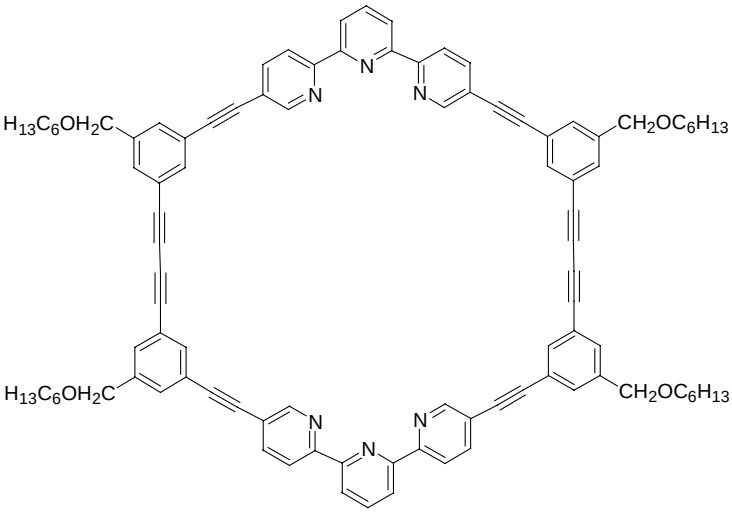
7.2.4 Compounds of Chapters 4.6 and 4.8

15,24,46,55-Tetrakis(hexyloxymethyl)-8,31,39,62,69,76-hexaaza-undecacyclo[58.2.2.1^{2,6}.2^{7,10}.1^{13,17}.1^{22,26}.2^{29,32}.1^{33,37}.2^{38,41}.1^{44,48}.1^{53,57}]hexaheptaconta-1(62),2,4,6(76),7,9,13,15,17(73),22,24,26(72),29,31,33,35,37(69),38,40,44,46,48(66),53,55,57(65),60,63,67,70,74-triacontaen-11,18,20,27,42,49,51,58-octayne **111**

$C_{98}H_{90}N_6O_4$, M = 1415.83.



To a solution of $PdCl_2(PPh_3)_2$ (30 mg, 0.043 mmol) and CuI (8 mg, 0.043 mmol) in piperidine/THF (100 ml / 150 ml), a solution of **80a** (344 mg, 485 mmol) in THF (25 ml) was added over a period of 4 days under stirring on air. It was stirred for two more days, the solvent evaporated, the soluble part of the residue dissolved in CH_2Cl_2, extracted with water (50 ml) and the aqueous phase again extracted with CH_2Cl_2 (50 ml). The combined organic phases were dried over $MgSO_4$, the solvent evaporated and the residue freeze-dried to give 1.00 g of a brownish solid material. By preparative GPC, cycle **111** (28 mg, 0.020 mmol, 8 %), oligomer **[111]$_{1.5}$** (26 mg, 0.012 mmol, 8 %), and oligomer **[111]$_2$** (11 mg, 0.004 mmol, 3 %) were isolated as yellow, amorphous materials.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.44 (s, 4 H, tpy-6,6''-H), 8.37 (s br, 4 H, tpy-3,3''-H), 8.14 (d, 4 H, ^{3}J = 7.0 Hz, tpy-3',5'-H), 7.72 (s br, 4 H, tpy-4,4''-H), 7.66 (t, 2 H, ^{3}J = 7.5 Hz, tpy-4'-H), 7.29 (s, 4 H, phenyl-H), 7.17 (s, 8 H, phenyl-H), 4.33 (s, 8 H, benzyl-H), 3.49 (t, 8 H, ^{3}J = 6.7 Hz, α-CH_2), 1.67 (quintet, 8 H, hexyl-β-CH_2), 1.34-1.44 (m, 24 H, γ-, δ-, ε-CH_2), 0.94 (t, 3 H, ^{3}J = 6.8 Hz, hexyl-CH_3).

MS (**MALDI**, THA): m/z (%) = 1513.81 $[M+CH_3+C_6H_{12}]^+$, 1477.82 $[M+Na+K]^+$, 1453.90 $[M+K]^+$, 1437.89 $[M+Na]^+$, 1429.90 $[M+CH_3]^+$, 1415.90 $[M+H]^+$, 1329.78 $[M-C_6H_{13}]^+$.

*Cyclic oligomer **[111]$_{1.5}$***

$C_{147}H_{135}N_9O_6$, M = 2123.74

MS (**MALDI**, THA): m/z (%) = 2145.34 $[M+Na]^+$, 2137.28 $[M+CH_3]^+$, 2123.32 $[M+H]^+$.

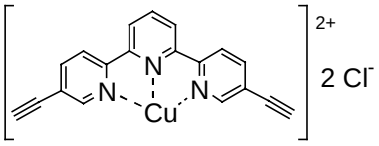
*Cyclic oligomer **[111]$_2$***

$C_{196}H_{180}N_{12}O_8$, M = 2831.66

MS (**MALDI**, THA): m/z (%) = 2908.92 $[M+Cu+CH_3]^+$, 2894.92 $[M+Cu]^+$, 2846.82 $[M+CH_3]^+$, 2832.42 $[M+H]^+$, 2761.53 $[M-C_5H_{11}]^+$, 2746.76 $[M-C_6H_{12}]^+$, 2675.88 $[M-C_5H_{11}-C_6H_{12}]^+$, 2660.95 $[M-2C_6H_{12}]^+$. Only a spectrum in the linear mode (i.e., with less resolution than in the reflector mode) could be obtained. The different isotopes could therefore not be resolved.

*(5,5''-Diethynyl-2,2':6',2''-terpyridine-κ^3N,N,N)copper(II) chloride **112***

$C_{19}H_{11}Cl_2CuN_3$, M = 415.77



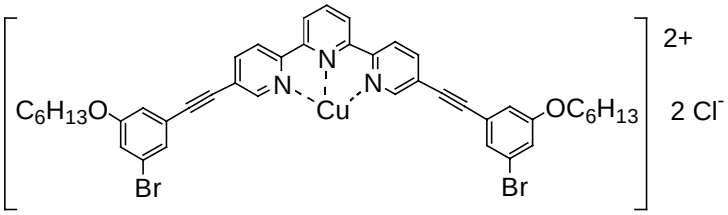
34 (50 mg, 0.12 mmol) was dissolved in degassesed, dried methanol (15 ml) under reflux. Via a septum, a solution of $CuCl_2 \bullet 2H_2O$ (20 mg, 0.20 mmol) in methanol (7 ml) was added. The color of the greenish solution became darker. After 5 min. of refluxing, the solution was allowed to cool to room temperature. A voluminous brownish precipitate was observed, which transformed during some minutes into green crystalline material. This was collected by filtration and washed with methanol, then ether to yield **112** (33 mg, 0.074 mmol, 67 %). As this Cu(II)-complex is paramagnetic, no NMR spectra were recorded.

MS (**EI**, 250 eV, 70°C): m/z (%) = 283 (2.8), 282 (20.3), 281 (100.0), 280 (9.3), 279 (1.4), 278 (1.2) $[M-Cu-2Cl]^+$.

MS (**FAB(+)**, DMSO-MNBA-Matrix): m/z (%) = 383 (16.7), 382 (21.0), 381 (80.3), 380 (29.0), 379 (100.0), 378 (4.5) $[M-Cl]^+$, 347 (8.6), 346 (30.9), 345 (18.3), 344 (64.5), 343 (4.2) $[M-2Cl]^+$.

*{5,5''-Bis[(3-bromo-5-hexoxyphenyl)ethynyl]-2,2':6',2''-terpyridine-κ^3N,N,N}copper(II) chloride **113***

$C_{43}H_{41}Br_2CuCl_2N_3O_2$, M = 926.07



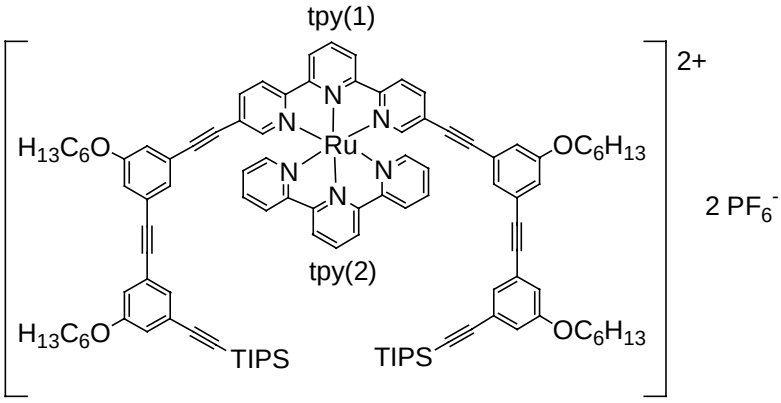
The procedure was analogous to that described for **112**, with methanol replaced by acetone for reasons of solubility of **36** (**36**: 39 mg, 0.049 mmol;

$CuCl_2 \cdot 2H_2O$: 8.4 mg, 0.049 mmol; acetone: 10 ml/5 ml). **113** (46 mg, 0.05 mmol, quant.) was isolated as green crystalline material.

MS (**FAB(+)**, DMSO/MNBA-Matrix): m/z (%) = 895 (6.9), 894 (13.5), 893 (31.1), 892 (31.2), 891 (68.6), 890 (34.3), 889 (66.1), 888 (14.6), 887 (27.1) $[M\text{-}Cl]^+$, 858 (5.8), 857 (8.1), 856 (16.7), 855 (11.1), 854 (21.9), 853 (6.4), 852 (12.1) $[M\text{-}2Cl]^+$.

*(5,5‘‘-Bis{[3-({3-[(triisopropylsilyl)ethynyl]-5-hexoxyphenyl}ethynyl)-5-hexoxyphenyl]-ethynyl}-2,2‘:6‘,2‘‘-terpyridine-κ^3N,N,N)(2,2‘:6‘,2‘‘-terpyridine-κ^3N,N,N)ruthenium(II) hexafluorophosphate **117***

$C_{108}H_{126}F_{12}N_6O_4P_2RuSi_2$, M = 2019.40



Under N_2, **89b** (317 mg, 0.227 mmol) was heated in dioxane (20 ml) to 120°C. ethylene glycol (ca. 6 ml) was dropwise added until the two phases became a single phase. **114**[175] (100 mg, 0.227 mmol) was added, and the mixture refluxed overnight. The brownish precipitate of **114** had then nearly vanished, and the solution was deeply red-brown. The mixture was poured into an aqueous NH_4PF_6 solution (50 ml) and stirred for 30 min. The dark-brown precipitate was filtered, thoroughly washed with water, and dissolved in dichloromethane. After repeated column chromatography over silica gel (first with CH_3CN/conc. KNO_3(aqu.)/H_2O 20:1:3, then 40:3:1), 100 mg (0.050 mmol, 22 %) of **117** was obtained as red-brownish solid. After another precipitation from NH_4PF_6 solution, 58 mg of **117** (0.030 mmol, 13 %) was isolated.[186]

^{1}H-NMR (500 MHz, CD_3CN): δ = 8.75 (d, 2 H, ^3J = 8.5 Hz, tpy-3’,5’-H), 8.71 (d, 2 H, ^3J = 8.0 Hz, tpy-3’,5’-H), 8.48 (d, 2 H, ^3J = 8.5 Hz, tpy-3,3’’-H) , 8.46 (d, 2 H, ^3J = 8.5 Hz, tpy-3,3’’-H), 8.42 (t, 1 H, ^3J = 8.0 Hz, tpy-4’-H), 8.35 (t, 1 H, ^3J = 8.0 Hz, tpy-4’-H), 7.96 (dd, 2 H, ^3J = 8.5 Hz, ^4J = 1.5 Hz, tpy(1)-4,4’’-H), 7.90 (dt, 2 H, ^3J = 7.8 Hz, ^4J = 1.0 Hz, tpy(2)-4,4’’-H), 7.41 (d, 2 H, ^4J = 2.0 Hz, tpy(1)-6,6’’-H), 7.34 (d, 2 H, ^3J = 5.0 Hz, tpy(2)-6,6’’-H), 7.17 (t, 2 H, ^3J = 6.0 Hz, tpy(2)-5,5’’-H), 7.16 (s, 2 H, phenyl-H), 7.11 (s, 2 H, phenyl-H), 7.06 (m, 2 H, phenyl-H), 7.01 (m, 2 H, phenyl-H), 6.99 (m, 2 H, phenyl-H), 6.94 (m, 2 H, phenyl-H), 3.95 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 3.90 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 1.66-1.74 (m, 8 H, β-CH_2), 1.36-1.44 (m, 8 H, γ-CH_2), 1.28-1.32 (m, 8 H, δ-,ε- CH_2), 1.11 (s, 42 H, silyl-H),

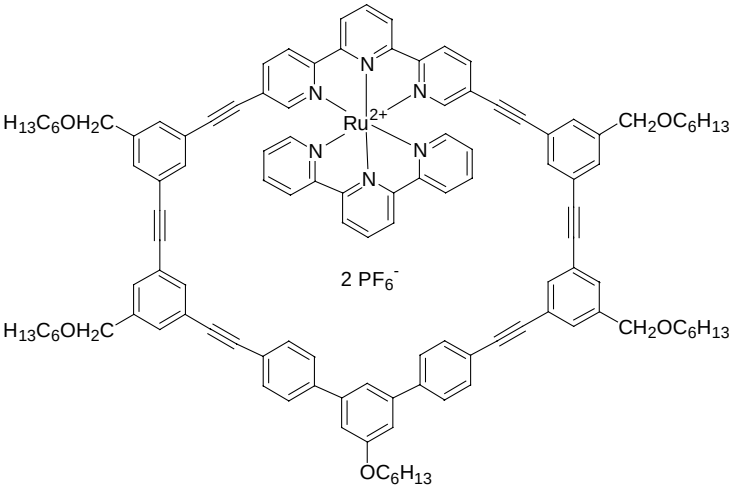
0.86 (t, 12 H, ^3J =7.5 Hz, hexyl-CH_3). The assignment of the tpy-signals is not proven by 2-D spectra, but derives from comparison with literature data.[176]

^{13}C-NMR (125.8 MHz, CD_3CN): δ = 160.27, 159.10, 158.10, 156.44, 156.10, 155.15, 153.81, 141.06, 139.35, 137.38, 137.00, 128.64, 128.05, 127.66, 125.81, 125.69, 125.50, 125.37, 125.14, 125.05, 125.02, 124.62, 123.93, 119.92, 119.31 (2 signals), 119.22, 107.03, 96.39, 92.49, 89.96, 89.27, 85.12, 69.58, 69.53, 32.32, 32.29, 29.86, 29.79, 26.38, 26.35, 23.37, 23.35, 19.10, 14.36, 12.21.

MS (**MALDI**, THA): m/z (%) = 1728.93 $[M\text{-}2PF_6]^+$,1874.94 $[M\text{-}PF_6\text{+}H]^+$.

{33-Hexoxy-15,22,44,51-tetrakis(hexoxymethyl)-8,58,72-triazaundecacyclo[54.2.2.1^{2,6}.2^{2,7}.1^{13,17}.1^{20,24}.2^{27,30}.1^{31,35}.2^{36,39}.1^{42,46}.1^{49,53}]diheptaconta-1(58),2,4,6(72),7,9,13,15,17(69),20,22,24(68),27,29,31,33,35(65),36,38,42,44,46(62),49,51,53(61),56,59,63,66,70-triacontaen-11,18,25,40,47,54-hexayne-κ^{3}N,N,N}(2,2‘:6‘,2‘‘-terpyridine-κ^{3}N,N,N)ruthenium(II) hexafluorophosphate ***118***

$C_{118}H_{116}F_{12}N_6O_5P_2Ru$, M = 2089.25



The procedure was analogous to that described for **117**. **95a** (39 mg, 0.027 mmol), **114**[175] (12 mg, 0.027 mmol), dioxane (7 ml), ethylene glycol (ca. 2 ml). **118** (11 mg, 0.030 mmol, 13 %) was isolated as red-brown solid. The signals in the ^{1}H-NMR spectrum were too broad for assignment.

MS (**MALDI**, THA): m/z (%) = 2007.85 $[M\text{-}PF_6\text{-}H\text{+}Cu]^+$, 1945.84 $[M\text{-}PF_6\text{+}2H]^+$, 1861.82 $[M\text{-}2PF_6\text{-}H\text{+}Cu]^+$, 1800.78 $[M\text{-}2PF_6\text{+}2H]^+$.