine 25 ml, at 80 °C for 24 h. The compound was purified by column chromatography through silica gel (hexane/ethyl acetate 6:1) to give 0.5 g of **88a** (63%) as colourless oil.

Rf = 0.42 (hexane/ethyl acetate 4:1).

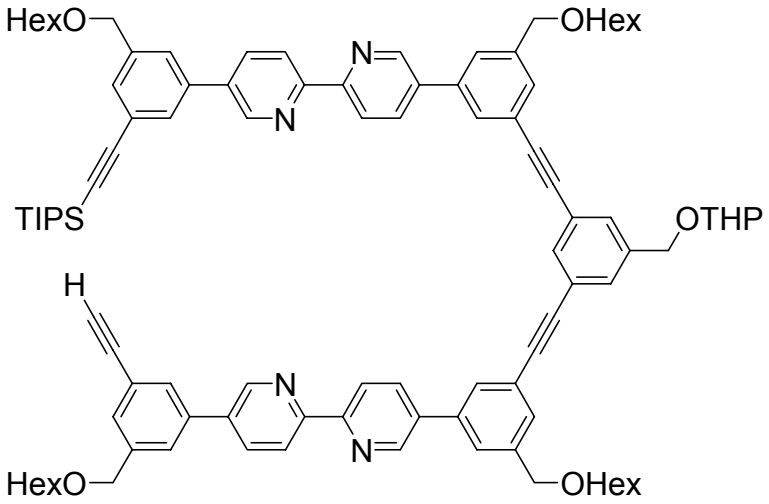
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.26 (s, 9 H, $Si(CH_3)_3$), 0.80-0.92 (m, 12 H, CH_3), 1.13 (s, 21 H, $Si(C_3H_7)_3$), 1.25-1.50 (m, 24 H, γ-, δ-, ε-CH_2), 1.53-1.90 (m, 14 H, β-CH_2, THP), 3.45-3.65 (m, 9 H, α-CH_2, THP), 3.85-3.97 (m, 1 H, THP), 4.49 (d, ^2J = 12

Hz, 1 H, benzyl-H), 4.51 (s, 2 H, benzyl-H), 4.53 (s, 2 H, benzyl-H), 4.56 (s, 4 H, benzyl-H), 4.73 (t, 1 H, THP), 4.79 (d, ^2J = 12 Hz, 1 H, benzyl-H),7.48 (s, 2 H, phenyl-H), 7.55 (s, 6 H, phenyl-H), 7.59 (s, 2 H, phenyl-H), 7.65 (s, 2 H, phenyl-H), 7.68 (s, 1 H, phenyl-H), 7.73 (s, 2 H, phenyl-H), 7.97-8.10 (m, 4 H, py-H), 8.47-8.55 (m, 4 H, py-H), 8.90 (s, 2 H, py-H), 8.93 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = -0.24, 11.14, 13.90, 18.50, 19.08, 22.46, 25.26, 25.71, 29.52, 29.56, 30.31, 31.51, 61.81, 67.64, 70.67, 70.75, 71.95, 88.97, 89.53, 91.07, 94.67, 97.69, 104.48, 106.46, 120.74, 123.31, 123.73, 123.85, 124.25, 125.77, 125.83, 128.94, 129.24, 129.37, 130.03, 130.43, 133.52, 134.87, 135.23, 135.33, 137.56, 137.62, 137.73, 139.07, 139.81, 140.01, 147.36, 154.60, 154.65.

MS (**FAB**) *m/z* (%): 1587.1 (100), $[M+H]^+$, 1501.8 (84), $[M-Hex]^+$, 1486.4 (32), $[M-OHex]^+$.

*5-(3-(2-(3-(2(3-(6-(5-(3-ethynyl-5-((hexyloxy)methyl)phenyl)pyridin-2-yl)pyridine-3-yl)-5-((hexyloxy)methyl)phenyl)ethynyl)-5-((tetrahydro-2H-pyran-2-yloxy)methyl)phenyl)ethynyl)-5-((hexyloxy)methyl)phenyl)-2-(5-(3-((hexyloxy)methyl)5-(2-(triisopropylsilyl)ethynyl)phenyl)pyridin-2-yl)pyridine (**88b**):*



88a (0.44 g, 0.28 mmol), a catalytic amount of 1M NaOH solution, THF 10 ml, methanol 10 ml, stirring for 24 h to give 0.40 g (98 %) of **88b** as a white solid which can be use without further purification.

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.87 (t, 12 H, CH_3), 1.13 (s, 21 H, $Si(C_3H_7)_3$), 1.20-1.50 (m, 24 H, γ-, δ-, ε-CH_2), 1.55-1.95 (m, 14 H, β-CH_2, THP), 3.13 (s, 1 H, acetyl-H), 3.48-3.59 (m, 9 H, α-CH_2, THP), 3.80-4.00 (m, 1 H, THP), 4.51 (d, ^2J = 12 Hz, 1 H, benzyl-H), 4.55 (s, 4 H, benzyl-H), 4.59 (s, 4 H, benzyl-H), 4.74 (t, 1 H, THP), 4.80 (d, ^2J = 12 Hz, 1 H, benzyl-H), 7.48 (s, 1 H, phenyl-H), 7.51 (s, 1 H, phenyl-H), 7.54

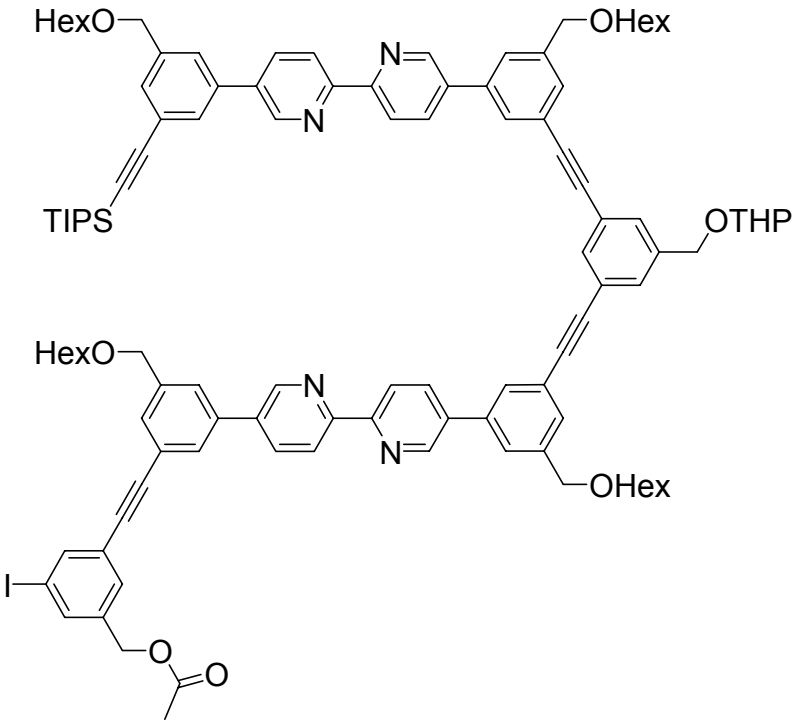
(s, 2 H, phenyl-H), 7.56 (s, 3 H, phenyl-H), 7.61 (s, 3 H, phenyl-H), 7.66 (s, 1 H, phenyl-H), 7.68 (s, 2 H, phenyl-H), 7.73 (s, 2 H, phenyl-H), 8.00-8.10 (m, 4 H, py-H), 8.52 (d, ^3J = 8 Hz, 4 H, py-H), 8.91 (s, 2 H, py-H), 8.94 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = 11.24, 13.99, 18.61, 19.19, 22.55, 25.35, 25.82, 29.63, 30.42, 31.60, 61.99, 67.78, 70.85, 72.00, 72.11, 77.77, 83.15, 89.06, 89.56, 91.25, 97.83, 106.47, 120.92, 122.99, 123.42, 123.87, 124.37, 125.97, 126.35, 129.13, 129.58, 130.21, 130.61, 133.65, 135.12, 135.46, 137.78, 137.82, 137.90, 139.16, 139.90, 140.12, 147.54, 154.78.

MS (**FAB**) *m/z* (%): 1514.6 (100), $[M+H]^+$, 1428.8 (74.83), $[M-Hex]^+$.

EA: for $C_{101}H_{120}N_4O_6Si$ (1514.14): calcd.: C 80.12, H 7.99, N 3.70; found: C 80.17, H 7.64, N 3.43.

*Compound (**88c**):*



88b (0.39 g, 0.25 mmol), **89** (1 g, 2.55 mmol), toluene (35 ml), TEA (25 ml), 60 °C, 24 h, gave 0.3 g of **88c** (67%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, 12 H, CH_3), 1.12 (s, 21 H, $Si(C_3H_7)_3$), 1.15-1.45 (m, 24 H, γ-, δ-, ε-CH_2), 1.50-1.90 (m, 14 H, β-CH_2, THP), 2.09 (s, 3 H, CH_3) 3.45-3.60 (m, 9 H, α-CH_2, THP), 3.85-4.00 (m, 1 H, THP), 4.45-4.60 (m, 9 H, benzyl-H), 4.72 (t, 1 H, THP), 4.76 (d, ^2J = 13 Hz, 1 H, benzyl-H), 4.99 (s, 2 H, benzyl-H), 7.46 (s, 2 H, phenyl-H), 7.49 (s, 1 H, phenyl-H), 7.52 (s, 5 H, phenyl-H), 7.56 (s, 3 H, phenyl-H), 7.61 (s, 1 H, phenyl-H), 7.64 (s, 1 H, phenyl-H), 7.67 (s, 2 H, phenyl-H),

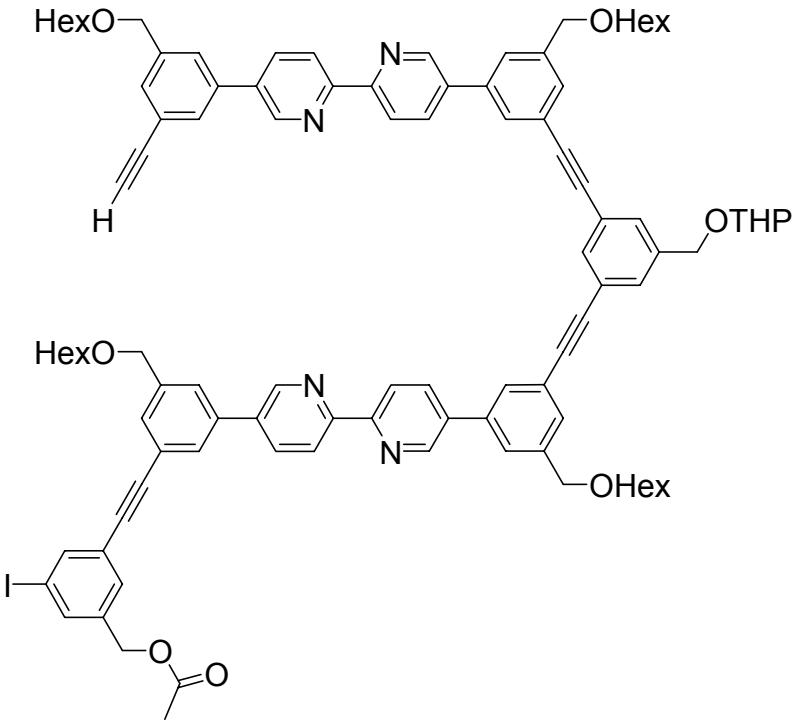
7.70 (s, 2 H, phenyl-H), 7.81 (s, 2 H, phenyl-H), 7.95-8.08 (m, 4 H, py-H), 8.50 (d, ^3J = 9 Hz, 4 H, py-H), 8.90 (d, 4 H, ^4J = 2 Hz, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 11.24, 13.92, 18.58, 19.18, 20.69, 22.50, 25.35, 25.78, 29.62, 30.40, 31.57, 61.95, 64.50, 67.76, 70.78, 70.86, 72.06, 87.75, 89.07, 89.59, 90.58, 91.23, 93.63, 97.84, 106.55, 120.88, 123.43, 123.85, 124.36, 125.15, 125.88, 126.14, 129.04, 129.47, 130.20, 130.53, 133.61, 135.00, 135.25, 135.38, 135.50, 136.65, 137.74, 137.88, 138.12, 139.20, 139.67, 139.93, 140.15, 140.21, 147.49, 154.74, 154.81, 170.25.

MS (**FAB**) *m/z* (%): 1788.9 (100), 1705.2 (18), 1689.6 (39).

EA: for $C_{110}H_{127}IN_4O_8Si$ (1788.197): calcd.: C 73.88, H 7.16, N 3.13; found: C 73.46, H 7.15, N 3.00.

*Compound (**88d**):*



88c (0.26 g, 0.17 mmol), Bu_4NF (54 mg), THF (20 ml). Purification of the compound by column chromatographay through silica gel (hexane/ethyl acetate 3 : 1) to give 0.23 g of **88d** (98%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, 12 H, CH_3), 1.15-1.45 (m, 24 H, γ-, δ-, ε-CH_2), 1.50-1.90 (m, 14 H, β-CH_2, THP), 2.06 (s, 3 H, CH_3) 3.12 (s, 1 H, acetylene-H), 3.45-3.60 (m, 9 H, α-CH_2, THP), 3.80-3.95 (m, 1 H, THP), 4.45-4.60 (m, 9 H, benzyl-H), 4.72 (t, 1 H, THP), 4.75 (d, ^2J = 13 Hz, 1 H, benzyl-H), 4.96 (s, 2 H, benzyl-H), 7.43 (s, 2 H, phenyl-H), 7.46 (s, 1 H, phenyl-H), 7.50 (s, 4 H, phenyl-H), 7.53 (s, 4 H,

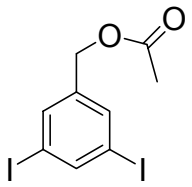
phenyl-H), 7.59 (s, 1 H, phenyl-H), 7.60 (s, 1 H, phenyl-H), 7.64 (s, 2 H, phenyl-H), 7.67 (s, 2 H, phenyl-H), 7.79 (s, 2 H, phenyl-H), 7.90-8.08 (m, 4 H, py-H), 8.41-8.50 (m, 4 H, py-H), 8.83 (s, 1 H, py-H), 8.87 (s, 3 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.92, 19.18, 20.70, 22.50, 25.34, 25.78, 29.61, 30.40, 31.56, 61.97, 64.52, 67.77, 70.87, 71.96, 72.02, 72.07, 77.75, 83.16, 87.75, 89.06, 89.58, 90.57, 93.63, 97.85, 120.90, 122.96, 123.42, 123.85, 125.15, 125.97, 126.17, 126.26, 129.05, 129.53, 130.21, 130.54, 133.62, 134.99, 135.27, 135.40, 136.66, 137.86, 138.12, 139.19, 139.69, 140.14, 140.19, 147.48, 154.78, 170.30.

MS (**FAB**): 1632.7 (100), 1546.2 (20), 1442.3 (23).

EA: for $C_{101}H_{107}IN_4O_8$ (1631.85): calcd.: C 74.38, H 6.61, N 3.43;
found: C 71.84, H 6.22, N 3.22.

*3,5-diiodobenzyl acetate (**89**):*



To a mixture of 3,5-diiodophenylmethanol (2.92 g, 8.1 mmol), triethylamine (4 ml) and catalytic amounts of 4,4-dimethylaminopyridine (0.15 g) in 80 ml dry DCM, fresh distilled acetyl chloride (1.3 g, 16.5 mmol) was added at 0 °C and the resulting mixture was stirred for 5 h at this temperature. Then water was added and the phases were separated. The organic phase was dried over $MgSO_4$. The solvent was removed and the compound was purified by column chromatography through silica gel (hexane/ethyl acetate 6:1) to give 3 g of **89** (95%) as a white solid.

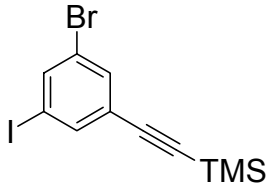
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 2.10 (s, 3 H, CH_3), 4.95 (s, 2 H, benzyl-H), 7.62 (s, 2 H, phenyl-H), 7.97 (s, 1 H, phenyl-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 20.79, 64.02, 94.74, 136.08, 139.86, 144.72, 170.23.

MS (**EI**) *m/z* (%): 401.8 (31), 359.4 (52), 342.7 (8).

EA: for $C_9H_8I_2O_2$ (401.97): calcd.: C 26.89, H 2.01,
found: C 26.93, H 1.83,

*(2-(3-bromo-5-iodophenyl)ethynyl)trimethylsilane (**97**):*



To a stirred suspension of **96** (3 g, 9.03 mmol) in dry diethylether (50 ml) a solution of 1.6 M of BuLi in hexane (6 ml, 9.6 mmol) was added droppwise at -78°C. After 2 h, diiodoethan (3.36 g, 11.92 mmol) was added and the mixture was let to warm to 20°C. Then water (40 ml) was added, the phases were separated. The aqueous phase was extracted with diethylether (2 × 50 ml) and the combined organic phases were dried over $MgSO_4$. The solvent was removed and the residue chromatographied over silica gel using as eluent hexane/ethylacetate (100:1) to give **97** as a colorless oil (2 g, 60 %).

R_f (hexane/ethylacetate 100:1) = 0.68.

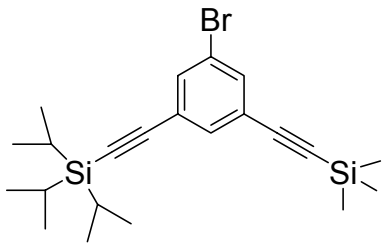
^{1}H NMR ($CDCl_3$): δ = 0.27 (s, 9 H, CH_3) 7.54 (s, 1 H, phenyl-H), 7.72 (s, 1 H, phenyl-H), 7.72 (s, 1 H, phenyl-H).

^{13}C-NMR ($CDCl_3$, 63 MHz): δ = -0.16, 93.74, 97.45, 101.51, 122.36, 126.47, 133.81, 138.99, 139.52.

MS (**EI**): *m/z* (%): 378 (39.89), 365 (100).

EA: for $C_{11}H_{12}BrISi$: calcd.: C 34.85, H 3.19;
found: C 34.81, H 3.22.

*1-bromo-3-(2-(triisopropylsilyl)ethynyl)-5-(2-(trimethylsilyl)ethynyl)benzene (**98**):*



A heavy-walled flask containing aryl iodide **97** (4.89 g, 12.9 mmol) and 100 ml triethylamine was degassed few times. To the degassed solution triisopropylsililacetylene (2 g, 14.2 mmol), $[Pd(PPh_3)_4]$ (335 mg) and CuI (48 mg) were added and the mixture degassed once more. It was then sealed with a teflon screw cap and stirred for 24 h at room temperature. The solvent was removed and the reaction mixture purified by column chromatography through silica gel (hexane) to give 5 g of **98** (90%) as colourless oil.

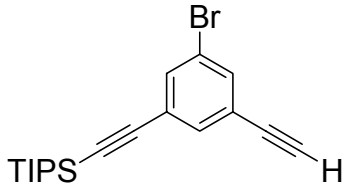
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.24 (s, 9H, CH_3), 1.12 (s, 21H, TIPS), 7.49 (s, 1H, Ph-H), 7.58 (s, 2H, Ph-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = -0.20, 11.23, 18.64, 93.19, 96.55, 102.46, 104.41, 121.64, 125.02, 125.37, 133.86, 134.37, 134.56.

MS (**EI**) m/z (%):417 (6.83) [M^+-CH_3], 389 (44.39) [M^+-C_3H_7].

HRMS (M^+-CH_3) calcd for $C_{21}H_{30}{}^{79}BrSi_2$: 417.10693; found 417.10822.

*(2-(3-bromo-5-ethynylphenyl)ethynyl)triisopropylsilane (**99**):*



To a stirred solution of **98** (4.00 g, 9.26 mmol) in a mixture of THF/methanol 1:1 (40 ml), a catalytic amount of 1M NaOH solution was added. After complete consumption of the starting material, the reaction mixture was diluted with diethyleter (50 ml) and brine (20 ml) and the phases were separated. The aqueous phase was extracted with diethyleter (20 ml), and the combined organic phases were dried over $MgSO_4$, The solvent was removed and the resulting oil purified by column chromatography trough silica gel (hexane/ethyl acetate 9:1) to give 3.13 g of **99** (97.8%) as colourless oil.

R_f = 0.75 (hexane/ethylacetate 9:1).

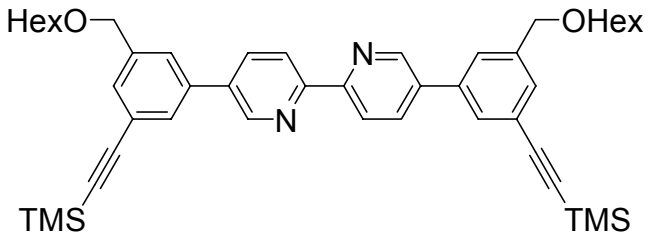
^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.10 (s, 21 H, $Si(C_3H_7)_3$), 3.10 (s, 1 H, acetyl-H), 7.47 (s, 1 H, phenyl-H), 7.55 (s, 1 H, phenyl-H), 7.58 (s, 1 H, phenyl-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 11.28, 18.64, 79.04, 81.35, 93.38, 104.34, 121.74, 124.04, 125.52, 134.08, 134.52, 134.91;

MS (**EI**): m/z (%): 362.2 (31.81), 319.1 (100), 249 (33.85).

HRMS for $C_{19}H_{25}BrSi$: calcd.: 360.09088;
found 360.09133.

*5.5'-Bis-(3-hexyloxymethyl-5-trimethylsilanylethynyl-phenyl)-[2,2']-bipyridyl (**100a**):*



76 (1.73 g, 2.20 mmol), $Pd(PPh_3)_4$ (0.02 equiv per coupling), CuI (0.02 equiv per coupling), dry triethylamine (35 ml), dry toluene (20 ml), trimethylsilylacetylene (0.74 g, 7.57 mmol). The solvent was removed and the reaction mixture was purified by column chromatography trough silica gel (hexane/ethyl acetate 6:1) to give 1.44 g of **100a** (90%) as white solid.

R_f = 0.42 (hexane/ethyl acetate 6:1).

M.p. 89 °C.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.24 (s, 18 H, $Si(CH_3)_3$), 0.85 (t, 6 H, CH_3), 1.21-1.41 (m, 12 H, γ, δ, ε- CH_2), 1.61 (mc, 4 H, β- CH_2), 3.49 (t, 4 H, α-CH_2), 4.51 (s, 4 H, benzyl-CH_2), 7.48 (s, 2 H, phenyl-H), 7.56 (s, 2 H, phenyl-H), 7.66 (s, 2 H, phenyl-H), 7.99 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 2 H, py-H), 8.49 (d, ^3J = 8 Hz, 2 H, py-H), 8.89 (s, 2 H, py-H).

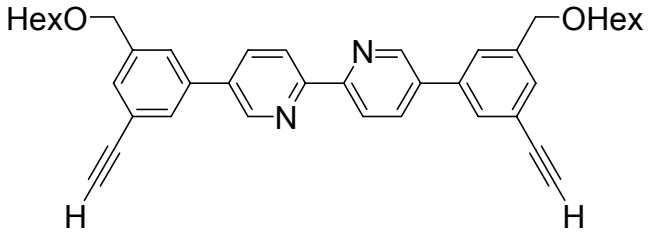
^{13}C NMR ($CDCl_3$, 63 MHz): δ = -0.12, 13.98, 22.55, 25.81, 29.63, 31.6, 70.79, 72.09, 94.84, 104.53, 120.87, 124.00, 126.07, 129.46, 130.53, 135.07, 135.47, 137.77, 139.94, 147.53, 154.79.

MS (**EI**, 80eV) *m/z* (%): 728 (27), 628 (100).

HRMS: for $C_{46}H_{60}N_2O_2Si_2$: calcd.: 728.419336,

Found: 728.41638.

*5,5'-Bis-(3-ethynyl-5-hexyloxymethyl-phenyl)-[2,2']-bipyridyl (**100b**):*



100a (1.4 g, 1.92 mmol), THF (30 ml), methanol (30 ml). The compound was purified by column chromatography through silica gel (hexane/ethyl acetate 6:1) to give 1.09 g of **100b** (97%) as a white solid.

R_f = 0.65 (hexane/ethyl acetate 3:1).

M.p. 92 °C.

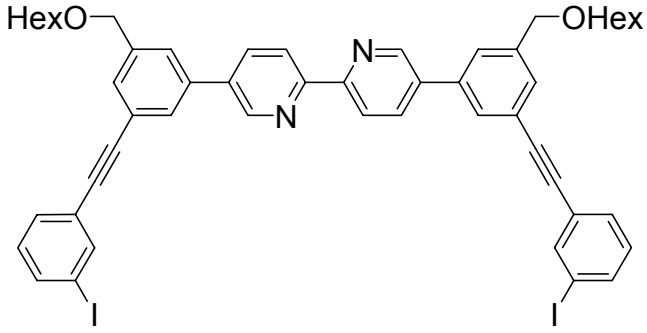
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, 6 H, CH_3), 1.21-1.45 (m, 12 H, γ-, δ-, ε-CH_2), 1.62 (mc., 4 H, β-CH_2), 3.12 (s, 2 H, acetylene-H), 3.50 (t, 4 H, α-CH_2), 4.52 (s, 4 H, benzyl-CH_2), 7.50 (s, 2 H, phenyl-H), 7.60 (s, 2 H, phenyl-H), 7.69 (s, 2 H, phenyl-H), 8.00 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 2 H, py-H), 8.49 (d, ^3J = 8 Hz, 2 H, py-H), 8.89 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.01, 22.58, 25.84, 29.67, 31.64, 70.92, 72.09, 77.78, 83.17, 120.99, 123.04, 126.48, 129.71, 130.71, 135.19, 135.46, 137.95, 140.13, 147.59, 154.87.

MS (**EI**, 80 eV) *m/z* (%): 584 (80), 499 (33), 484 (100), 383 (56).

EA: for $C_{40}H_{44}N_2O_2$ (584.80): calcd.: C 82.15, H 7.58, N 4.79;
found: C 82.06, H 7.28, N 4.65.

*5,5'-Bis-[3-hexyloxymethyl-5-(3-iodo-phenylethynyl)-phenyl]-[2,2']-bipyridyl (**100c**):*



100b (2.00 g, 3.42 mmol), 1,3-diiodobenzene (23 g, 70 mmol), toluene (230 ml), triethylamine (230 ml), $Pd(PPh_3)_4$ (0.04 equiv) and CuI (0.04 equiv), 3 d. The solvent was removed and the crude product was purified by column chromatography through silica gel (hexane/ethyl acetate 6:1) to give 2.00 g of **100c** (60%) as white solid.

R_f = 0.17 (hexane/ethyl acetate 6:1).

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, 6 H, CH_3), 1.23-1.42 (m, 12 H, γ-, δ-, ε-CH_2), 1.65 (m, 4 H, β-CH_2), 3.53 (t, 4 H, α-CH_2), 4.56 (s, 4 H, benzyl-CH_2), 7.06 (t, 2 H, phenyl-H), 7.42 (d, 2 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 7.53 (s, 2 H, phenyl-H),

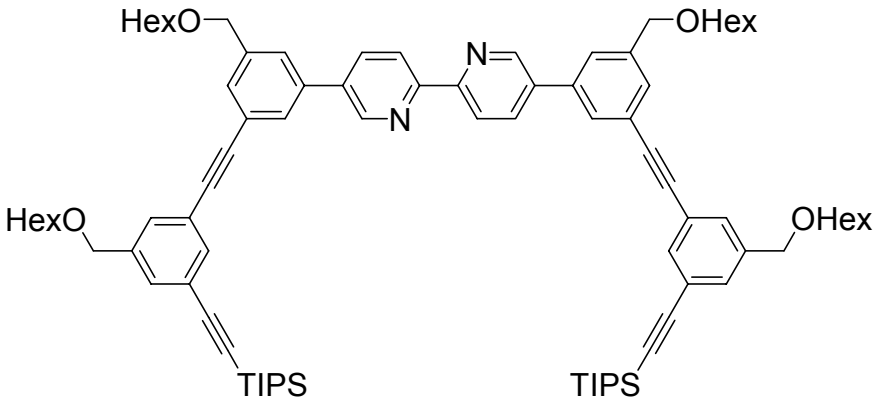
7.59 (d, 2 H, phenyl-H), 7.64 (s, 2 H, phenyl-H), 7.83 (s, 2 H, phenyl-H), 7.96 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 2 H, py-H), 8.54 (d, ^3J = 8 Hz, 2 H, py-H), 8.94 (d, ^4J = 2 Hz, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.00, 22.58, 25.84, 29.68, 31.64, 70.95, 72.13, 88.18, 90.26, 93.67, 121.01, 123.70, 125.07, 126.22, 129.16, 129.81, 130.22, 130.69, 135.16, 135.51, 137.38, 138.00, 140.17, 140.21, 147.59, 154.88.

MS (**EI**, 80 eV) *m/z* (%): 988.9 (57.17), 988.0 (96.83), 888.9 (43.63), 887.9 (100), 761.9 (26.69), 127.9 (45.09), 42.0 (49.08).

HRMS: for $C_{52}H_{50}I_2N_2O_2$: calcd.: 988.19617;
Found: 988.19436.

*5,5'-Bis-(3-hexyloxymethyl-5-{3-hexyloxymethyl-5-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenyl)-[2,2']-bipyridinyl (**101a**):*



92a (X^3 = CH_2OHex) (3.41 g, 8.6 mmol), **74a** or **76** (2.90 mmol), tryethylamine (40 ml), toluene (20 ml). Column chromatography trough silica gel (hexane/ethyl acetate 10:1) to give 3.07 g of **101a** (80%) as a colourless oil.

R_f = 0.48 (hexane/ethyl acetate 4:1).

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.92 (t, 12 H, CH_3), 1.12 (s, 42 H, $Si(C_3H_7)_3$), 1.30-1.48 (mc, 24 H, γ-, δ-, ε-CH_2), 1.64 (mc, 8 H, β-CH_2), 3.28 (m, 8 H, α-CH_2), 4.40 (s, 4 H, benzyl-CH_2), 4.60 (s, 4 H, benzyl-CH_2), 7.42 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.56 (s, 2 H, phenyl-H) 7.60 (s, 2 H, phenyl-H) 7.70 (s, 2 H, phenyl-H) 7.72 (s, 2 H, phenyl-H), 8.04 (d, ^3J = 8 Hz, 2 H, py-H), 8.52 (d, ^3J = 8 Hz, 2 H, py-H), 8.96 (s, 2 H, py-H).

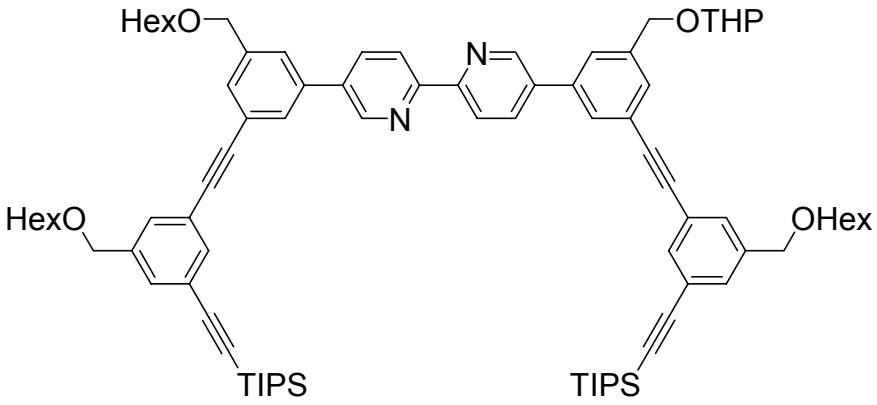
^{13}C NMR ($CDCl_3$, 63 MHz): δ = 11.28, 14.03, 18.64, 22.61, 25.84, 29.67, 31.67, 70.81, 70.95, 71.92, 72.22, 89.17, 89.42, 91.41, 106.05, 121.03, 123.25, 123.98,

126.14, 129.25, 130.30, 130.43, 130.91, 134.15, 135.26, 135.63, 138.04, 139.37, 140.18, 147.67, 154.95.

MS (**EI**, 80 eV) *m/z* (%) = 1326 (10) [M^+], 1282 (100).

HRMS for $C_{88}H_{120}N_2O_4Si_2$: calcd.: 1280.81607;
Found: 1280.81120.

*5'-(3-Hexyloxymethyl-5-{3-hexyloxymethyl-5-[(triisopropylsilanyl)-ethynyl]-phenylethynyl}-phenyl)-5-[3-[3-hexyloxymethyl-5-(1-isopropyl-2,4-dimethyl-siletan-1-ylethynyl)-phenylethynyl]-5-(tetrahydro-pyran-2-yloxymethyl)-phenyl]-[2,2']bipyridinyl (**101b**):*



74c (1.78 g, 2.56 mmol), **92a** (X^3 = CH_2OHex) (3.01 g, 7.60 mmol), tryethylamine (40 ml), toluene (20 ml). Column chromatography trough silica gel (hexane/ethyl acetate 6:1) gave 2.79 g of **101b** (82%) as colourless oil.

$\mathbf{R_f}$ = 0.36 (hexane/ethyl acetate 3:1).

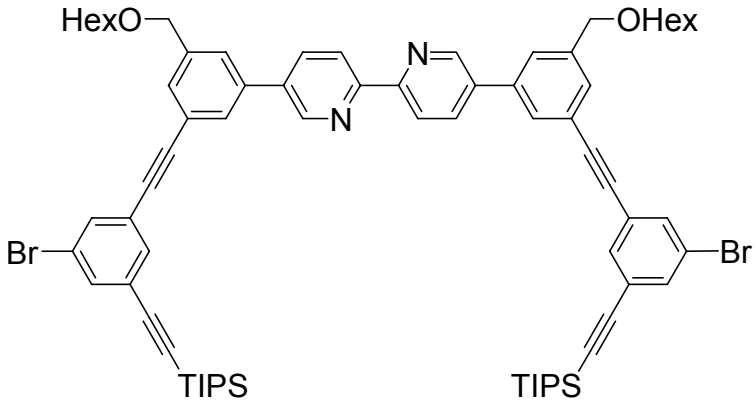
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.86 (t, 9 H, CH_3), 1.12 (s, 42 H, $Si(C_3H_7)_3$), 1.23-1.42 (mc, 18 H, β-, γ-, δ-CH_2), 1.50-1.90 (mc, 12 H, β-CH_2, 6 H-THP), 3.45-3.6 (m, 7 H, α-CH_2, THP), 3.90 (m, 1 H, THP), 4.39 (s, 4 H, benzyl-H), 4.51 (s, 2 H, benzyl-H), 4.56 (d, ^2J = 12 Hz, 1 H, benzyl-H), 4.73 (t, 1 H, THP), 4.88 (d, ^2J = 12 Hz, 1 H, benzyl-H), 7.41 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.53 (s, 1 H, phenyl-H), 7.56 (s, 2 H, phenyl-H), 7.61 (s, 3 H, phenyl-H), 7.71 (s, 2 H, phenyl-H), 7.53 (d, ^3J = 8 Hz, 2 H, py-H), 8.00 (d, ^3J = 8 Hz, 2 H, py-H), 8.91 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 11.17, 13.93, 18.19, 19.20, 22.51, 25.34, 25.74, 29.56, 30.41, 31.55, 61.98, 66.90, 68.03, 70.67, 70.81, 71.75, 72.04, 89.07, 89.37, 91.22, 97.86, 105.98, 120.89, 123.13, 123.83, 12589, 126.11, 129.03, 130.26, 130.71, 133.97, 135.02, 135.39, 137.79, 139.30, 139.68, 140.10, 147.42, 154.64.

MS (**FAB**) *m/z* (%): 1327 (7.20), $[M+H]^+$, 496 (32.29).

EA: for $C_{87}H_{116}N_2O_5Si_2$ (1326.03): calcd.: C 78.80, H 8.82, N 2.11;
found: C 78.42, H 8.83, N 1.94.

*5-(3-(2-(3-bromo-5-(2-triisopropylsilyl)ethynyl)phenyl)ethynyl)-5-((hexyloxy)methyl)phenyl)-2-((5-(3-(2-(3-bromo-5-(2-(triisopropylsilyl)ethynyl)phenyl)ethynyl)-5-((hexyloxy)methyl)phenyl)pyridine-2-yl)pyridine (**101c**):*



Diiodocompound **76** (1g, 1.26 mmol), free acetylene compound **99** (0.92 g, 2.54 mmol), triethylamnie (30 ml), toluene (15 ml). The compound was purified by column chromatography through silica gel (hexane/ethylacetate 9:1) gave 1.3 g of **101c** (84%) as white solid.

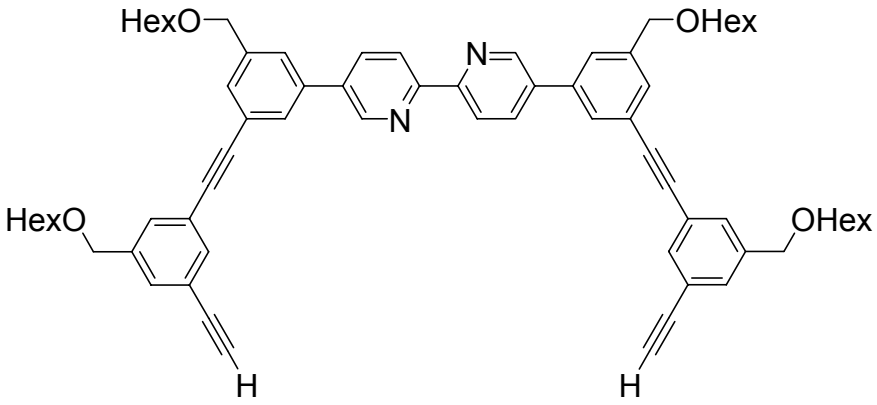
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.88 (t, 6 H, CH_3), 1.12 (s, 42 H, $Si(C_3H_7)_3$), 1.29-1.37 (m, 12 H, γ-, δ-, ε-CH_2), 1.52-1.66 (m, 4 H, β-CH_2), 3.47 (t, 4 H, α-CH_2), 4.45 (s, 4 H, benzyl-H), 7.45 (s, 2 H, phenyl-H), 7.50 (s, 2 H, phenyl-H), 7.53 (s, 4 H, phenyl-H), 7.63 (s, 2 H, phenyl-H), 7.89 (d, ^3J = 8 Hz, 2 H, py-H), 8.58 (d, ^3J = 8 Hz, 2 H, py-H), 0.88 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = 11.19, 14.02, 18.59, 22.60, 25.86, 29.68, 31.65, 70.95, 72.09, 87.62, 90.74, 93.28, 104.39, 121.00, 121.80, 123.42, 124.90, 125.49, 126.32, 129.16, 130.23, 133.58, 133.95, 134.40, 135.13, 135.40, 137.96, 140.24, 147.52, 154.79.

MS (**FAB+**): *m/z* (%): 1255.5 (100) $[M^+]$.

EA. for $C_{74}H_{90}Br_2N_2O_2Si_2$ (1255.5): calcd.: C 70.79, H 7.23, N 2.23;
Found: C 70.68, H 7.24, N 2.11.

*5,5'-Bis[3-(3-ethynyl-5-hexyloxymethyl-phenylethynyl)-5-hexyloxymethyl-phenyl]-[2,2']bipyridinyl (**102a**):*



101a (2.72 g, 2.05 mmol), ammoniumfluoride trihydrate (1.36 g, 4.25 mmol). The compound was purified by column chromatography through silica gel (ethyl acetate/hexane 1:6) to give 1.97 g of **102a** (95%) as a white solid.

R_f = 0.07 (ethyl acetate/hexane 1:3).

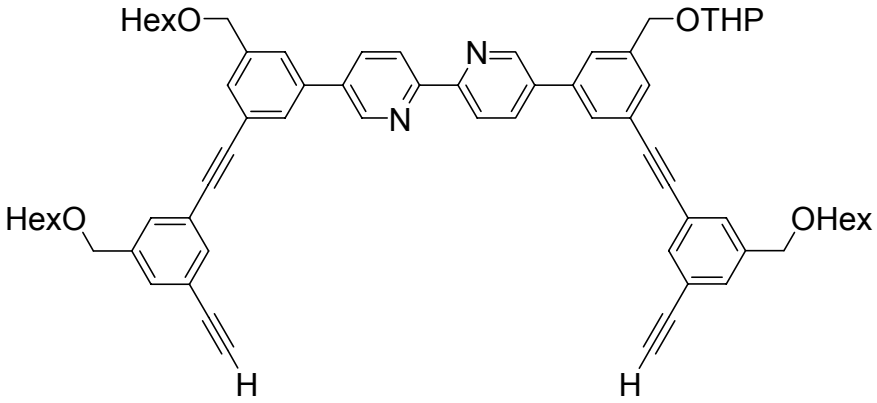
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.89 (t, 12 H, CH_3), 1.29 (mc, 24 H, β-, γ-, δ-CH_2), 1.63 (mc, 8 H, β-CH_2), 3.1 (s, 2 H, acetylene-H), 3.50 (m, 8 H, α-CH_2), 4.46 (s, 4 H, benzyl-CH_2), 4.59 (s, 4 H, benzyl-CH_2), 7.42 (s, 2 H, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.57 (s, 2 H, phenyl-H) 7.59 (s, 2 H, phenyl-H) 7.62 (s, 2 H, phenyl-H) 7.72 (s, 2 H, phenyl-H), 8.04 (d, ^3J = 9 Hz, 2 H, py-H), 8.55 (d, ^3J = 9 Hz, 2 H, py-H), 8.95 (s, 2 H, py-H)

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.04, 22.62, 25.85, 25.90, 29.69, 31.68, 70.89, 70.99, 71.85, 72.24, 88.97, 121.07, 122.59, 123.57, 123.95, 126.24, 129.28, 130.32, 130.92, 134.16, 135.29, 135.71, 138.1, 139.64, 140.25, 147.70, 153.57, 154.99.

MS (**FAB**) *m/z* (%): 1014 (100), 926 (57.53).

EA: for $C_{70}H_{80}N_2O_4$ (1013.40):	calcd.:	C 82.96,	H 7.96,	N 2.76
	found:	C 81.21,	H 7.59,	N 2.53.

*5'-[3-(3-Ethynyl-5-hexyloxymethyl-phenylethynyl)-5-hexyloxymethyl-phenyl]-5-[3-(3-ethynyl-5-hexyloxymethyl-phenylethynyl)-5-(tetrahydro-pyran-2-yloxymethyl)-phenyl]-[2,2']bipyridinyl (**101b**):*



101a (2.90 g, 2.19 mmol), ammoniumfluoride trihydrate (1.45 g, 4.52 mmol). The compound was purified by column chromatography through silica gel (hexane/ethyl acetate 1:3) to give 2.15 g **102b** (97%) as a white solid.

R_f = 0.36 (ethyl acetate/hexane 1:3).

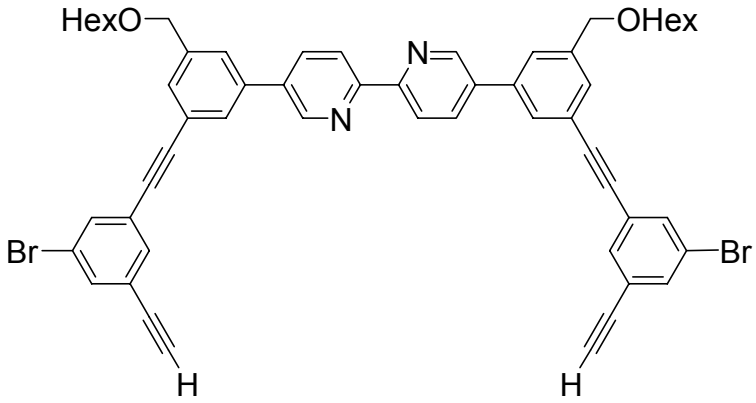
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.86 (t, 9 H, CH_3), 1.18-1.38 (mc, 18 H, γ-, δ-, ε-CH_2), 1.50-2.00 (mc, 12 H, β-CH_2, THP), 3.09 (s, 2 H, acetylene-H), 3.35-3.57 (m, 7 H, α-CH_2, THP), 3.91 (m, 1 H, THP), 4.39 (s, 4 H, benzyl), 4.47 (s, 2 H, benzyl), 4.51 (d, ^2J = 12 Hz, 1 H, benzyl), 4.71 (t, 1 H, THP), 4.82 (d, ^2J = 12 Hz, 1 H, benzyl), 7.36 (s, 2 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 7.5 (s, 2 H, phenyl-H) 7.55 (s, 4 H, phenyl-H) 7.65 (s, 2 H, phenyl-H) 7.94 (d, ^3J = 8 Hz, 2 H, py-H), 8.48 (d, ^3J = 8 Hz, 2 H, py-H), 8.86 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 13.87, 19.17, 22.45, 25.29, 25.74, 29.51, 30.37, 31.49, 61.93, 67.98, 70.66, 71.56, 71.50, 77.81, 82.63, 88.86, 89.52, 97.85, 120.81, 122.42, 123.25, 123.70, 123.73, 125.82, 126.05, 128.93, 130.00, 130.18, 130.58, 130.68, 131.03, 133.89, 134.86, 135.21, 137.73, 139.47, 139.67, 140.07, 147.34, 154.63.

MS (**FAB**) *m/z* (%) = 1013 (12.30), 927 (6.35).

EA: for $C_{69}H_{76}N_2O_5$ (1013.35): calcd.: C 81.78, H 7.56, N 2.76,
found: C 81.22, H 7.34, N 2.38.

*5-(3-(2-(3-bromo-5-ethynylphenyl)ethynyl)-5-((hexyloxy)methyl)phenyl)-2-(5-(3-(2-(3-bromo-5-ethynylphenyl)ethynyl)-5-((hexyloxy)methyl)phenyl)pyridine-2-yl)pyridine (**102c**):*



Tetrabutylammonium fluoride trihydrate (1.5 g, 4.67 mmol), **101c** (2.65 g, 2.11 mmol), THF (50 ml). The resulting oil was purified by column chromatography through silica gel (hexane/ethyl acetate 4:1) gave 0.83 g of **102c** (85%) as a white solid.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, 6 H, CH_3), 1.23-1.50 (m, 12 H, δ-,ε-, γ-CH_2), 1.65 (m, 4 H, β-CH_2), 3.17 (s, 2 H, acetyl-H), 3.54 (t, 4 H, α-CH_2), 4.56 (s, 4 H, benzyl-H), 7.51 (s, 2 H, phenyl-H), 7.59 (overlapped, 6 H, phenyl-H), 7.65 (s, 2 H, phenyl-H), 7.70 (s, 2 H, phenyl-H), 8.03 (d, ^3J = 8 Hz, 2 H, py-H), 8.56 (d, ^3J = 8 Hz, 2 H, py-H), 8.92 (s, 2 H, py-H).

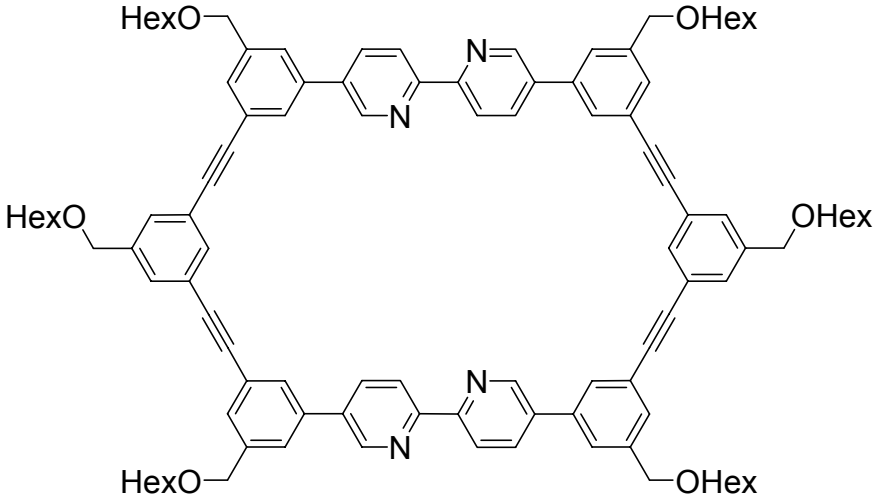
^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.00, 22.59, 25.86, 29.69, 31.65, 71.00, 72.09, 79.19, 81.26, 87.45, 90.93, 121.11, 121.89, 123.38, 124.18, 125.10, 126.41, 129.19, 130.28, 133.65, 134.56, 135.22, 135.46, 137.97, 140.31, 147.50, 154.72.

MS (**FAB**) m/z (%): 943.2 (100) [M^+], 857.9 (19.18) [M^+-C_6H_{13}].

EA: for $C_{56}H_{50}Br_2N_2O_2$ (942.82): calcd.: C 71.34, H 5.35, N 2.97;
Found: C 70.54, H 5.25, N 2.59.

7.2.2. Compounds of chapter 4.3.

*Macrocycle (**103a**):*



102a (300 mg, 0.30 mmol), **76** (236 mg, 0.30 mmol), triethylamine (100 ml), toluene (100 ml), $[Pd(PPh_3)_4]$ (0.04 equiv.), and CuI (0.04 equiv.). Gave 83 mg of **103a** (19%) as white powder.

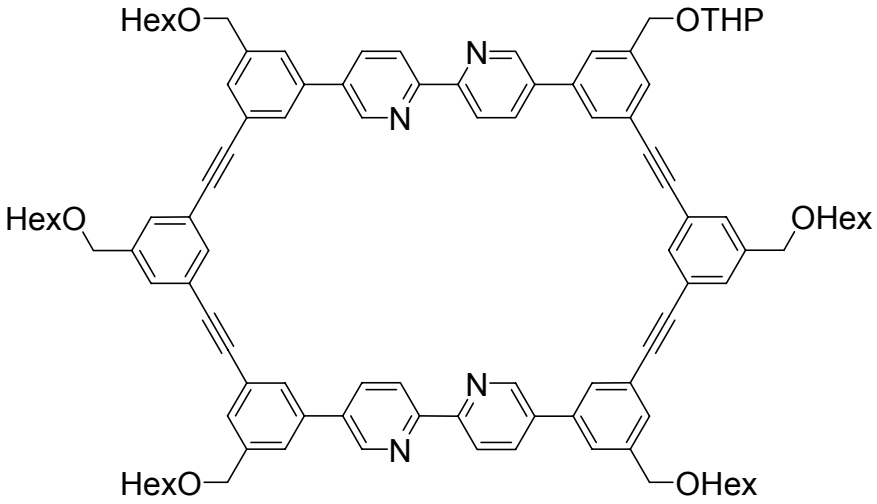
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.91 (t, 18 H, CH_3), 1.20-1.49 (mc, 36 H, γ-, δ-, ε-CH_2), 1.67 (mc, 12 H, β-CH_2), 3.53 (m, 12 H, α-CH_2), 4.51 (s, 4 H, benzyl-CH_2), 4.59 (s, 8 H, benzyl-CH_2), 7.5 (s, 4 H, phenyl-H), 7.55 (s, 4 H, phenyl-H), 7.62 (s, 4 H, phenyl-H) 7.75 (s, 6 H, phenyl-H), 8.06 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 4 H, py-H), 8.53 (d, ^3J = 8 Hz, 4 H, py-H), 8.96 (s, 4 H, py-H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 14.03, 22.63, 23.91, 25.89, 29.14, 29.74, 31.70, 70.90, 70.98, 71.99, 72.27, 89.23, 89.70, 121.11, 123.55, 124.04, 125.91, 129.55, 129.99, 130.16, 134.48, 135.12, 135.40, 137.92, 139.65, 140.25, 147.59, 154.96.

MS (**FAB**) m/z (%) = 1546 (100), 1460 (57.85).

EA: for $C_{106}H_{120}N_4O_6$ (1546.11): calcd.: C 82.34, H 7.82, N 3.62;
found: C 81.27, H 7.54, N 3.50.

*Macrocycle (**103b**):*



102b (1.84 g, 1.82 mmol), **76** (1.44 g, 1.82 mmol), triethylamine (600 ml), toluene (600 ml), [$Pd(PPh_3)_4$] (80 mg, 0.04 equiv), copper iodide (13 mg, 0.04 equiv). Gave 0.66 g of cycle **103b** (23%) as white solid.

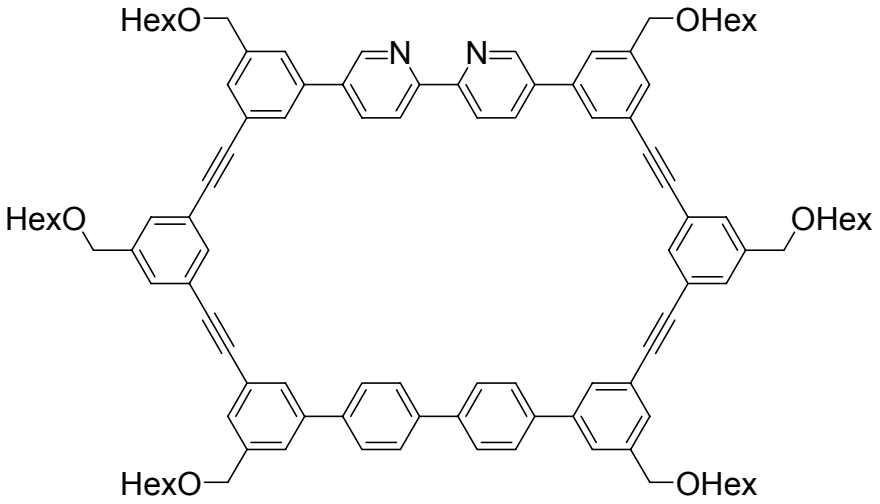
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 15 H, CH_3), 1.20-1.44 (mc, 30 H, γ-, δ-, ε-CH_2), 1.50-2.00 (mc, 16 H, THP, β-CH_2), 3.40-3.64 (m, 11 H, THP, α-CH_2), 3.92 (m, 1 H, THP), 4.46 (s, 4 H, benzyl-H), 4.52 (s, 7 H, THP, benzyl-H), 4.76 (t, 1 H, THP), 5.84 (d, 1 H, benzyl-H), 7.36-7.6 (m, 12 H, phenyl-H), 7.68 (s, 6 H, phenyl-H), 8.00 (dd, 4 H, ^3J = 8 Hz, py-H), 8.52 (d, 4 H, ^3J = 8 Hz, py-H), 8.88 (s, 4 H, py-H).

^{13}C NMR ($CDCl_3$, 126 MHz): δ =14.05, 19.42, 22.65, 25.49, 25.92, 28.73, 30.61, 31.72, 62.29, 68.24, 70.93, 71.04, 71.99, 72.20, 89.35, 89.56, 98.15, 121.56, 123.45, 124.07, 125.51, 129.15, 130.14, 134.35, 135.32, 135.43, 136.96, 139.51, 139.77, 140.18, 146.69, 153.36.

MS (**FAB**) m/z (%) = 1546 (19.72), 1462 (6.81).

EA: for $C_{105}H_{116}N_4O_7$ (1546.07): calcd.: C 81.57, H 7.56, N 3.62;
found: C 81.18, H 7.42, N 3.76.

*Macrocycle (**103c**):*



A solution of **102a** (993 mg, 0.98 mmol) and **83** (771 mg, 0.98 mmol) in a mixture of triethylamine (320 ml) and toluene (320 ml) was carefully degassed. Then [$Pd(PPh_3)_4$] (85 mg, 0.04 equiv) and CuI (14 mg, 0.04 equiv) were added and the reaction was stirred at 60°C for 4 d and then at 95°C for 1 d. The solvent was removed and purification of the residue by GPC gave 302 mg (20%) of **103c** as a white powder.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.93 (m, 18 H, CH_3), 1.38 (m, 36 H, γ-, δ-, ε-CH_2), 1.69 (m, 12 H, β-CH_2), 3.55 (m, 12 H, α-CH_2), 4.45 (s, 4 H, benzyl-H), 4.48 (s, 4 H, benzyl-H), 4.53 (s, 4 H, benzyl-H), 7.40 (s, 6 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.56 (s, 4 H, phenyl-H), 7.66 (m, 14 H, phenyl-H), 8.03 (d, ^3J = 6.4 Hz, 2 H py-H), 8.51 (d, ^3J = 6.6 Hz, 2 H, py-H), 8.91 (s, 2 H, py-H).

^{13}C-NMR ($CDCl_3$, 63 MHz): δ = 14.02, 22.63, 25.91, 29.75, 31.71, 70.84, 70.91, 71.02, 72.00, 72.19, 72.39, 88.72, 89.36, 89.53, 90.15, 121.57, 123.41, 123.51, 123.70, 124.07, 125.56, 125.76, 127.17, 127.27, 129.12, 129.49, 129.97, 130.07, 131.84, 134.35, 135.49, 137.05, 138.72, 139.44, 139.53, 139.64, 140.20, 140.46, 146.74.

MS (**FAB**) m/z (%) = 1544 (100), 1459 (59.21).

EA: for $C_{108}H_{122}N_2O_6$ (1544.13): calcd.: C 84.01, H 7.96, N 1.81;
found: C 82.26, H 7.54, N 1.50.

*Compound (**[103c]$_2$**):*

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.80 (t, 32 H, CH_3), 1.10-1.45 (m, 72 H, γ-, δ-, ε-CH_2), 1.50-1.60 (m, 24 H, β-CH_2), 3.40-3.58 (m, 24 H, α-CH_2), 4.45 (s, 8 H, benzyl-

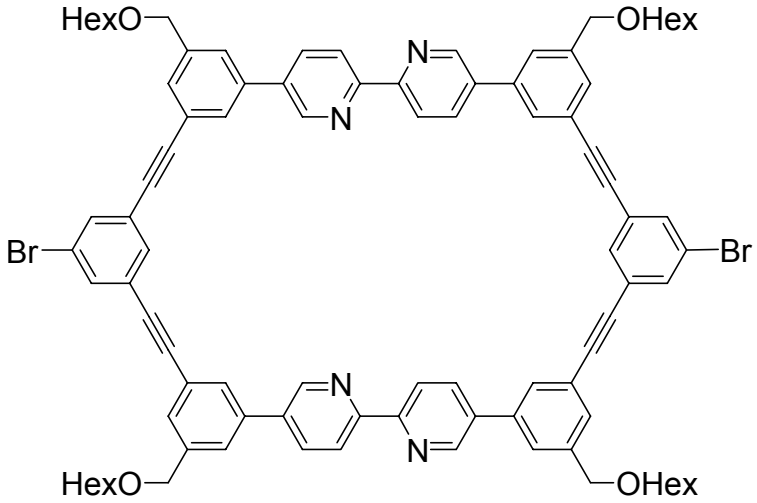
H), 4.54 (s, 16 H, benzyl-H, 7.40-7.75 (m, 52 H, phenyl-H), 8.00 (m, 4 H, py-H), 8.45 (m, 4 H, py-H), 8.85 (s, 4 H, py-H).

MS (**MALDI-TOF**): *m/z*: 3100.82 $[M+CH_3]^+$, 3086.88 $[M+H]^+$, 3000.69 $[M-C_6H_{13}]^+$; monoisotopic mass calcd for $C_{216}H_{245}O_{12}N_4^+$: 3086.87, found: 3086.88.

*Macrocycle (**10**):*

100b (1.12 g, 1.92 mmol), **100c** (1.9 g, 1.92 mmol), triethylamine (600 ml), toluene (800 ml), $Pd(PPh_3)_4$ (0.04 equiv), copper iodide (0.04 equiv), gave 540 mg of cycle (28%).

*Macrocycle (**103d**)*



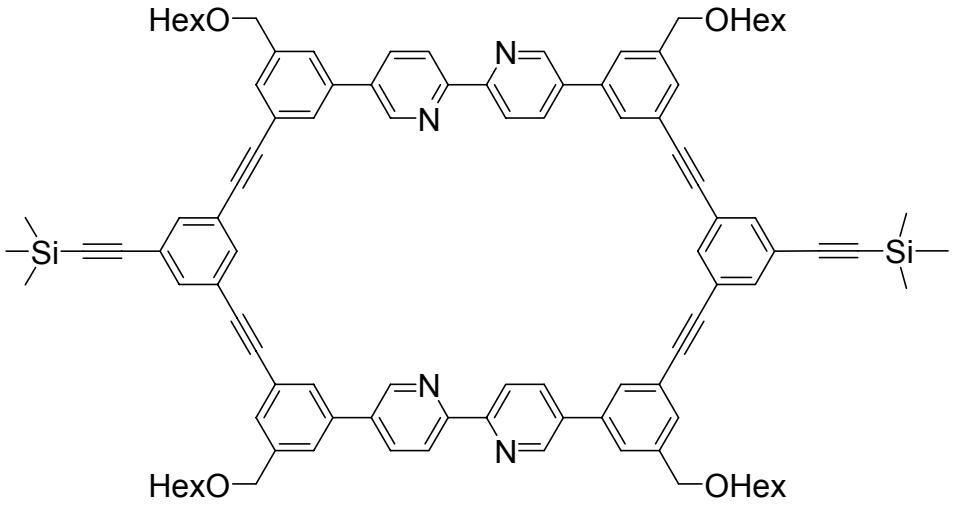
A solution of **102c** (1.72 g, 1.82 mmol), **76** diiodocomp(1.43 g, 1.82 mmol), TEA (650 ml), and toluene (650 ml). Purification of the residue by GPC gave 0.21 g of **103d** (16%) as white solid.

1H NMR (D-toluene, 500 MHz, 90°C): δ = 1.12 (t, 12 H, CH_3), 1.53 (m, 16 H, δ-, ε-CH_2), 1.64 (m, 8 H, γ-CH_2), 1.88 (m, 8 H, β-CH_2), 3.69 (t, 8 H, α-CH_2), 4.61 (s, 8 H, benzyl-H), 7.69 (s, 4 H, phenyl-H), 7.75 (s, 4 H, phenyl-H), 7.77 (s, 4 H, phenyl-H), 7.89 (d, ^3J = 7 Hz, 4 H, py-H), 7.92 (s, 4 H, phenyl-H), 7.98 (s, 2 H, phenyl-H), 8.87 (d, ^3J = 7 Hz, 4 H, py-H), 9.12 (s, 4 H, py-H).

^{13}C NMR: was not measured because of the low solubility of the substance even at high temperature.

MS (**MALDI-TOF**,dithranol): m/z: 1537.71 $[M+Cu]^+$, 1475.23 $[M]^+$.

*Macrocycle (**103e**):*

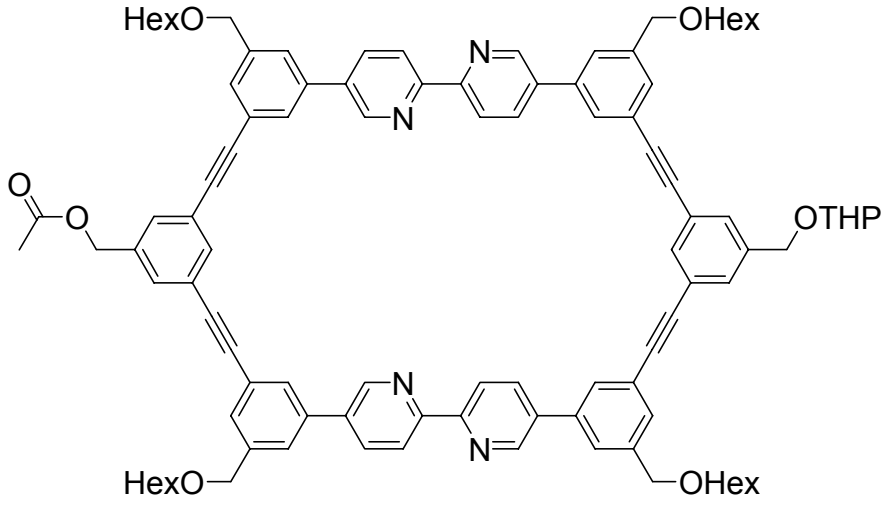


Macrocycle **103d** (30 mg, 0.02 mmol), trimethylsilylacetylene (10 mg, 0.1 mmol), triethylamnie (30 ml), toluene (30 ml), Pd cat (60 mg), CuI (10 mg) were charged in a flask and was degassed several times. Then the reaction was stirred at 60°C for 1 d. The solvent was removed and the compound was purified by column chromatography through silica gel (DCM/methanol 9:1)to give 0.02 mg of **103e** (66%) as white solid.

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.27 (s, 18 H, $Si(CH_3)_3$), 0.89 (t, 12 H, CH_3), 1.26-1.45 (m, 24 H, γ-, δ-, ε-CH_2), 1.55-1.75 (m, 8 H, β-CH_2), 3.54 (t, 8 H, α-CH_2), 4.58 (s, 8 H, benzyl-H), 7.51 (s, 4 H, phenyl-H), 7.60 (s, 8 H, phenyl-H), 7.74 (s, 6 H, phenyl-H), 8.05 (d, ^3J = 8 Hz, 4 H, py-H), 8.52 (d, ^3J = 8 Hz, 4 H, py-H), 8.94 (s, 4 H, py-H).

MS (**FAB+**) *m/z* (%): 1511.7 (1.46) $[M+H]^+$, 1440.3 (15.78) $[M-C_5H_{11}]^+$, 1225.0 (100) $[M-2C_5H_{11}-2Si(CH_3)_3]^+$.

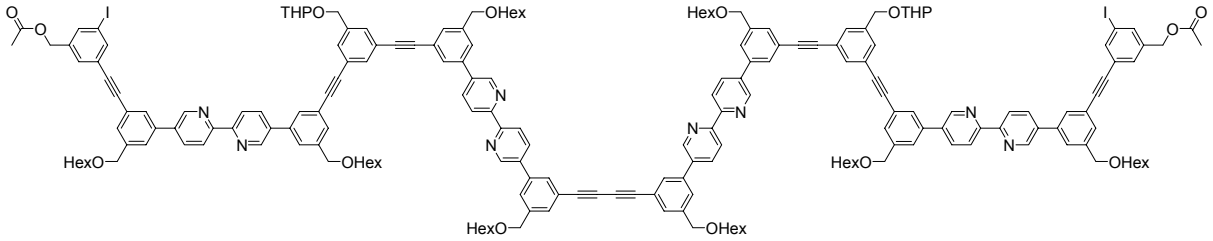
*Macrocycle (**103g**):*



To a solution of $Pd(PPh_3)_4$ and CuI in toluene (50 ml) and TEA (50 ml) at 65 °C, a solution of **88d** (0.25 g, 0.15 mmol) in toluene (20 ml) was added with a syringe pump within 24 h. Then the reaction mixture was stirred at this temperature for additional 4 d. The solvent was removed to give a brown solid. Purification by preparative GPC gave 1 mg of **103g** as a white solid.

MS (**MALDI-TOF**): *m/z*: 1503.57 $[M+H]^+$, 1565.48, 1606.5 $[M+Cu]^+$; monoizotopic mass calcd for $C_{101}H_{107}N_6O_8$: 1503.8; found: 1503.57

*Glaser coupling of **88d** to **104**:*



^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 24 H, CH_3), 1.20-1.50 (m, 48 H, γ-, δ-, ε-CH_2), 1.55-2.00 (m, 28 H, β-CH_2, THP), 2.12 (s, 6 H, CH_3), 3.43-3.65 (m, 18 H, α-CH_2, THP), 3.85-4.00 (m, 2 H, THP), 4.51 (d, ^2J = 13 Hz, 2 H, benzyl-H), 4.57 (s, 8 H, benzyl-H), 4.59 (s, 8 H, benzyl-H), 4.74 (t, 2 H, THP), 4.80 (d, ^2J = 13 Hz, 2 H, benzyl-H), 5.03 (s, 4 H, benzyl-H), 7.49 (s, 2 H, phenyl-H), 7.54 (s, 6 H, phenyl-H), 7.56 (s, 6 H, phenyl-H), 7.58-7.63 (m, 8 H, phenyl-H), 7.66 (s, 2 H, phenyl-H), 7.68 (s, 2 H, phenyl-H), 7.71 (s, 2 H, phenyl-H), 7.74 (s, 6 H, phenyl-H), 7.85 (s, 2 H, phenyl-H), 8.05 (d, ^3J = 8 Hz, 8 H, py-H), 8.54 (d, ^3J = 8 Hz, 8 H, py-H), 8.94 (s, 8 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.98, 19.33, 20.82, 22.60, 25.49, 25.90, 29.75, 30.57, 31.69, 62.17, 64.67, 67.95, 71.04, 72.09, 72.20, 72.26, 74.48, 81.54, 87.67, 89.19, 89.66, 90.69, 93.68, 98.05, 121.10, 122.78, 123.60, 123.67, 124.08, 125.37, 126.19, 126.41, 126.98, 129.27, 130.05, 130.27, 130.33, 130.40, 130.72, 131.00, 133.76, 135.22, 136.85, 138.15, 138.31, 139.37, 139.90, 140.36, 140.42, 147.72, 155.02, 170.45.

MS (**MALDI-TOF**): *m/z*: 3260 $[M+H]^+$.

*Glaser macrocycle (**106**):*

First route:

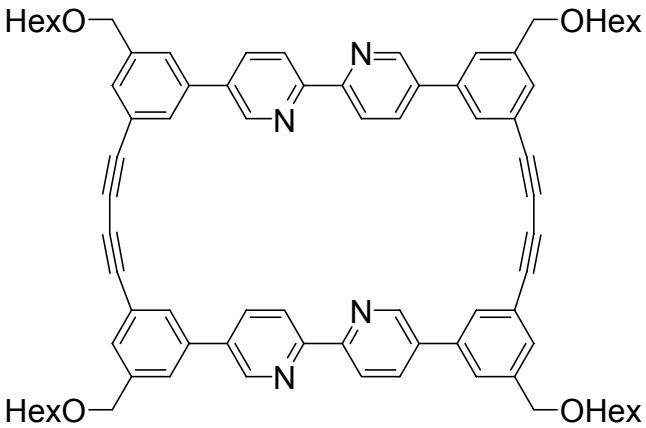
$Cu_2(OAc)_4$ (1.29 g) was dissolved in worm pyridine (320 ml) and the solution was degassed. To this a degassed solution of **100b** (170 mg, 0.3 mmol) in pyridine (20 ml) was slowly added over 5 h. After the complete addition of **100b**, the reaction mixture was stirred at r. t. for 14 d. The solvent was removed and the residue dissolved in DCM and treated with a solution of KCN (2.4 g in 300 ml water). The suspension was stirred until the blue-green colour disappeared. Then the phases were separated and the organic phase was washed several times with water. The organic phase was dried over $MgSO_4$ and the solvent removed. The compounds were isolated by preparative GPC to give **106**, $\mathbf{[106]_{1.5}}$, and $\mathbf{[106]_2}$.

Second route:

A solution of **100b** (170 mg, 0.3 mmol) in pyridine (20 ml) was slowly added over a period of 92 h to a solution of CuCl (2.25 g) and $CuCl_2$ (0.45 g) in 250 ml pyridine at r. t. After all the compound was added, the reaction was stirred at r. t. for another 2 d. Then the solvent was removed and the residue dissolved in DCM (200 ml) and treated with a solution of KCN (8.8 g in 300 ml water). The phases were separated and the organic phase was washed several times with water. It was then dried over $MgSO_4$ and the solvent removed. The macrocycles were isolated by preparative GPC. Additional purification by column chromatography through silica gel was also done (first column with DCM/methanol 9:1 and second column with DCM/ethyl acetate/acetone/methanol/TEA 20:8:2:2:1).

The results from this two cyclization reactions were very similar and gave **106** 8 mg (5%), $\mathbf{[106]_{1.5}}$ 18 mg (10 %), and $\mathbf{[106]_2}$ 14 mg (8%).

*Macrocycle (**106**):*

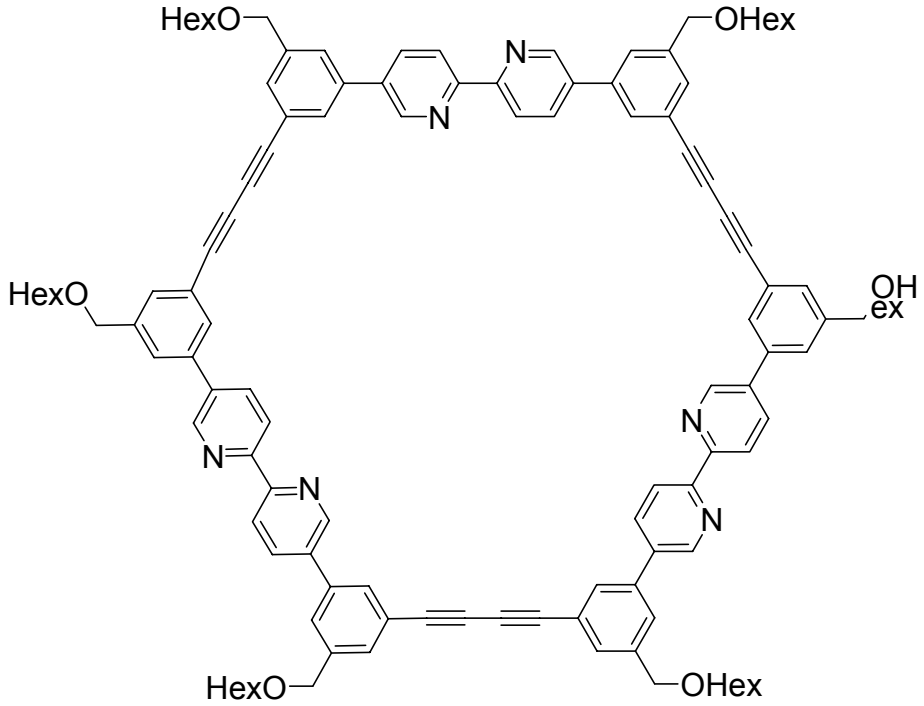


^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.88 (t, 12 H, CH_3), 1.20-1.40 (m, 24 H, γ-, δ-, ε-CH_2), 1.55-1.68 (m, 8 H, β-CH_2), 3.53 (t, 8 H, α-CH_2), 4.55 (s, 8 H, benzyl-H), 7.35 (s, 4 H, phenyl-H), 7.61 (s, 4 H, phenyl-H), 7.74 (s, 4 H, phenyl-H), 7.93 (d, ^3J = 8 Hz, 4 H, py-H), 8.48 (d, ^3J = 8 Hz, 4 H, pyridyl -H), 8.82 (s, 4 H, pyridyl -H).

^{13}C NMR (CDCl3, 270 MHz): δ = 14.05, 22.62, 25.89, 29.72, 31.69, 71.03, 72.18, 75.87, 84.48, 120.83, 122.88, 125.99, 127.61, 135.14, 135.51, 135.62, 138.57, 140.35, 147.77, 154.78.

MS (**FAB**): *m/z* (%): 1165.4 (100), 1079 (35), 1063.4 (33); monoizotopic mass calcd for $C_{80}H_{85}N_4O_4^+$: 1165.65, found 1165.4 $[M+H]^+$.

*Macrocycle **([106]$_{1.5}$)**:*



^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.91 (t, 18 H, CH_3), 1.20-1.40 (m, 36 H, γ-,δ-, ε-CH_2), 1.55-1.56 (m, 12 H, β-CH_2), 3.52 (t, 12 H, α-CH_2), 4.43 (s, 12 H, benzyl-H), 7.34 (s, 6 H, phenyl-H), 7.38 (s, 6 H, phenyl-H), 7.50 (s, 6 H, phenyl-H), 7.80 (d, ^3J = 8 Hz, 6 H, pyridyl -H), 8.30 (d, ^3J = 8 Hz, 6 H, pyridyl -H), 8.67 (s, 6 H, pyridyl -H).

MS (FAB): *m/z* (%): 1748.5 (100), $[M+H]^+$; monoizotopic mass calcd. for $C_{120}H_{127}N_6O_6^+$: 1748.97, found: 1749 $[M+H]^+$.

MS (**MALDI-TOF**): *m/z*: 1749 $[M+H]^+$.

HR-MALDI for $C_{120}H_{127}N_6O_6$: calcd.: 1747.974;
found: 1447.976.

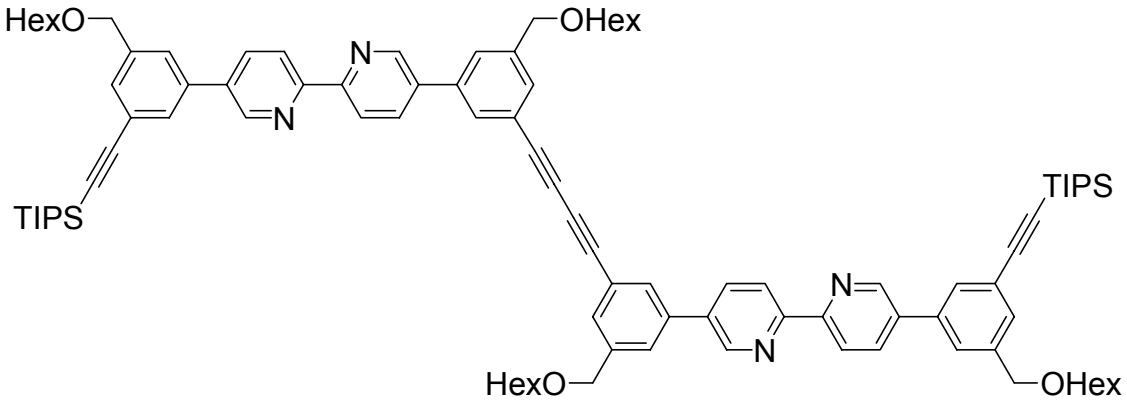
*Macrocycle (**[106]$_2$**):*

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.88 (t, 24 H, CH_3), 1.15-1.40 (m, 48 H, γ-, δ-, ε-CH_2), 1.55-1.75 (m, 16 H, β-CH_2), 3.52 (t, 16 H, α-CH_2), 4.56 (s, 16 H, benzyl-H), 7.55 (s, 8 H, phenyl-H), 7.63 (s, 8 H, phenyl-H), 7.73 (s, 8 H, phenyl-H), 8.02 (d, ^3J = 8 Hz, 8 H, pyridyl -H), 8.51 (d, ^3J = 8 Hz, 8 H, pyridyl -H), 8.90 (s, 8 H, pyridyl -H).

^{13}C NMR ($CDCl_3$, 500 MHz): δ = 14.04, 22.62, 25.89, 29.72, 31.69, 71.10, 72.08, 74.40, 81.41, 121.20, 122.73, 127.03, 130.19, 131.04, 135.39, 135.52, 138.18, 140.44, 147.61, 154.90.

MS (**MALDI-TOF**): *m/z* : 2330.2 $[M+H]^+$; monoisotopic mass calcd. for $C_{160}H_{169}N_8O_8^+$: 2330.31, found 2330.2 $[M+H]^+$.

*2-(5-(3-((hexyloxy)methyl)-5-(2-(triisopropylsilyl)ethynyl)phenyl)pyridin-2-yl)-5-(3-((hexyloxy)methyl)-5-(4-(3-((hexyloxy)methyl)-5-(6-(5-(3-((hexyloxy)methyl)-5-(2-(triisopropylsilyl)ethynyl)phenyl)pyridin-2-yl)pyridin-3-yl)phenyl)buta-1,3-diynyl)phenyl)pyridine (**105a**):*



To a solution of $PdCl_2(PPh_3)_2$ (2 mg, 0.003 mmol) and CuI (0.5 mg) in piperidine / THF (1 ml / 3 ml) a solution of **86c** (50 mg, 0.067 mmol) in THF (1 ml) was added. The reaction mixture was stirred for 2 days at r. t. Then the solvent was removed and the compound purified by column chromatography through silica gel (solvent hexane/ethyl acetate 4 : 1) to give 30 mg of **105a** (61%) as a colourless oil.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 12 H, CH_3), 1.14 (s, 21 H, TIPS), 1.20-1.50 (m, 24 H, γ-, δ-, ε-CH_2), 1.55-1.75 (m, 8 H, β-CH_2), 3.45-3.57 (m, 8 H, CH_2), 4.55 (s, 4 H, benzyl-H), 4.56 (s, 4 H, benzyl-H), 7.48 (s, 2 H, phenyl-H), 7.56 (s, 2 H, phenyl-H), 7.57 (s, 2 H, phenyl-H), 7.64 (s, 2 H, phenyl-H), 7.66 (s, 2 H, phenyl-H), 7.74 (s, 2 H, phenyl-H), 8.03 (d, ^3J = 8 Hz, 4 H, py-H), 8.52 (dd, ^3J = 8 Hz, ^4J = 2 Hz, 4 H, py-H), 8.91 (s, 4 H, py-H).

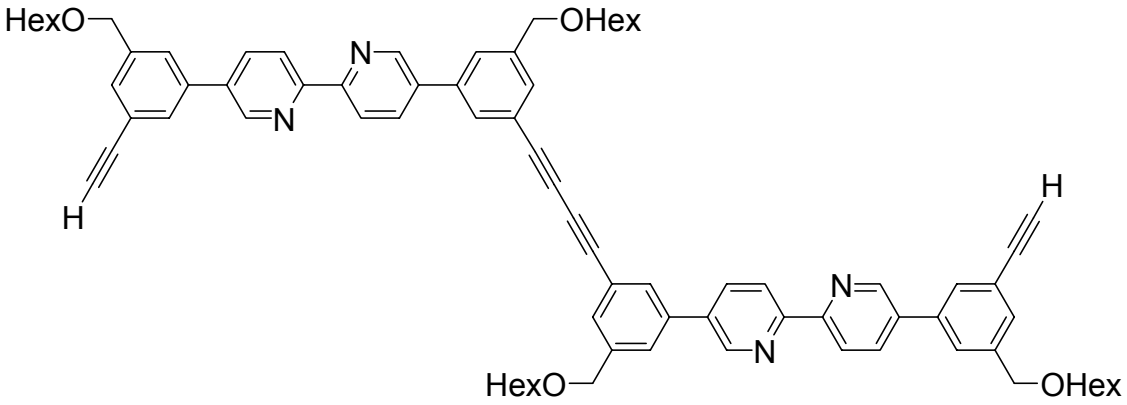
^{13}C NMR ($CDCl_3$, 63 MHz): δ = 11.36, 14.01, 18.68, 22.61, 25.90, 29.72, 31.68, 70.94, 71.06, 72.09, 72.23, 74.42, 81.48, 91.42, 106.59, 121.02, 122.73, 124.55, 126.08, 126.99, 129.70, 130.07, 130.71, 130.99, 135.24, 135.34, 135.79, 137.94, 138.27, 140.04, 140.46, 147.65, 147.73, 154.86, 155.17.

MS (EI) m/z (%) = 1478.9 (27) [M]+, 1395.7 (6.23),

MS (**FAB**) *m/z* (%) = 1481.4 (100) $[M+H]^+$, 1393.5 (27) $[M-Hex]^+$.

HRMS: for $C_{98}H_{126}N_4O_4Si_2$: calcd.: 1478.93176;
found: 1478.9411.

*2-(5-(3-ethynyl-5-((hexyloxy)methyl)phenyl)pyridin-2-yl)-5-(3-(4-(3-(6-(5-(3-ethynyl-5-((hexyloxy)methyl)phenyl)pyridin-2-yl)pyridin-3-yl)-5-((hexyloxy)methyl)phenyl)buta-1,3-diynyl)-5-((hexyloxy)methyl)phenyl)pyridine (**105**):*



105a (30 mg, 0.02 mmol), tetrabutylammonium fluoride trihydrate (14 mg, 0.02 mmol) in 5 ml THF were stirred over night. The compound was purified by column chromatography through silica gel using as solvent hexane / ethyl acetate 4 :1 to give 20 mg of **106** (87%) as a white solid.

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.87 (t, 12 H, CH_3), 1.20-1.45 (m, 24 H, γ-, δ-, ε-CH_2), 1.55-1.75 (m, 8 H, β-CH_2), 3.13 (s, 2 H, acetyl-H), 3.40-3.60 (m, 8 H, α-CH_2), 4.55 (s, 4 H, benzyl-H), 4.56 (s, 4 H, benzyl-H), 7.50 (s, 2 H, phenyl-H), 7.55 (s, 2 H, phenyl-H), 7.61 (s, 2 H, phenyl-H), 7.63 (s, 2 H, phenyl-H), 7.86 (s, 2 H, phenyl-H), 7.71 (s, 2 H, phenyl-H), 7.73 (s, 2 H, phenyl-H), 8.02 (d, ^3J = 8 Hz, 4 H, py-H), 8.51 (d, ^3J = 8 Hz, 4 H, py-H), 8.91 (s, 4 H, py-H).

^{13}C NMR ($CDCl_3$, 270 MHz): δ = 14.01, 22.60, 25.87, 29.70, 31.68, 71.02, 72.09, 74.41, 77.77, 81.47, 83.18, 121.08, 122.68, 123.11, 126.53, 127.00, 129.76, 130.07, 130.77, 131.02, 135.28, 135.55, 137.98, 138.21, 140.22, 140.40, 147.63, 154.92.

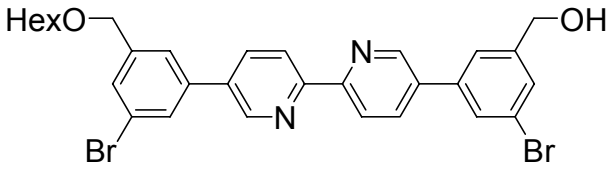
MS (**FAB**): *m/z* (%): 1182.5 (45) $[M+Na]^+$, 1167.8 (100) $[M+H]^+$, 1080.9 (65) $[M-Hex]^+$; monoizotopic mass calcd. for $C_{80}H_{86}N_4O_4$: 1167.67, found: 1167.70.

*Coupling of **105b** to **106**:*

To a solution of $PdCl_2(PPh_3)_2$ (1 mg) and CuI (0.15 mg) in piperidine / THF (35 ml / 12 ml) a solution of **105b** (20 mg, 0.017 mmol) was added. The reaction mixture was stirred for 7 days at r. t. Then the solvent was removed and the compound analysed by analytical GPC. The GPC curve of the raw product showed two peaks. First compound (40% from GPC) came at retention times which correspond to the tetramer and has the same ^1H NMR spectra. The second compound (50% from GPC) came at retention times which were intermediary to trimer and dimmer. These compounds are still under investigation.

7.2.3. Compounds of chapter 4.4.

*(3-bromo-5-(6-(5-(3-bromo-5-((hexyloxy)methyl)phenyl)pyridin-2-yl)pyridin-3-yl)phenyl)methanol (**107**):*



To a stirred solution of **74c** (1.5 g, 2.16 mmol) in THF/methanol 1:1 (60 ml), hydrochloric acid 35% (1 ml) was added. The reaction mixture was stirred at r. t. for 24 h. Then DCM (100 ml) and a saturated aqueous solution of $NaHCO_3$ (20 ml) were added and the phases separated. The aqueous one was extracted with dichloromethane (50 ml) and the combined organic phases were dried over $MgSO_4$. The solvent was removed to give 1.23 g of **107** (93%) as a white solid.

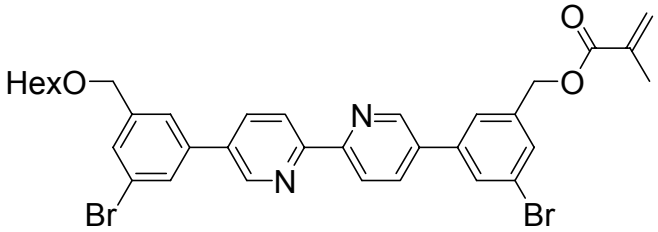
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.84 (t, 3 H, CH_3), 1.20-1.40 (m, 6 H, γ-, δ-, ε-CH_2), 1.62 (m, 2 H, β-CH_2), 3.34 (s, 1 H, OH), 3.50 (t, 2 H, α-CH_2), 4.52 (s, 2 H, benzyl-H), 4.72 (s, 2 H, benzyl-H), 7.46 (s, 4 H, phenyl-H), 7.56 (s, 1 H, phenyl-H), 7.64 (s, 1 H, phenyl-H), 7.82 (d, 1 H, py-H), 7.92 (d, 1 H, py-H), 8.40 (2d overlapped in t, 2 H, py-H), 8.72 (s, 1 H, py-H), 9.89 (s, 1 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.98, 22.56, 25.82, 29.63, 31.62, 64.05, 71.05, 71.82, 121.11, 123.21, 123.26, 123.83, 124.53, 128.80, 128.92, 129.40, 130.04, 134.88, 13.08, 135.13, 135.22, 139.44, 141.94, 144.21, 147.40, 147.48, 154.77.

MS (**EI**) *m/z* (%): 610 (40.30), 509.8 (99.11), 430.7 (100).

EA: for $C_{30}H_{30}Br_2N_2O_2$ (610.38): calcd.: C 59.03, H 4.95, N 4.59;
found: C 59.01, H 4.66, N 4.46.

*3-bromo-5-(6-(5-(3-bromo-5-((hexyloxy)methyl)phenyl)pyridin-2-yl)pyridin-3-yl)benzyl methacrylate (**108a**):*



To a mixture of alcohol **107** (50 mg, 0.08 mmol), triethylamine (30 µL), and catalytic amounts of 4,4-dimethylaminopyridine (1.3 mg) in dry dichloromethane (2 ml) freshly

distilled methacryloyl chloride (15 µL) was added at 0 °C and the resulting mixture stirred for 20 h before it was let to warm to r. t. Then a saturated solution of $NaHCO_3$ was added and the phases were separated. The organic one was washed with brine and dry over $MgSO_4$. The solvent was removed at r. t. and the compound dried to give 51 mg of **108a** (95%) as a white solid.

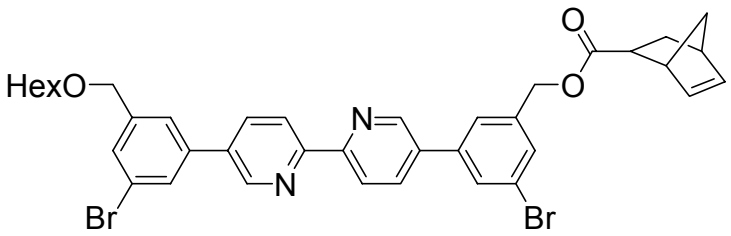
^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.88 (t, 3 H, CH_3), 1.3-1.45 (m, 6 H, γ-, δ-, ε-CH_2), 1.65 (m, 2 H, β-CH_2), 1.99 (s, 3 H, CH_3), 3.52 (t, 2 H, α-CH_2), 4.54 (s, 2 H, benzyl-H), 5.24 (s, 2 H, benzyl-H), 5.63 (s, 1 H, C=CH_2), 6.20 (s, 1 H, C=CH_2) 7.54 (s, 2 H, phenyl-H), 7.56 (s, 2 H, phenyl-H), 7.68 (s, 1 H, phenyl-H), 7.73 (s, 1 H, phenyl-H), 7.99 (d, ^3J = 8 Hz, 2 H, py-H), 8.51 (d, 2 H, ^3J = 8 Hz, py-H), 8.88 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.99, 18.31, 22.56, 25.82, 29.63, 31.60, 65.19, 71.00, 71.81, 121.10, 123.20, 124.59, 125.13, 126.31, 128.96, 129.69, 130.07, 130.41, 135.30, 141.93, 147.47, 155.01, 176.87.

MS (**EI**) *m/z* (%): 678 (71.9) [M^+], 578 (100), 497 (61.5).

HRMS: for $C_{34}H_{34}N_2O_3Br_2$: calcd.: 678.09155;
Found: 678.09355.

*Monomer (**108b**):*



Exo, endo-5-norbornene-2-carboxylic acid (115 µl, 0.5 mmol), **107** (0.3 g, 0.5 mmol), DMAP (0.12 g, 1 mmol), and dry dichloromethane (4 ml) were placed in a flask. DCC (0.2 g, 1 mmol) was added to the solution at 0 °C. The solvent was stirred under a nitrogen atmosphere at r. t. for 18 h. After removal of the solvent, the product was dissolved in acetone and a solution of 10 % HCl was added (pH = 7) followed by the addition of NH_4PF_6 (0.8 g). The resulting solid was collected and washed with water. The aqueous phase was extracted with dichloromethane (2 × 100 ml). The solvent was removed and the solid washed with ether. The ether phase was treated with triethyl amine and diluted with dichloromethane and water. The organic phase was separated and dried over $MgSO_4$ to give 0.4 g of **108b** (70%) as white solid.

^{1}H NMR mixture of *endo/exo* 3:1 (from integration of the benzyl protons) ($CDCl_3$, 270 MHz): *exo* δ = 0.75 (t, 3 H, CH_3), 1.10-1.55 (m, 10 H, β-, γ-, δ-, ε-CH_2, nornornene-

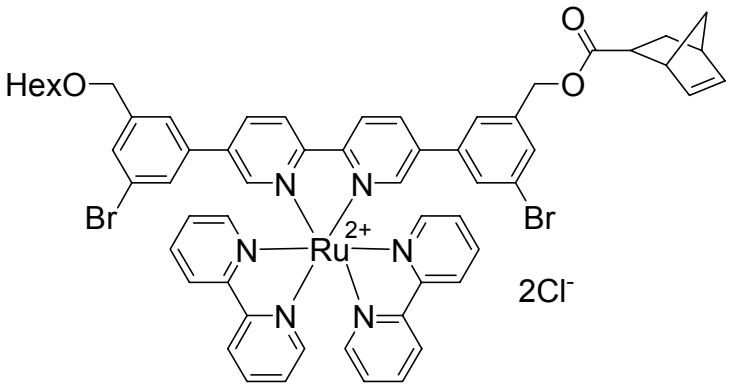
H), 1.58-1.68 (m, 2 H, norbornene-H), 2.15-2.25 (s, 1 H, norbornene), 2.85-3.00 (m, 2 H, norbornene), 3.36 (t, 2 H, α-CH_2), 4.36 (s, 2 H, benzyl-H), 5.01 (s, 2 H, benzyl-H), 5.95-6.30 (m, 2 H, norbornene), 7.35 (s, 4 H, phenyl-H), 7.49 (s, 1 H, phenyl-H), 7.53 (s, 1 H, phenyl-H), 7.75 (d, ^3J = 8 Hz, 2 H, py-H), 8.29 (d, ^3J = 8 Hz, 2 H, py-H), 8.67 (s, 2 H, py-H); *endo*: δ = 0.75 (t, 3 H, CH_3), 1.10-1.55 (m, 11 H, β-, γ-, δ-, ε-CH_2, nornornene), 1.72-1.90 (m, 2 H, norbornene), 2.78 (s, 1 H, norbornene), 3.12 (s, 1 H, norbornene), 3.36 (t, 2 H, α-CH_2), 4.36 (s, 2 H, benzyl-H), 4.96 (s, 2 H, benzyl-H), 5.75-5.80 (m, 1 H, norbornene), 6.03-6.10 (m, 1 H, norbornene), 7.35 (s, 4 H, phenyl-H), 7.49 (s, 1 H, phenyl-H), 7.53 (s, 1 H, phenyl-H), 7.75 (d, ^3J = 8 Hz, 2 H, py-H), 8.29 (d, ^3J = 8 Hz, 2 H, py-H), 8.67 (s, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz) for the *exo-endo* mixture: δ = 13.71, 22.27, 25.53, 28.96, 29.33, 30.13, 31.31, 41.33, 42.24, 42.71, 42.96, 45.48, 46.02, 46.30, 49.30, 64.37, 64.64, 66.64, 70.61, 71.37, 120.53, 122.80, 122.88, 122.92, 123.99, 124.45, 124.59, 126.45, 128.39, 128.98, 129.07, 129.50, 129.81, 129.93, 131.89, 132.18, 134.06, 134.43, 134.55, 135.28, 136.33, 137.53, 137.75, 139.03, 139.09, 139.15, 139.26, 139.32, 139.38, 141.67, 147.04, 147.08, 154.36, 154.63, 173.69, 175.23.

MS (**EI**, 80 eV) *m/z* (%): 730.2 (100), 665.4 (17), 344.6 (57).

HRMS ($C_{38}H_{38}N_2O_3{}^{79}Br_2$): calcd. 728.12673;
found 728.12494.

*[**108b**$Ru(bpy)_2(PF_6)_2$] (**108c**):*



A stirred solution of **108b** (0.33 g, 0.45 mmol) and $[Ru(bpy)_2Cl_2]\times 2H_2O$ (245 mg, 0.43 mmol) in a mixture of ethanol (8 ml) and H_2O (3 ml) was refluxed for 24 h. Then the solvent was removed and the residual orange material purified by column chromatography through silica gel (methanol/2M NH_4Cl/nitromethane 7:2:1). The combined orange fractions were diluted with CH_2Cl_2, the organic phase was separated, and the solvent removed to give an orange solid 0.36 g of **108c** (66%). A

small part of this solid was dissolved in methanol and added to a concentrated solution of NH_4PF_6. The precipitated solid was separated by filtration and washed with H_2O several times. The compound was characterized as PF_6 salt.

The product was obtained as a mixture of diastereoisomers with an *endo*/*exo* ratio of 1:3. Its ^{1}H NMR spectrum is therefore quite complex and the number of atoms which cause the signals are not given.

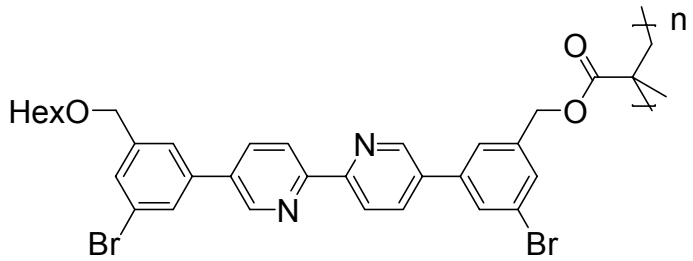
^{1}H NMR (D-acetonitrile, 270 MHz): δ = 0.89 (t, CH_3), 1.25-1.45 (m, γ-, δ-, ε-CH_2, norbornene-H), 1.58-1.62 (m, β-CH_2), 1.56-1.85 (m, norbornene-H), 2.93 (s, norbornene-H), 3.00-3.05 (m, norbornene-H), 3.21 (s, norbornene-H), 3.49 (t, α-CH_2), 4.46 (s, benzyl-H), 5.03 (s, norbornene-H), 5.08 (s, norbornene-H), 6.15-6.18 (m, norbornene-H), 7.33 (s, phenyl-H), 7.50-7.60 (m, py-H, phenyl-H), 7.65-7.70 (m, py-H), 7.79 (d, ^3J = 6 Hz, py-H), 7.82-7.88 (m, py-H), 8.05-8.15 (m, py-H), 8.25 (d, ^3J = 8 Hz, py-H), 8.51 (d, ^3J = 8 Hz, py-H), 8.61 (dd, ^3J = 8 Hz, ^4J = 3 Hz, py-H).

^{13}C NMR (D-acetonitrile, 126 MHz): δ = 14.10, 22.73, 25.94, 29.33, 29.77, 31.77, 42.72, 43.37, 45.99, 49.81, 64.60, 71.19, 71.46, 123.40, 124.51, 124.75, 124.95, 125.67, 128.14, 128.44, 129.02, 129.67, 131.57, 131.88, 132.35, 136.45, 136.55, 136.71, 136.96, 138.18, 138.38, 138.52, 138.91, 139.21, 140.46, 143.03, 144.06, 148.81, 151.96, 155.75, 156.73, 157.13, 175.83.

MS (**FAB**) *m/z* (%) $C_{58}H_{54}N_6O_3Br_2RuCl_2$: 1178.7 (18), 1158.1 (25), 1143.1 (88);

EA for $C_{58}H_{54}Br_2N_6O_3RuP_2F_{12}$ (1433.83): calcd.: C 48.59, H 3.79, N 5.86;
found: C 48.54, H 3.56, N 5.68.

*Polymerization of **108a** (**109**):*



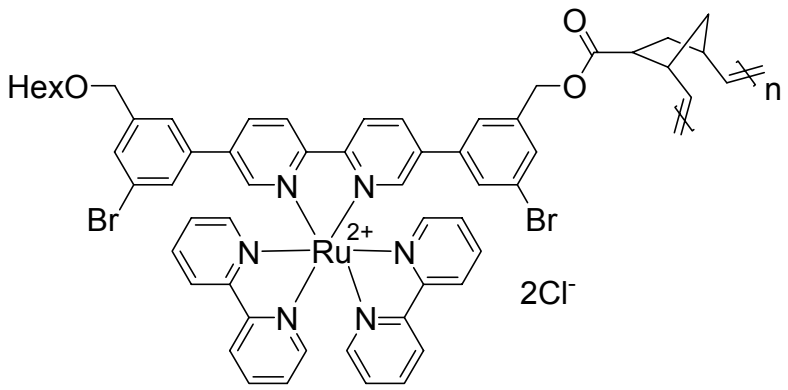
To a solution of **108a** (63 mg, 0.1 mmol) in freshly degassed toluene (50 µL) 100 µL (5 mol-%) of a 0.05 M AIBN solution in toluene were added. The mixture was stirred in a sealed tube at 80 °C for 24 h. The product was purified by preparative GPC to give 41 mg of **109** (65%).

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.81 (s, br, 3 H, CH_3), 1.23 (s, br, 6 H, γ-, δ-, ε-CH_2), 1.55 (s, br, 2 H, β-CH_2), 3.40 (s, 2 H, α-CH_2), 4.39 (s, 2 H, benzyl-H), 4.91 (s, 2 H,

benzyl-H), 7.46 (m, br, 6 H, phenyl-H), 7.69 (s, br, 2 H, py-H), 8.18 (s, br, 2 H, py-H), 8.62 (s, br, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 68 MHz): δ = 14.06, 22.55, 25.80, 29.65, 31.62, 71.00, 71.77, 120.87, 123.20, 124.34, 125.15, 129.37, 130.05, 130.90, 132.53, 133.86, 134.80, 139.49, 147.27, 154.53, 171.98.

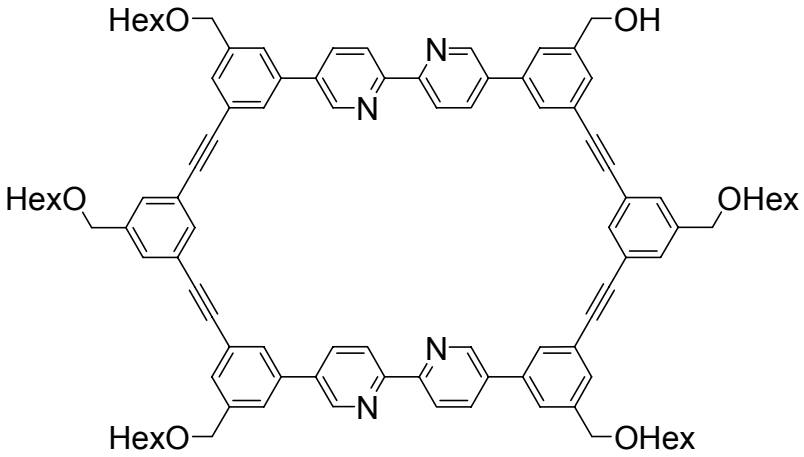
*Polymerizationof **108c** (**110**):*



Monomer **108c** (360 mg, 0.3 mmol) was dissolved in CH_2Cl_2 (0.5 ml) and stirred under nitrogen. The catalyst ([M]/[C] 20:1) was placed in a second flask containing dried and degassed CH_2Cl_2 (0.2 ml) and was added dropwise to the monomer solution which was then stirred for 2 h at r. t. followed by another 16 h at 40 °C. Nitromethane (1 ml) and ethyl vinyl ether were then added to the reaction mixture. The solvent was removed and the compound was dried at high vacuum pump.

^{1}H NMR (CD_3NO_2, 250 MHz): δ = 0.80 (br, 3 H, CH_3), 1.24 (br, 7 H, γ-,δ-, ε-CH_2, CH), 1.50-1.80 (br, 4 H, β-CH_2, CH_2), 2.30-3.00 (br, 4 H), 3.43 (br, 2 H, α-CH_2), 4.41 (s, 2 H, benzyl-H), 4.97 (br, 2 H, benzyl-H), 5.20-5.50 (br, 2 H, CH=), 7.30-7.60 (br, 10 H, phenyl-H, py-H), 7.90-8.15 (br, 10 H, py-H), 8.31 (br, 2 H, py-H), 8.53 (br, 4 H, py-H), 8.64 (br,2 H, py-H)

*Macrocycle (**111**):*



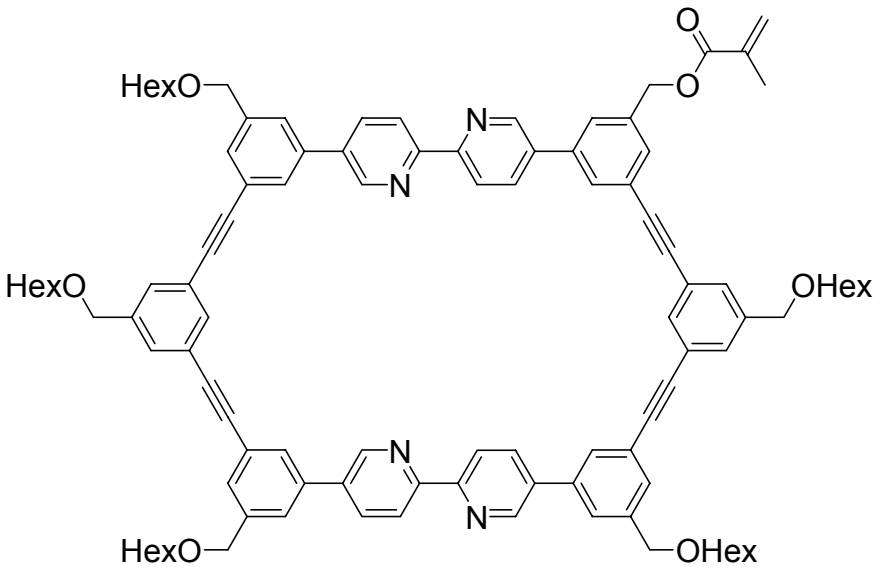
A solution of **103b** (0.47 g, 0.30 mmol) in DCM (150 ml) and methanol (50 ml) was treated with a solution of hydrochloric acid 25 % (1.5 ml). The mixture was stirred at ambient temperature for 24 h and then treated with a solution of $NaHCO_3$ (pH = 7). The phases were separated and the organic one was washed with brine and dried over $MgSO_4$ to give 0.43 g of **111** (98%) as a white solid.

^{1}H NMR ($CDCl_3$, 270 MHz): to prevent aggregation some triethylammonium hydrochloride salt (TEA·HCl) was added into the NMR tube: δ = 0.80-0.95 (m, 15 H, CH_3), 1.25-1.50 (m, 30 H, γ-, δ-, ε-CH_2), 1.60-1.70 (m, 10 H, β-CH_2), 3.43-3.52 (m, 10 H, α-CH_2), 4.44 (s, 4 H, benzyl-H), 4.50 (s, 6 H, benzyl-H), 4.72 (s, 2 H, benzyl-H), 7.41 (s, 4 H, phenyl-H), 7.44 (s, 3 H, phenyl-H), 7.49 (s, 1 H, phenyl-H), 7.51 (s, 3 H, phenyl-H), 7.59 (s, 1 H, phenyl-H), 7.64 (s, 6 H, phenyl-H), 7.96 (d, ^3J = 8 Hz, 4 H, py-H), 8.43 (d, ^3J = 8 Hz, 4 H, py-H), 8.86 (s, 4 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.04, 22.63, 25.90, 29.69, 31.72, 70.90, 71.12, 71.99, 72.23, 88.95, 89.48, 120.46, 123.21, 123.33, 123.43, 124.71, 128.49, 129.30, 129.83, 133.80, 134.07, 136.52, 136.69, 138.89, 139.02, 141.96, 146.69, 154.18.

MS (**FAB**) *m/z* (%): 1463 (100), $[M+H]^+$.

*Macromonomer (**112a**):*



To a mixture of alcohol **111** (0.2 g, 0.14 mmol), triethylamine (70 µL), and catalytic amounts of 4,4-dimethylaminopyridine (2.6 mg) in dry dichloromethane (60 ml) freshly distilled methacryloyl chloride (60 µL) was added at 0 °C and the resulting mixture stirred for 20 h. After letting it warm to r. t. a saturated solution of $NaHCO_3$ was added and the phases were separated. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed at r. t. The white solid was dissolved in the minimum amount of tetrahydrofurane and precipitated with methanol. The suspension was centrifugated, the white solid collected, and then dried at high vacuum to give 0.17 g of **112a** (82%) as a white solid.

^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.80-1.02 (m, 15 H, CH_3), 1.30-1.50 (m, 30 H, γ-, δ-, ε-CH_2), 1.60-1.75 (m, 10 H, β-CH_2), 2.02 (s, 3 H, CH_3), 3.45-3.60 (m, 10 H, α-CH_2), 4.48 (s, 4 H, benzyl-H), 4.50 (s, 6 H, benzyl-H), 5.19 (s, 2 H, benzyl-H), 5.66 (s, 1 H, C=CH_2), 6.24 (s, 1 H, C=CH_2), 7.49 (s, 4 H, phenyl-H), 7.52 (s, 3 H, phenyl-H), 7.55 (s, 1 H, phenyl-H), 7.59 (s, 4 H, phenyl-H), 7.73 (s, 5 H, phenyl-H), 7.77 (s, 1 H, phenyl-H), 8.04 (d, ^3J = 8 Hz, 4 H, py-H), 8.52 (d, ^3J =8 Hz, 4 H, py-H), 8.94 (s, 4 H, py-H).

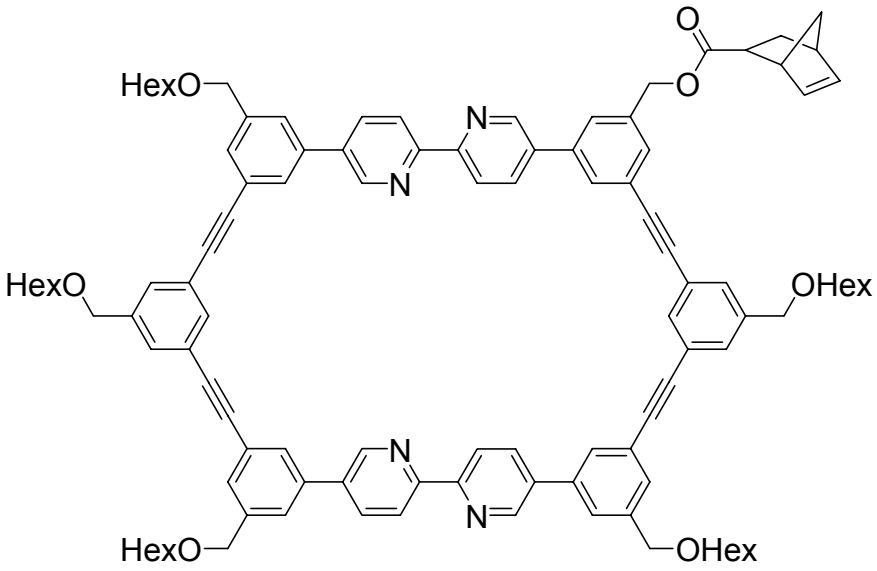
^{13}C NMR ($CDCl_3$, 68 MHz): δ = 14.04, 18.40, 22.62, 25.62, 29.74, 31.69, 65.66, 70.93, 71.93, 72.20, 89.09, 89.63, 120.85, 123.46, 123.83, 124.21, 125.49, 125.86, 126.17, 129.12, 129.78, 130.11, 134.22, 134.72, 136.02, 137.44, 137.74, 139.41, 139.92, 147.27, 154.65, 160.74.

MS (**MALDI-TOF**) 1529.87

MS (**FAB**) *m/z* (%): 1255.1 (100) $[M+Na]^+$.

EA: for $C_{104}H_{112}N_4O_7$ (1530.02): calcd.: C 81.64, H 7.38, N 3.66;
found: C 81.48, H 6.94, N 3.29.

*Macrocycle (**112b**):*



exo-5-Norbornene-2-carboxylic acid (50 mg, 0.36 mmol), **111** (0.22 g, 0.15 mmol), DMAP (44 mg, 0.36 mmol), and dry dichloromethane (50 ml) were placed in a flask. DCC (74 mg, 0.36 mmol) was added to the solution at 0 °C. The solution was stirred for 20 h, during which time the reaction warmed to r. t. The solvent was removed, the solid dissolved in the minimum amount of tetrahydrofurane, and the compound precipitated by addition of methanol. The suspension was centrifugated and the precipitate filtered and dried in vacuum to give 0.23 g of **112b** (96%) as a white solid.

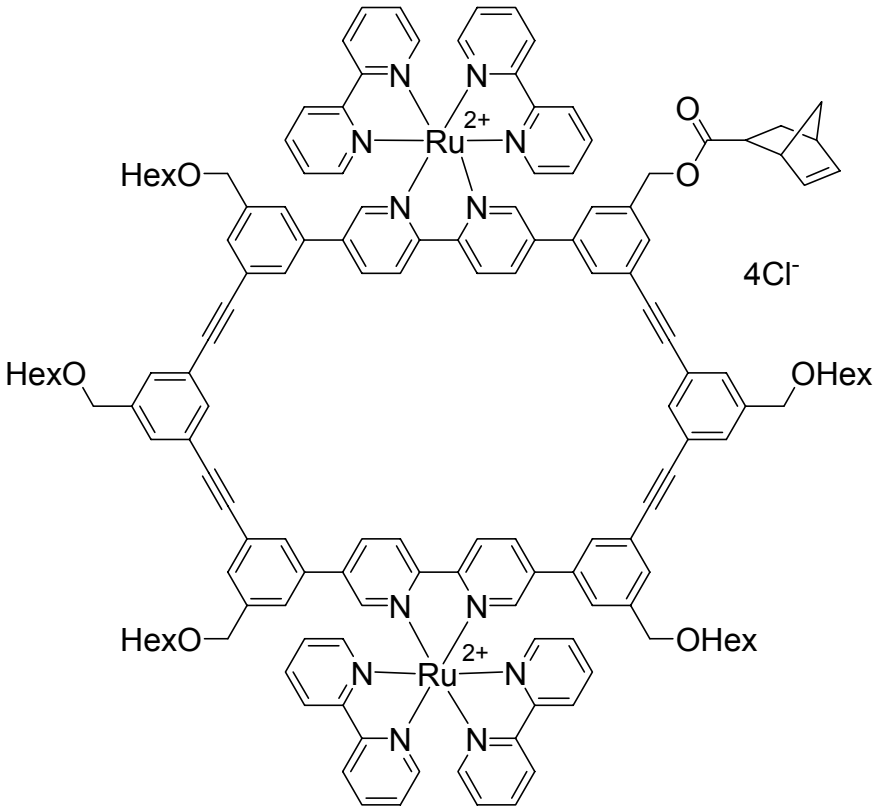
^{1}H NMR ($CDCl_3$, 270 MHz): δ = 0.80-0.95 (m, 15 H, CH_3), 1.25-1.50 (m, 32 H, γ-, δ-, ε-CH_2, norbornene), 1.58 (d, 1 H, norbornene), 1.60-1.72 (m, 10 H, β-CH_2), 1.95-2.05 (m, 1 H, norbornene), 2.30-2.40 (m, 1 H, norbornene), 2.95 (s, 1 H, norbornene), 3.12 (s, 1 H, norbornene), 3.50-3.65 (m, 10 H, α-CH_2), 4.50 (s, 4 H, benzyl-H), 4.55 (s, 6 H, benzyl-H), 5.17 (s, 2 H, benzyl-H), 6.14 (s, 2 H, norbornene), 7.46 (s, 5 H, phenyl-H), 7.48 (s, 4 H, phenyl-H), 7.54 (s, 4 H, phenyl-H), 7.67 (s, 4 H, phenyl-H), 7.71 (s, 1 H, phenyl-H), 7.99 (d, ^3J = 8 Hz, 4 H, py-H), 8.48 (d, ^3J = 8 Hz, 4 H, py-H), 8.90 (s, 4 H, py-H).

^{13}C NMR ($CDCl_3$, 500 MHz): δ = 13.99, 22.56, 25.88, 29.68, 30.45, 31.66, 41.62, 43.05, 46.35, 46.60, 70.82, 70.87, 71.90, 72.10, 88.94, 89.14, 89.33, 85.54, 120.50, 123.13, 123.33, 123.53, 123.88, 124.90, 125.35, 128.56, 129.11, 129.46, 129.85, 133.73, 133.90, 134.04, 134.13, 135.63, 136.87, 137.18, 138.05, 139.10, 139.45, 146.80, 154.24, 154.33, 154.54, 175.73.

MS (**FAB**): *m/z* (%) = 1583 (57).

EA: for $C_{108}H_{116}N_4O_7$ (1582.10): calcd.: C 81.99, H 7.39, N 3.54;
found: C 80.63, H 7.16, N 3.30.

*Macromonomer [(bpy)$_2$Ru(**112b**)Ru(bpy)$_2$](Cl)$_4$ (**112c**):*



A stirred suspension of **112b** (0.23 mg, 0.14 mmol) and [Ru(bpy)$_2$Cl$_2$]×2H$_2$O (155 mg, 0.30 mmol) in a mixture of dioxane (70 ml) and ethylene glycol (23 ml) was refluxed for 24 h. The solvent was removed and the residual orange material purified by column chromatography through silica gel (methanol/2M NH_4Cl/nitromethane 7:2:1). The combined orange fractions were diluted with DCM, the organic phase was separated, and the solvent removed to give 0.2 g of **112c** (54%) as an orange solid. A small amount of the complex was precipitated by adding a solution of the complex in methanol to a saturated solution of NH_4PF_6 in H_2O (1 ml). The precipitated solid was separated by filtration, washed with H_2O (4 × 2 ml), and dried in vacuum (this complex was used for characterization). The chloride complex was used for polymerization because of its higher solubility in DCM.

^{1}H NMR ($CDCl_3$, CD_3NO_2, 270 MHz): δ = 0.83 (t, 15 H, CH_3), 1.25-1.48 (m, 32 H, γ-, δ-, ε-CH_2, 2 norbornene-H), 1.50-1.59 (m, 12 H, β-CH_2, 2 norbornene-H), 2.18-2.25 (m, 1 H, norbornene-H), 2.90 (s, 1 H, norbornene-H), 2.98 (s, 1 H, norbornene H),

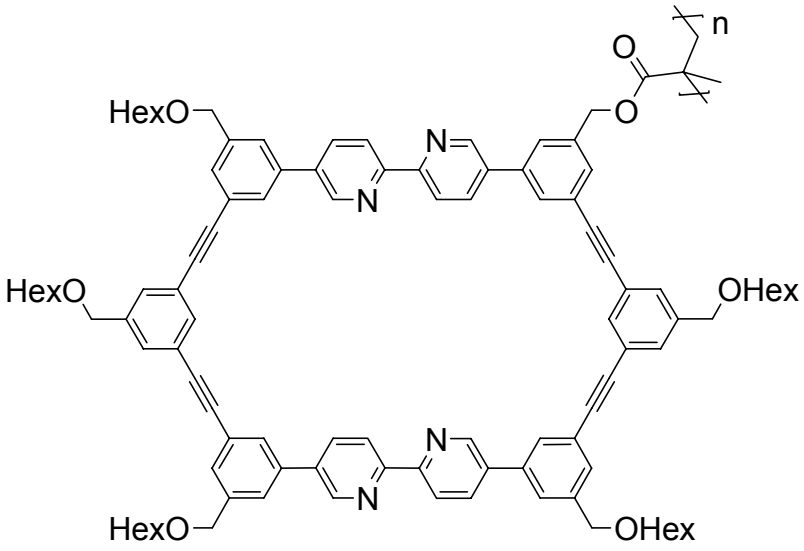
3.40-3.50 (m, 10 H, α-CH_2), 4.38 (s, 6 H, benzyl-H), 4.45 (s, 4 H, benzyl-H), 4.99 (s, 2 H, benzyl-H), 6.00-6.10 (m, 2 H, norbornene-H), 7.03 (s, 4 H, phenyl-H), 7.42-7.52 (m, 18 H, 8 py-H, 10 phehyl-H), 7.63 (s, 3H, phenyl-H), 7.69 (s, 1 H, phenyl-H), 7.75 (s, 4 H, phenyl-H), 7.81 (s, 8 H, py-H), 7.95 -8.07 (m, 8 H, py-H), 8.31 (d, ^3J = 8 Hz, 4 H, py-H), 8.42 (d, ^3J = 8 Hz, 8 H, py-H), 8.68 (d, ^3J = 8 Hz, 4 H, py-H).

^{13}C NMR ($CDCl_3$, CD_3NO_2, 63 MHz): δ = 13.84, 22.47, 25.66, 29.53, 30.32, 31.52, 41.51, 42.93, 46.22, 46.44, 70.82, 70.93, 71.57, 71.67, 88.97, 89.74, 123.17, 123.95, 124.27, 124.41,124.77, 124.88, 125.00, 127.89, 128.27, 129.93, 130.98, 132.68, 133.62, 134.61, 134.97, 135.45, 136.30, 137.76, 138.09, 138.19, 139.29, 139.84, 140.83, 147.80, 151.41, 151.65, 155.50, 156.33, 156.87, C=O missing.

MS (**MALDI-TOF**, dithranol) *m/z*: 2843.75 $[M\text{-}PF_6]^+$, 2785.82 $[M\text{-}PF_6\text{-}C_4H_9]^+$, 2698.82 $[M\text{-}2PF_6]^+$, 2553.86 $[M\text{-}3PF_6]^+$; monoisotopic mass calcd for: $C_{148}H_{148}N_{12}O_7Ru_2P_3F_{18}$ 2843.86, found 2843.75.

EA for $C_{148}H_{148}N_{12}O_7Ru_2P_4F_{24}$ (2988.83): calcd.: C 59.47, H 4.99, N 5.62;
found: C 58.82, H 4.96, N 5.31.

*Polymerization of **112a** (**113**):*

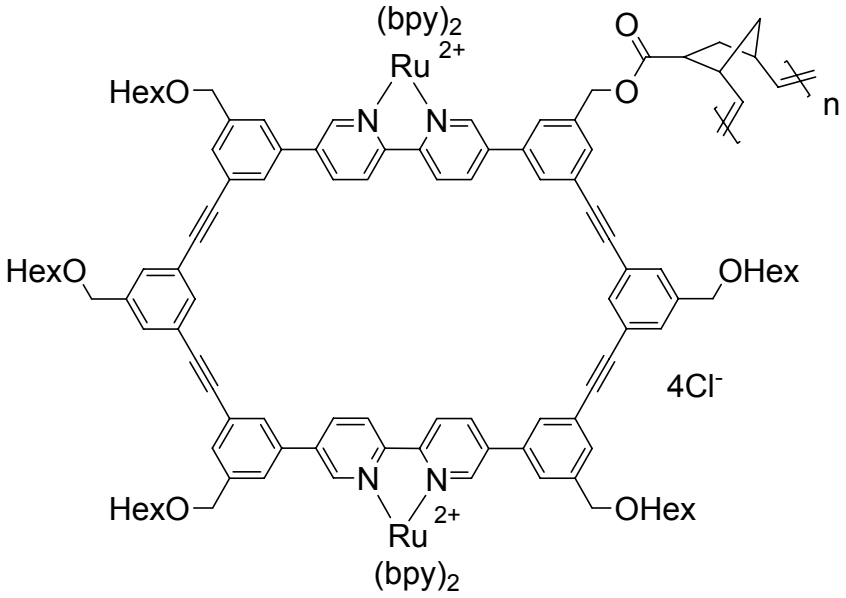


To a solution of monomer **112a** (0.17 mg, 0.11 mmol) in degassed benzene (1 ml), a 0.05M AIBN initiator solution in benzene (112 µL, 5 mol-%) was added. The resulting mixture was stirred in a sealed tube at 80 °C for 5 d. The purification of the oligomer was done by GPC using THF as solvent to give 108 mg of polymer **113** (62%).

^{1}H NMR (270 MHz, CD_2Cl_2): δ = 0.75-1.10 (br, 18 H, CH_3), 1.20-1.90 (br, 42 H, β-, γ-, δ-, ε-CH_2, CH_2), 3.25-3.70 (br, 12 H, 10 α-CH_2, 2 benzyl-H), 4.00-4.55 (br, 10 H, benzyl-H), 6.50-8.80 (br, 30 H, phenyl-H, py-H).

^{13}C NMR (CD_2Cl_2, 63 MHz): δ = 14.36, 21.37, 23.19, 26.50, 29.25, 30.33, 32.32, 71.46, 72.56, 89.34, 89.90, 120.50, 123.79, 128.47, 130.02, 133.84, 136.62, 139.68, 146.78, 154.29, 156.84, 172.30.

*Polymerization of **112c** (**114**):*



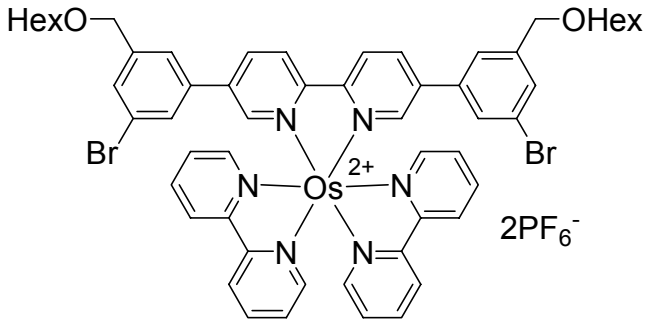
Monomer **112c** (100 mg, 0.04 mmol) was dissolved in CH_2Cl_2 (0.5 ml) and stirred under nitrogen. 130 µL of a catalyst stock solution prepared from 12 mg of $(Cy_3P)_2Cl_2Ru{=}CHPh$ in 1 ml DCM, corresponding to monomer/catalyst ratio of 20:1, was added dropwise to the monomer solution which was then stirred for 24 h. The product was dried at high vacuum.

^{1}H NMR ($CDCl_3/CD_3NO_2$): δ = 0.60-1.90 (br. 15 H, CH_3), 1.10-1.45 (br. 34 H, γ-, δ-, ε-CH_2, CH_2), 1.45-1.60 (br, 11 H, β-CH_2, CH), 1.60-2.0 (br, 2 H, CH), 3.80-3.50 (br, 10 H, α-CH_2), 4.3-4.48 (2 s, 10 H, benzyl-H), 4.60 (br, 2 H, benzyl-H), 4.85-5.10 (br, 1 H, =CH), 5.20-5.50 (br, 1 H, =CH), 7.0-7.23 (br, 4 H, Ph-H), 7.24-7.60, 7.60-7.90 (br, 34 H, py-H, Ph-H), 7.90-8.15 (br, 8 H, py-H), 8.15-8.45 (br, 4 H, py-H), 8.70-9.10 (br, 8 H, py-H), 9.10-9.40 (br, 8 H, py-H).

^{13}C NMR ($CDCl_3$, CD_3NO_2): δ = 13.36, 22.05, 25.58, 25.72, 26.21, 26.40, 29.11, 31.10, 34.26, 45.44, 70.50, 71.21, 88.67, 89.29, 122.80, 123.93, 124.78, 125.89, 127.38, 127.77, 129.73, 130.59, 134.22, 134.67, 136.36, 137.69, 138.74, 139.66, 140.38, 147.43, 150.95, 155.45, 156.32, 156.83, C=O missing.

7.2.4. Compounds of Chapter 4.5.

*$[bpy)_2Os$(**74a**)$](PF_6)_2$ (**115**):*



$[Os(bpy)_2Cl_2]$ (41 mg, 0.072 mmol) and **74a** (50 mg, 0.072 mmol) were dissolved in ethanol (20 ml) and the mixture was stirred under nitrogen at reflux for 3 d. The solvent was removed to give a dark green residue which was purified by column chromatography through neutral aluminium oxide (CH_2Cl_2/methanol 95:5). The green fraction was collected and the solvent removed. The solid was dissolved in methanol (1 ml) and added to a solution of NH_4PF_6 (240 mg) in water (2 ml). The precipitated solid was separated by filtration, washed with water (5 x 2 ml) and dried in vacuum to give 41 mg (38%) of complex **115** as a green solid.

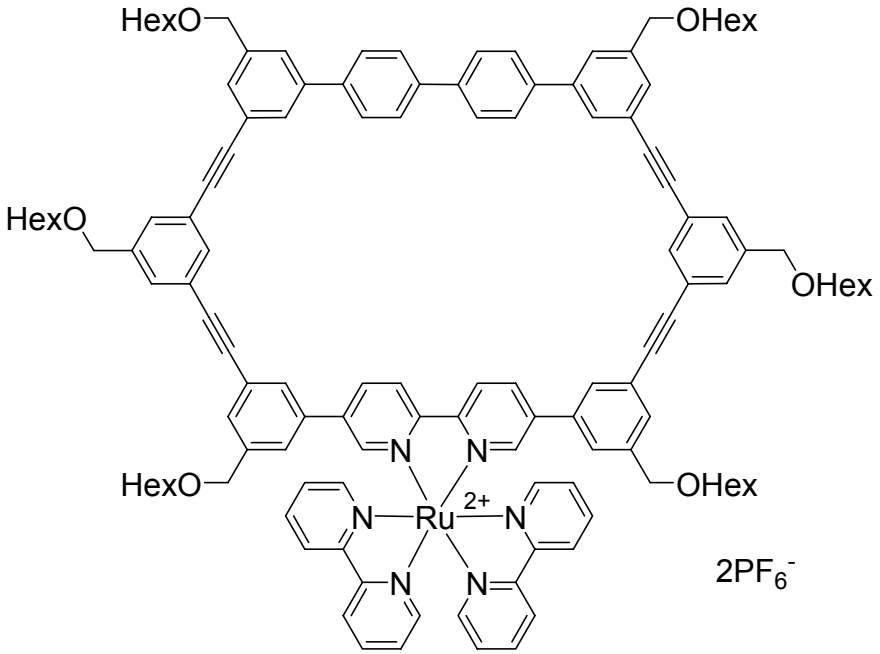
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.86 (t, 6 H, CH_3), 1.27-1.36 (m, 12 H, γ-, δ-, ε-CH_2), 1.59 (m, 4 H, β-CH_2), 3.47 (t, 4 H, α-CH_2), 4.45 (s, 4 H, benzyl-H), 7.24 (s, 4 H, phenyl-H), 7.44 (t, 4 H, py-H), 7.53 (s, 2 H, phenyl-H), 7.56 (s, 2 H, py-H), 7.78 (d, ^3J = 5.5 Hz, 2H, py-H), 7.77-7.82 (m, 6 H, py-H), 7.93 (d, ^3J = 7.5 Hz, 2 H, py-H) 8.36 (d, ^3J = 8 Hz, 4 H, py-H), 8.48 (d, ^3J = 9 Hz, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 14.06, 22.61, 25.80, 29.66, 31.65, 71.17, 71.32, 123.43, 124.04, 124.39, 124.85, 124.98, 128.86, 129.36, 131.57, 135.68, 136.19, 137.24, 137.69, 139.90, 142.91, 147.42, 151.11, 151.32, 157.45, 157.87, 158.55.

MS (**FAB**): *m/z* (%): 1343 (2.13) $[M+H-PF_6]^+$, 1198 (2.38) $[M+H-2PF_6]^{+\cdot}$

EA: for $C_{56}H_{58}Br_2F_{12}N_6O_2OsP_2$ (1487.07): calcd.: C 45.23, H 3.93, N 5.65;
found: C 44.43, H 4.07, N 5.53.

*[(bpy)$_2$Ru(**103c**)][PF$_6$)$_2$ (**116a**):*



A stirred solution of **103c** (50 mg, 0.032 mmol) and [Ru(bpy)$_2$]Cl$_2$×2H$_2$O (24 mg, 0.066 mmol) in dioxane (5 ml), propylene glycol (3 ml) and ethanol (3 ml) was refluxed for 24 h under nitrogen. The solvent was removed and the brown-orange solid purified by column chromatography through silica gel (CH_2Cl_2/methanol 95:5). The solvent was removed to give an orange solid which was dissolved in 1 ml methanol. This solution was added to a solution of NH_4PF_6 (50 mg) in H_2O (2 ml). The precipitated solid was separated by filtration, washed with H_2O (4 × 2 ml) and dried in vacuum to give 40 mg (56%) of **116a** as an orange solid. R_f = 0.54 (dichloromethane/methanol = 95:5).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.89 (m, 18 H, CH_3), 1.25-1.42 (m, 36 H, γ-, δ-, ε-CH_2), 1.53-1.70 (m, 12 H, β-CH_2), 3.47 (t, 4 H, α-CH_2), 3.52 (m, 8 H, α-CH_2), 4.40 (s, 4 H, benzyl-H), 4.49 (s, 4 H, benzyl-H), 4.54 (s, 2 H, benzyl-H), 7.05 (s, 2 H, phenyl-H), 7.42 (s, 2 H, phenyl-H), 7.45 (s, 4 H, phenyl-H), 7.46 (s, 2 H, phenyl-H) 7.48 (s, 2 H, phenyl-H), 7.90 (t, ^3J = 6.5 Hz, 2 H, py-H), 7.54 (s, 2 H, phenyl-H), 7.56 (t, ^3J = 6.5 Hz, 2 H, py-H), 7.62 (s, 2 H, py-H), 7.63-7.69 (mc, 4 H, phenyl-H), 7.71-7.74 (m, 6 H, phenyl-H), 7.77 (s, 2 H, phenyl-H), 7.84 (d, ^3J = 4.5 Hz, 2 H, py-H), 7.87 (d, ^3J = 4.5 Hz, 2 H, py-H), 7.92 (t, ^3J = 7 Hz, 2 H, py-H), 7.99 (t, ^3J = 7 Hz, 2 H, py-H), 8.07 (d, ^3J = 8 Hz, 2 H, py-H), 8.33 (2d overlapped, ^3J = 8 Hz, 4 H, py-H), 8.51 (d, ^3J = 8.5 Hz, 2 H, py-H).

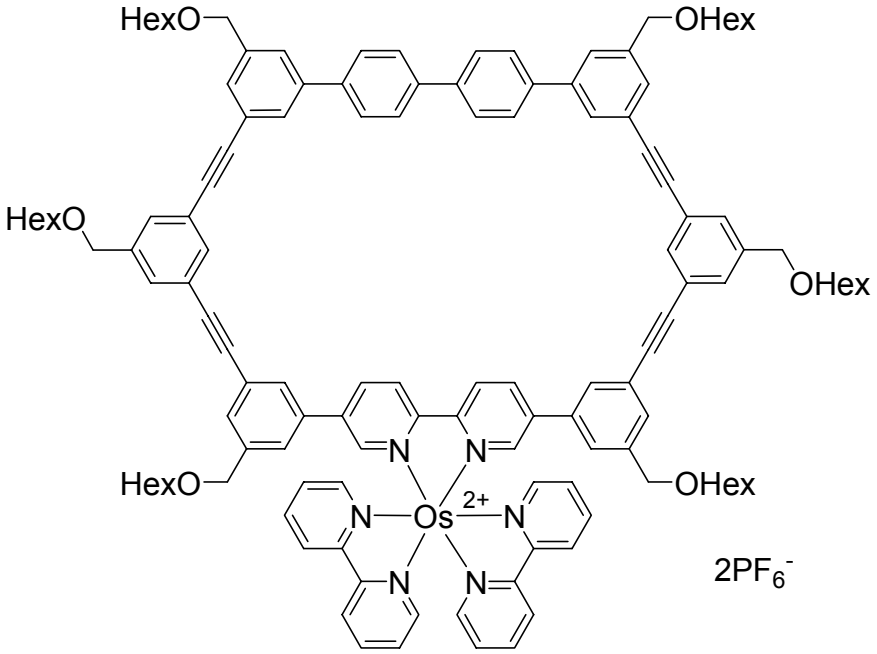
^{13}C NMR ($CDCl_3$, 500 MHz): δ = 14.19, 22.76, 25.98, 29.86, 31.82, 71.00, 71.08, 71.19, 71.76, 72.05, 72.48, 88.82, 89.17, 90.15, 90.40, 123.61, 123.85, 124.62,

124.82, 125.39, 127.35, 127.51, 128.39, 128.95, 129.58, 129.84, 130.11, 130.22, 130.26, 131.16, 134.69, 134.94, 136.52, 137.80, 138.25, 138.81, 139.50, 139.74, 139.90, 140.60, 141.07, 148.03, 151.99, 152.32, 155.30, 156.15, 156.75.

MALDI-TOF *m/z*: 2103 $[M\text{-}PF_6]^+$, 2025 $[M+Na\text{-}PF_6\text{-}OC_6H_{13}]^+$, 1958 $[M\text{-}2PF_6]^+$.

EA: for $C_{128}H_{138}N_6O_6RuP_2F_{12}$ (2247.50): calcd.: C 68.40, H 6.19, N 3.74;
found: C 67.13, H 6.19, N 3.41.

*$[(bpy)_2Os$(**103c**)$](PF_6)_2$ (**116b**):*



A stirred solution of **103c** (40 mg, 0.026 mmol) and $[Os(bpy)_2]Cl_2\times 2H_2O$ (17 mg, 0.030 mmol) in butanol (15 ml) was refluxed for 5 d. The solvent was removed and the brown-green solid purified by column chromatography on neutral aluminium oxide (CH_2Cl_2/methanol 95:5) to remove unreacted macrocycle. Then the complex was eluted off the column using methanol. The green fraction was collected and the solvent removed to give a green solid which was disolved in methanol (2 ml). This solution was added to a solution of NH_4PF_6 (86 mg) in H_2O (2 ml). The precipitated solid was separated by filtration, washed with H_2O (4 × 3 ml), and dried in vacuum to give 30 mg (50%) of **116b** as a green solid.

^{1}H NMR ($CDCl_3$ 500 MHz): δ = 0.88 (m, 18 H, CH_3), 1.24-1.44 (m, 36 H, γ-, δ-, ε-CH_2), 1.56-1.72 (m, 12 H, β-CH_2), 3.47 (t, 4 H, α-CH_2), 3.52 (m, 8 H, α-CH_2), 4.42 (s, 4 H, benzyl-H), 4.48 (s, 4 H, benzyl-H), 4.54 (s, 4 H, benzyl-H), 7.05 (s, 2 H, phenyl-H), 7.42 (s, 4 H, phenyl-H), 7.45-7.53 (m, 10 H, 6 phenyl-H, 4 py-H), 7.56 (s, 4 H, 2

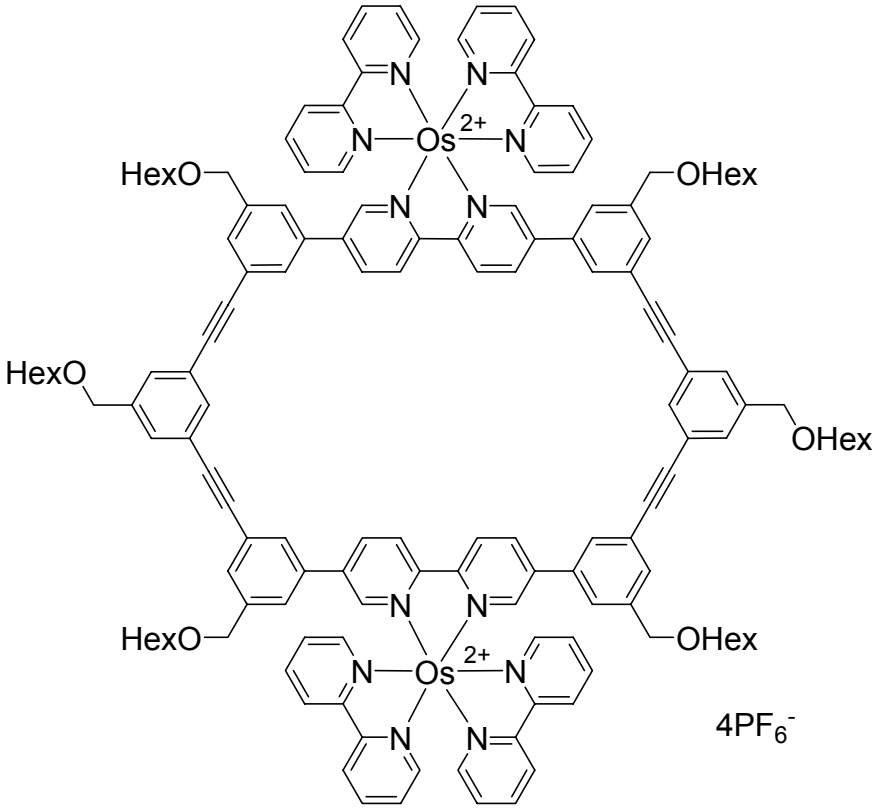
py-H, 2 phenyl-H), 7.64-7.84 (m, 20 H, 12 phenyl-H, 8 py-H), 7.91 (d, ^3J = 8 Hz, 2 H, py-H), 8.32 (t, ^3J = 9 Hz, 4 H, py-H), 8.5 (d, ^3J = 8 Hz, 2 H, py-H).

^{13}C NMR ($CDCl_3$, 500 MHz): δ = 14.16, 22.74, 25.97, 29.83, 31.81, 71.00, 71.06, 71.17, 71.75, 72.00, 72.48, 88.8, 88.84, 90.16, 90.40, 99.57, 102.14, 116.68, 123.28, 123.6, 123.85, 123.97, 124.39, 124.57, 125.00, 125.47, 126.05, 127.36, 127.50, 128.87, 129.19, 129.35, 129.57, 129.80, 130.22, 131.16, 132.54, 134.56, 134.89, 135.92, 136.51, 137.11, 137.63, 138.81, 138.99, 139.53, 139.74, 139.89, 140.26, 140.62, 141.06.

MS (**MALDI-TOF**): 2192 $[M\text{-}PF_6]^+$, 2047 $[M\text{-}2PF_6]^+$.

EA: for $C_{128}H_{138}N_6O_6OsP_2F_{12}$ (2336.66): calcd.: C 65.79, H 5.95, N 3.60;
found: C 64.23, H 5.75, N 3.29.

*$[(bpy)_2Os($**10**$)Os(bpy)_2](PF_6)_4$ (**117**):*



A stirred solution of macrocycle **10** (37.2 mg, 0.03 mmol) and $[Os(bpy)_2]Cl_2\times 2H_2O$ (50 mg, 0.09 mmol) in butanol (15 ml) was refluxed for 5 d under nitrogen. The solvent was removed and the brown-green solid was purified by column chromatography through neutral aluminium oxide using as eluent dichloromethane/methanol (95:5) to remove unreacted macrocycle and $[Os(bpy)_2]Cl_2$, followed by methanol to wash the complex off the column. After removal of the

solvent the green solid was dissolved in 2 ml methanol. To this a solution of NH_4PF_6 (55 mg in water 2 ml) was added. The precipitated solid was separated by filtration, washed with H_2O (5 × 3 ml), and dried in vacuum to give 43.5 mg of the complex **117** (53%) as a green solid.

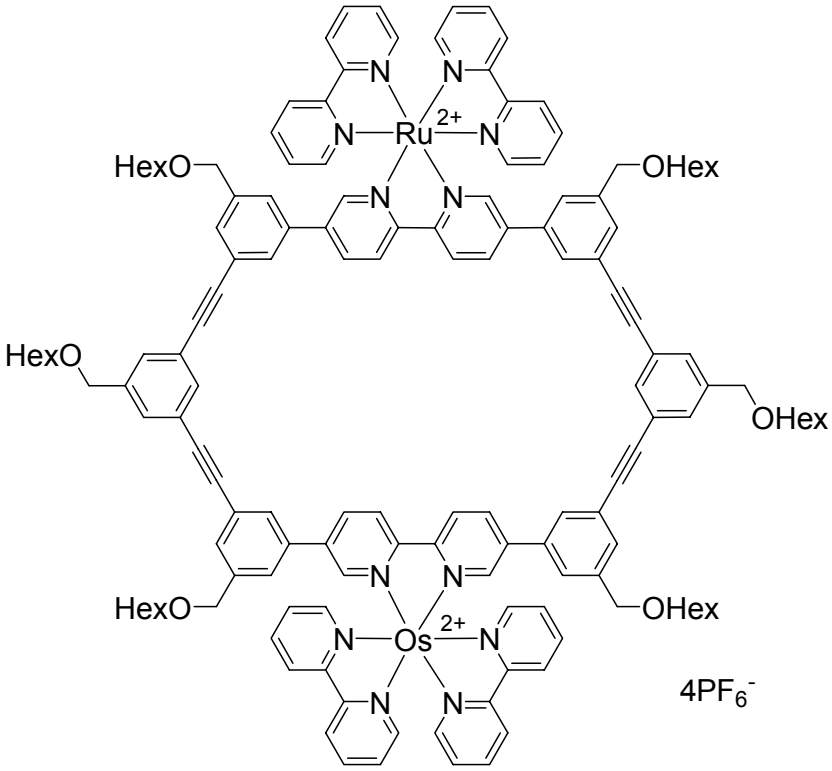
R_f = 0.63 (methanol/2M NH_4Cl/nitromethane 7:2:1).

^{1}H NMR (nitromethane-D_3, 500 MHz): δ = 0.84 (t, 12 H, CH_3), 1.25-1.47 (m, 24 H, γ, δ, ε-CH_2), 1.1.50-1.68 (m, 8 H, β-CH_2), 3.47 (t, 8 H, α-CH_2), 4.42 (s, 8 H, benzyl-CH_2), 7.17 (s, 4 H, phenyl-H), 7.36 (m, 4 H, py-H), 7.42 (m, 4 H, py-H), 7.45 (m, 2 H, phenyl-H), 7.55 (m, 8 H, phenyl-H), 7.86 (m, 4 H, phenyl-H), 7.88 (s, 2 H, phenyl-H), 7.92-7.99 (m, 16 H, py-H), 8.01 (s, 4 H, py-H), 8.29 (d, 4 H, ^3J = 8 Hz, py-H), 8.51 (d, 4 H, ^3J = 8 Hz, py-H), 8.58 (d, 4 H, ^3J = 8 Hz, py-H), 8.70 (d, 4 H, ^3J = 8 Hz, py-H).

^{13}C NMR (nitromethane-D_3, 500 MHz): δ = 14.44, 23.70, 26.92, 30.72, 32.74, 71.87, 72.61, 90.42, 90.48, 124.59, 125.30, 125.71, 125.78, 125.85, 126.75, 128.49, 129.35, 129.39, 130.55, 131.22, 132.19, 132.48, 136.36, 137.20, 138.59, 140.62, 142.64, 149.17, 151.96, 152.31, 152.37, 159.44, 160.43, 160.74.

MALDI-TOF: 2758 $[M\text{-}PF_6]^+$, 2613 $[M\text{-}2PF_6]^+$, 2468 $[M\text{-}3PF_6]^+$, 1966 $[M\text{-}3PF_6\text{-Os-}2bpy]^+$, 1821 $[M\text{-}4PF_6\text{-Os-}2bpy]^+$; monoisotopic mass calcd for $C_{132}H_{124}N_{12}O_4Os_2P_3F_{12}$: 2757.80; found 2757.87.

*$[(bpy)_2Ru($**10**$)Os(bpy)_2](PF_6)_4$ (**118**):*



A stirred solution of **10** (80 mg, 0.06 mmol), and $[Os(bpy)_2Cl_2]$ (28 mg, 0.05 mmol) in 7 ml butanol was refluxed for 3 d. The solvent was removed and the residual green material purified by column chromatography, first through neutral aluminium oxide (dichloromethane/methanol 90:10) to remove the unreacted macrocycle and the unreacted Os source. The green fraction was collected and the solvent removed. The second column was done through silica gel eluting first with methanol/2M NH_4Cl/nitromethane 7:2:1. The binuclear Os complex was isolated first, followed then by the mononuclear Os complex which was washed off the column by dichloromethane/methanol 3:4. The solvent was removed and the precipitate (NH_4Cl and the complex) washed with dichloromethane and filtrated to give a green solution. The solvent was removed and the green solid $[(bpy)_2Os(\mathbf{10})]Cl_2$ (10 mg, 10%) was partially characterised.

MS (**MALDI-TOF**, dithranol): *m/z*: 1821.04 $[M\text{-}2Cl]^+$, 1735.89 $[M\text{-}2Cl\text{-}C_6H_{13}]^+$.

^{1}H NMR ($CDCl_3$, 500 MHz, 20 °C): the signals are broad; characteristic for this complex are the two different signals for benzylic-H at δ = 4.43 and 4.52.

A solution of $[(bpy)_2Os(\mathbf{1})]Cl_2$ (6 mg, 0.003 mmol) and $[Ru(bpy)_2Cl_2]\cdot 2H_2O$ (3 mg, 0.006 mmol) in ethanol (1 ml), methanol (0.5 ml), water (0.5 ml) was refluxed for 24 h. The solvent was removed and the residue purified by column chromatography through silica gel (methanol/2M NH_4Cl/nitromethane). The green fraction was collected and the solvent removed. The precipitate was washed with dichloromethane. The green solution was collected and the solvent removed. The solid was then dissolved in methanol (0.5 ml) and added to a concentrated solution of NH_4PF_6 (1 ml). The green precipitate was collected and washed with water (3 × 0.5 ml), and dried in vacuum to give 7 mg of **118** (83%).

R_f (methanol/2M NH_4Cl/nitromethan) = 0.86.

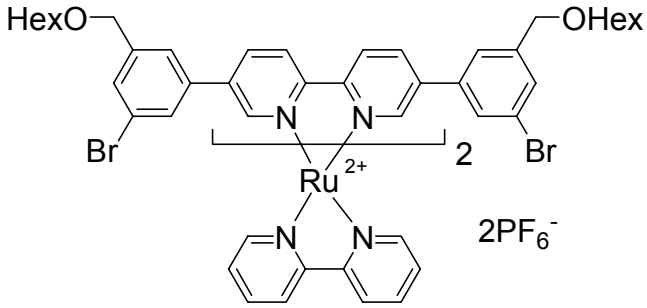
^{1}H NMR (CD_3NO_2, 500 MHz): δ = 0.85 (t, 12 H, CH_3), 1.23-1.34 (m, 24 H, γ-, δ-, ε-CH_2), 1.55-1.65 (m, 8 H, β-CH_2), 3.48 (t, 8 H, α-CH_2), 4.48 (s, 8 H, benzyl-CH_2), 7.18 (s, 2 H, phenyl-H), 7.20 (s, 2 H, phenyl-H), 7.34 (2 dd overlapped in a t, ^3J = 6 Hz, 2 H, py-H), 7.42 (2 dd overlapped in a t, 2 H, py-H), 7.43 (2 dd overlapped in a t, 2 H, py-H), 7.47 (d, ^3J = 8 Hz, 2 H, phenyl-H), 7.51 (2 dd overlapped in a t, 2 H, py-H), 7.55-7.60 (m, 8 H, phenyl-H), 7.82 (s, 2 H, phenyl-H), 7.83 (s, 2 H, phenyl-H), 7.85 (s, 2 H, phenyl-H), 7.86 (2 dd overlapped in a t, 2 H, py-H), 7.91 (d, ^3J = 6 Hz, 2 H, py-H), 7.96-8.00 (m, 6 H, py-H), 8.01 (d, ^4J = 2 Hz, 2 H, py-H), 8.03-8.08 (m, 4 H, py-H), 8.09 (d, ^4J = 2 Hz, 2 H, py-H), 8.16 (2 dd overlapped in a t, 2 H, py-H), 8.28 (dd,

^3J = 8 Hz, ^4J = 2 Hz, 2 H, py-H), 8.48 (dd, ^3J = 8.5 Hz, ^4J = 2 Hz, 2 H, py-H), 8.49-8.54 (2d overlapped in a t, ^3J = 8 Hz, 4 H, py-H), 8.56-8.61 (2d, overlapped in a t, ^3J = 8 Hz, 4 H, py-H), 8.71 (d, ^3J = 8.5, 2 H, py-H), 8.73 (d, ^3J = 8.5 Hz, 2 H, py-H).

^{13}C NMR (CD_3NO_2): is quite complex because of the diastereoizomeric mixture and couldn't be resolved.

MS (**MALDI-TOF**, dithranol): 2669.77 $[M\text{-}PF_6]^+$, 2524.84 $[M\text{-}2PF_6]^+$; monoisotopic mass calcd for $C_{132}H_{124}O_4N_{12}F_{18}OsP_3Ru^+$: 2669.745, found: 2669.77.

*$[(bpy)_2Ru($**74a**$)](PF_6)_2$ (**119a**):*



A solution of **74a** (76 mg, 0.11 mmol) and $[Ru(bipy)Cl_3]_x$ (20 mg, 0.055 mmol) in dioxane (2 ml), ethanol (3.5 ml), water (1.5 ml) was refluxed for 24 h. The solvent was removed and the residual orange material purified by column chromatography through silica gel (methanol/2M NH_4Cl/nitromethane 7:2:1). The combined orange fractions were diluted with chloroform and the organic phase was separated, and the solvent removed. The orange precipitate was then dissolved in the minimal amount of methanol (2 ml) and added to a solution of NH_4PF_6 (200 mg) in water (3 ml). The precipitated solid was separated by filtration, washed with water (6 ml), and dried in vacuum to give 88 mg (83%) of complex **119a** as an orange solid.

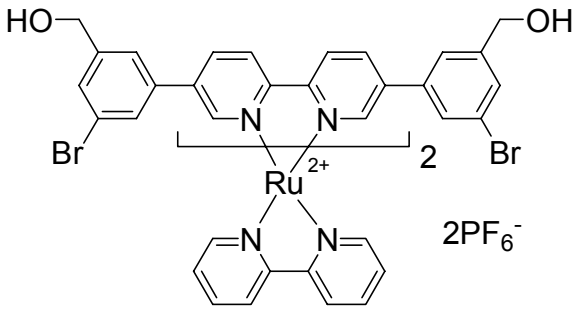
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.79 (t, 12 H, CH_3), 1.14-1.3 (m, 24 H, γ-, δ-, ε-CH_2) 1.45 (m, 4 H, β-CH_2), 1.5 (m, 4 H, β-CH_2), 3.33 (t, 4 H, α-CH_2), 3.42 (t, 4 H, α-CH_2), 4.33 (s, 4 H, benzyl-CH_2), 4.4 (s, 4 H, benzyl-CH_2), 7.13 (s, 4 H, phenyl-H), 7.21(s, 4 H, phenyl-H), 7.44 (s, 2 H, phenyl-H), 7.5 (s, 2 H, phenyl-H), 7.58 (s, 2 H, py-H), 7.67 (d, 4 H, py-H), 7.9 (s, 2 H, py-H), 7.98 (s, 2 H, py-H), 8.13 (s, 4 H, py-H), 8.45 (s, 2 H, py-H), 8.64 (s, 4 H, py-H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ = 13.91, 22.47, 25.65, 25.68, 29.48, 31.52, 71.18, 123.35, 123.59, 124.40, 124.84, 125.13, 125.50, 128.66, 131.46, 135.94, 136.22, 136.33, 136.72, 138.34, 139.36, 142.69, 143.05, 147.98, 152.15, 155.11, 155.81, 156.35.

MS (**FAB**): *m/z* (%): 1791 $[M\text{-}PF_6]^+$ (100), 1646 $[M\text{-}2 \times PF_6]^{2+}$ (90.29).

EA: for $C_{82}H_{92}Br_4N_6O_4P_2F_{12}Ru$ (1936.26): calcd.: C 50.86, H 4.79, N 4.34;
found: C 51.04, H 4.73, N 4.11.

*$[(bpy)_2Ru($**74b**$)](PF_6)_4$ (**119b**):*



A stirred solution of **74b** (150 mg, 0.21 mmol) and and $[Ru(bpy)Cl_3]_x$ (39 mg, 0.10 mmol) in dioxane (4 ml), ethanol (4 ml), water (2 ml) was refluxed for 24 h. The solvent was removed and the residual orange material purified by column chromatography through silica gel (methanol/2M NH_4Cl/nitromethane 7:2:1). The combined orange fractions were diluted with chloroform, the organic phase separated, and the solvent removed. The orange precipitate was then dissolved in methanol (20 ml) and added to a solution of NH_4PF_6 (200 mg) in water (3 ml). The precipitated solid was separated by filtration, washed with water (6 ml), and dried in vacuum to give 144 mg (84%) complex **119b** as an orange solid.

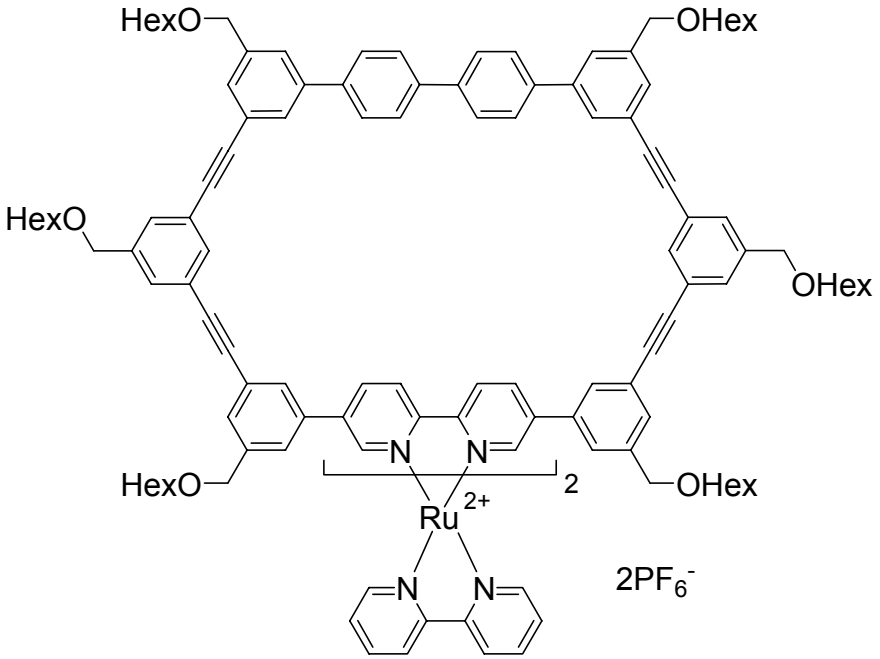
^{1}H NMR (DMSO, 500 MHz): δ = 4.45 (s, 4 H, benzyl-CH_2), 4.54 (s, 4 H, benzyl-CH_2), 5.39 (s, 4 H, -OH), 7.43 (s, 4 H, phenyl-H), 7.56 (s, 2 H, phenyl-H), 7.61 (s, 2 H, py-H, 4 H, phenyl-H), 7.65 (s, 2 H, phenyl-H), 7.86 (s, 2 H, py-H), 7.92 (s, 2 H, py-H), 8.11 (d, 2 H, py-H), 8.27 (t, 2 H, py-H), 8.62 (d, 2 H, py-H), 8.69 (d, 2 H, py-H), 8.88 (d, 2 H, py-H), 8.95 (d, 2 H, py-H), 9.02 (d, 2 H, py-H).

^{13}C NMR (DMSO, 126 MHz): δ = 62.26, 122.85, 124.35, 125.14, 128.13, 130.29, 135.82, 136.13, 136.73, 137.06, 137.33, 137.86, 138.24, 146.84, 149.31, 149.66, 153.03, 155.77, 156.16, 157.30.

MS (**FAB**): *m/z* (%): 1451 (2.21) $[M\text{-}PF_6]^+$, 1306 (3.28) $[M\text{-}PF_6]^{2+}$.

EA: for $C_{58}H_{40}F_{12}Br_4N_6O_4P_2Ru$ (1595.59): calcd.: C 43.66, H 2.53, N 5.27;
found: C 44.06, H 2.84, N 5.15.

*[(bpy)Ru(**103c**)$_2$](PF$_6$)$_2$ (**120**):*



A stirred suspension of **103c** (20 mg, 0.013 mmol) and [Ru(bpy)Cl3]x (2.3 mg, 0.006 mmol) in dioxane/ethanol/water (2:2:1, 5 ml) was refluxed for 4 d. During this time a change of colour from blue to dark red was observed. Then 20 µl of 4-ethylmorpholin was added and the reaction stirred for another 1 h. The solvent was removed and the compound was purified by column chromatography through silica gel (DCM/methanol 9:1). The orange fraction was collected, the solvent removed. The solid was then dissolved in methanol (0.3 ml) and added to a saturated solution of NH_4PF_6. The complex precipitated, was filtrated and washed several times with water, dried in vacuum to give 6 mg of **120** (25%)as an orange solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.89 (br., 32 H, CH_3), 1.25-1.50 (br., 72 H, γ-, δ-, ε-CH_2), 1.64 (br., 24 H, β-CH_2), 3.25 (br., 24 H, α-CH_2), 4.42 (s, 8H, benzyl-CH_2), 4.51 (s, 8 H, benzyl-CH_2), 4.55 (s, 8 H, benzyl-CH_2), 7.00 (s, 4 H, phenyl-H), 7.25-7.50 (m, br., 20 H, phenyl-H), 7.50-7.90 (br., 32 H, py-H, phenyl-H), 8.06 (br., 6 H, py-H), 8.27 (s, br., 4 H, py-H), 8.39 (s, br., 2 H, py-H), 8.66 (s, br., 4 H, py-H).

MS (**MALDI-TOF**): *m/z*: 3503.76 $[M+CH_3-PF_6]^+$, 3489.84 $[M-PF_6]^+$, 3445.83 $[M-PF_6-C_3H_7]^+$, 3359.82 $[M+H-CH_3-2PF_6]^+$, 3344.84 $[M+H-2PF_6]^+$; monoisotopic mass calcd for $C_{223}H_{245}F_6N_6O_{12}PRu^+$: 3445.74, found: 3445.83.

7.3. Crystallografic Data

Table 16: Crystal data and structure refinement for **103c** and **106**.

	103c	**106**
Empirical formula	C106 H120 N4 O6	C80 H84 N4 O4
Formula weight	1546.06	1165.51
Temperature	173(2) K	173(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions a	10.814(5) Å	8.357(7) Å
b	14.096(7) Å	10.787(11) Å
c	15.079(8) Å	18.555(18) Å
α	74.812(13)°	95.68(2)°.
β	89.180(12)°	100.89(2)°.
γ	78.124(12)°	102.76(2)°.
Volume	2168.9(19) $Å^3$	1584(3) $Å^3$
Z	1	1
Density (calculated)	1.184 Mg/m^3	1.222 Mg/m^3
Absorption coefficient	0.072 mm^{-1}	0.075 mm^{-1}
F(000)	832	624
Crystal size	0.8 x 0.2 x 0.03 mm^3	0.80 x 0.20 x 0.03 mm^3
Theta range for data collection	1.40 to 20.90°	1.96 to 20.93°.
Index ranges	-7<=h<=10, -14<=k<=14, -15<=l<=14	-6<=h<=8, -10<=k<=9, -18<=l<=18
Reflections collected	11115	5641
Independent reflections	4547 [R(int) = 0.2386]	3307 [R(int) = 0.2682]
Completeness to theta = 20.90°	98.8 %	98.0 %
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	4547 / 27 / 527	3307 / 0 / 280
Goodness-of-fit on F^2	0.877	0.745
Final R indices [I>2sigma(I)]	R1 = 0.1030, wR2 = 0.2381	R1 = 0.0872, wR2 = 0.0773
R indices (all data)	R1 = 0.2646, wR2 = 0.3237	R1 = 0.3102, wR2 = 0.1126
Extinction coefficient	0.0130(11)	0.00136(14)
Largest diff. peak and hole	0.548 and -0.279 $e.Å^{-3}$	0.234 and -0.291 $e.Å^{-3}$