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[58.2.2.12,6.27,10.113,17.122,26.229,32.133,37.238,41.144,48.153,57]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

\[ \text{C}_{98}\text{H}_{90}\text{N}_{6}\text{O}_{4}, \text{ M = 1415.83.} \]

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\(_2\)Cl\(_2\), extracted with water (50 ml) and the aqueous phase again extracted with CH\(_2\)Cl\(_2\) (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\text{H-NMR} (500 \text{ MHz, CDCl}_3): \delta = 8.44 (\text{s, 4 H, tpy-6,6''-H}), 8.37 (\text{s br, 4 H, tpy-3,3''-H}), 8.14 (\text{d, 4 H, }^3\text{J = 7.0 Hz, tpy-3',5'-H}), 7.72 (\text{s br, 4 H, tpy-4,4''-H}), 7.66 (\text{t, 2 H, }^3\text{J = 7.5 Hz, tpy-4'-H}), 7.29 (\text{s, 4 H, phenyl-H}), 7.17 (\text{s, 8 H, phenyl-H}), 4.33 (\text{s, 8 H, benzyl-H}), 3.49 (\text{t, 8 H, }^3\text{J = 6.7 Hz, }\alpha\text{-CH}_2), 1.67 (\text{quintet, 8 H, hexyl-}\beta\text{-CH}_2), 1.34-1.44 (\text{m, 24 H, }\gamma, \delta, \epsilon- \text{CH}_2), 0.94 (\text{t, 3 H, }^3\text{J = 6.8 Hz, hexyl-CH}_3).\]


\text{Cyclic oligomer [111]\(_{1.5}\)}
\[ \text{C}_{147}\text{H}_{135}\text{N}_{9}\text{O}_{6}, \text{ M = 2123.74} \]

\text{MS (MALDI, THA): m/z (\%) = 2145.34 [M+Na]^+, 2137.28 [M+CH}_3]^+, 2123.32 [M+H]^+.}
Cyclic oligomer [III]$_2$
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$_5$H$_{11}$]$^+$, 2746.76 [M-C$_6$H$_{12}$]$^+$, 2675.88 [M-C$_5$H$_{11}$-C$_6$H$_{12}$]$^+$, 2660.95 [M-2C$_6$H$_{12}$]$^+$. 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$^3$N,N,N)copper(II) chloride 112

C$_{19}$H$_{11}$Cl$_2$CuN$_3$, M = 415.77

34 (50 mg, 0.12 mmol) was dissolved in degassed, dried methanol (15 ml) under reflux. Via a septum, a solution of CuCl$_2$•2H$_2$O (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$^3$N,N,N}copper(II) chloride 113

C$_{43}$H$_{41}$Br$_2$CuCl$_2$N$_3$O$_2$, 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;
7.2.4 Compounds of Chapter 4.8

CuCl$_2$•2H$_2$O: 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-Cl]$^+$, 858 (5.8), 857 (8.1), 856 (16.7), 855 (11.1), 854 (21.9), 853 (6.4), 852 (12.1) [M-2Cl]$^+$.

(5,5’’-Bis[(3-[tris(isopropylsilyl)ethynyl]-5-hexoxyphenyl)ethynyl]-5-hexoxyphenyl[ethynyl]-2,2’:6’,2’’-terpyridine-$\kappa^{3}$N,N,N)(2,2’:6’,2’’-terpyridine-$\kappa^{3}$N,N,N)ruthenium(II) hexafluorophosphate 117

C$_{108}$H$_{126}$F$_{12}$N$_{6}$O$_{4}$P$_{2}$RuSi$_{2}$, 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** (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$_{4}$PF$_{6}$ 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$_{3}$CN/conc. KNO$_{3}$(aqu.)/H$_{2}$O 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$_{4}$PF$_{6}$ solution, 58 mg of **117** (0.030 mmol, 13 %) was isolated.

**$^1$H-NMR (500 MHz, CD$_{3}$CN):** $\delta$ = 8.75 (d, 2 H, $^3$J = 8.5 Hz, tpy-3’,5’-H), 8.71 (d, 2 H, $^3$J = 8.0 Hz, tpy-3’,5’-H), 8.48 (d, 2 H, $^3$J = 8.5 Hz, tpy-3’,3’-H), 8.42 (t, 1 H, $^3$J = 8.0 Hz, tpy-4’-H), 8.35 (t, 1 H, $^3$J = 8.0 Hz, tpy-4’-H), 7.96 (dd, 2 H, $^3$J = 8.5 Hz, $^4$J = 1.5 Hz, tpy(1)-4,4’’-H), 7.90 (dt, 2 H, $^3$J = 7.8 Hz, $^4$J = 1.0 Hz, tpy(2)-4,4’’-H), 7.41 (d, 2 H, $^4$J = 2.0 Hz, tpy(1)-6,6’’-H), 7.34 (d, 2 H, $^3$J = 5.0 Hz, tpy(2)-6,6’’-H), 7.17 (t, 2 H, $^3$J = 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, $^3$J = 6.5 Hz, $\alpha$-CH$_{2}$), 3.90 (t, 4 H, $^3$J = 6.5 Hz, $\alpha$-CH$_{2}$), 1.66-1.74 (m, 8 H, $\beta$-CH$_{2}$), 1.36-1.44 (m, 8 H, $\gamma$-CH$_{2}$), 1.28-1.32 (m, 8 H, $\delta$-CH$_{2}$), 1.11 (s, 42 H, silyl-H),
The assignment of the tpy-signals is not proven by 2-D spectra, but derives from comparison with literature data.\textsuperscript{176}

\textbf{13C-NMR} (125.8 MHz, CD\textsubscript{3}CN): $\delta$ = 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.

\textbf{MS (MALDI, THA)}: \(m/z\) (%) = 1728.93 [M-2PF\textsubscript{6}]\(^+\), 1874.94 [M-PF\textsubscript{6}+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]2^{2,30}.1^{31}1^{35}.2^{36}1^{39}.I^{42}4^{46}.I^{49}5^{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-\(\kappa^3N,N,N\}(2,2':6',2''-terpyridine-\(\kappa^3N,N,N\))ruthenium(II)

\textit{Hexafluorophosphate 118}

C\textsubscript{118}H\textsubscript{116}F\textsubscript{12}N\textsubscript{6}O\textsubscript{5}P\textsubscript{2}Ru, M = 2089.25

The procedure was analogous to that described for 117. \textit{95a} (39 mg, 0.027 mmol), 114\textsuperscript{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 \textsuperscript{1}H-NMR spectrum were too broad for assignment.

\textbf{MS (MALDI, THA)}: \(m/z\) (%) = 2007.85 [M-PF\textsubscript{6}+H+Cu]\(^+\), 1945.84 [M-PF\textsubscript{6}+2H]\(^+\), 1861.82 [M-2PF\textsubscript{6}+H+Cu]\(^+\), 1800.78 [M-2PF\textsubscript{6}+2H]\(^+\).