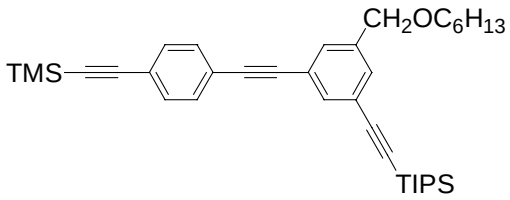
7.2.3 Compounds of Chapter 4.5

1-Hexoxymethyl-3-({4-[(trimethylsilyl)ethynyl]phenyl}ethynyl)-5-[(triisopropylsilyl)ethynyl]benzene ***99***

$C_{37}H_{52}OSi_2$, M = 568.99



The procedure was analogous to that described for **43b** (**98**:[31] 8.62 g, 34.1 mmol; **45a**:[32] 13.50 g, 34.1 mmol; CuI: 194 mg, 1.02 mmol; $Pd[P(Ph_3)]_4$: 1.18 g, 1.02 mmol; triethylamine: 250 ml; reaction time: 3 days; reaction temperature: 70°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **99** (15.11 g, 26.56 mmol, 78 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.71 (hexane/ethyl acetate 40:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.53 (t, 1 H, ^4J = 1.3 Hz, aryl-H), 7.42 (s, 5 H, aryl-H), 7.39 (d, 1 H, ^4J = 1.3 Hz, aryl-H), 4.44 (s, 2 H, benzyl-H), 3.45 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 1.55-1.63 (quintet, 2 H, $^3J \approx 7$ Hz, β-CH_2), 1.28-1.38 (m, 6 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.87 (t, 3 H, ^3J = 6.7 Hz, hexyl-CH_3), 0.24 (s, 9 H, TMS-H).

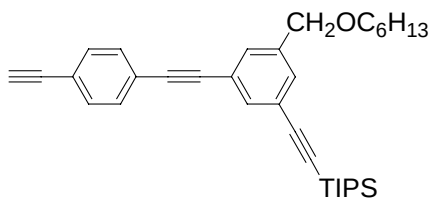
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.35, 134.07, 131.88, 131.34, 130.91, 130.35, 123.95, 123.22, 123.07, 106.03, 104.58, 96.35, 91.40, 90.43, 89.47, 71.90, 70.79, 31.66, 29.66, 25.84, 22.61, 18.65, 14.03, 11.28, -0.11.

MS (**EI**, 80 eV, 180°C): m/z (%) = 571 (7.5), 570 (21.2), 569 (40.8), 568 (62.0) $[M]^+$, 527 (19.8), 526 (47.9), 525 (100) $[M\text{-}C_3H_7]^+$, 497 (9.5) $[M\text{-}C_5H_{11}]^+$.

EA:	Calc.:	C:78.10	H:9.21
	Found:	C:77.82	H:8.99.

1-Hexoxymethyl-3-[(4-ethynylphenyl)ethynyl]-5-[(triisopropylsilyl)ethynyl]benzene ***100***

$C_{34}H_{44}OSi$, M = 496.81



The procedure was analogous to that described for **45b** (**99**: 11.58 g, 20.35 mmol; dichloromethane: 70 ml; methanol: 70 ml). The solvent was evaporated, the crude product dissolved in dichloromethane (100 ml), and washed with water (100 ml). The aqueous phase was extracted with dichloromethane (2 × 100 ml), the

combined organic layers were dried over $MgSO_4$ and the solvent evaporated to afford **100** (9.98 g, 20.09 mmol, 99 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.56 (hexane/ethyl acetate 40:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.54 (t, 1 H, ^{4}J = 1.4 Hz, aryl-H), 7.45 (s, 4 H, aryl-H), 7.43 (s, 1 H), 7.40 (t, 1 H, ^{4}J = 1.3 Hz, aryl-H), 4.45 (s, 2 H, benzyl-H), 3.46 (t, 2 H, ^{3}J = 6.7 Hz, α-CH_2), 3.16 (s, 1H, ethynyl-H), 1.56-1.63 (quintet, 2 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.30-1.41 (m, 6 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.87 (t, 3 H, ^{3}J = 6.7 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.36, 134.04, 132.03, 131.45, 130.92, 130.34, 123.94, 123.45, 123.15, 122.06, 106.01, 91.39, 90.49, 89.26, 83.18, 78.98, 71.86, 70.77, 31.64, 29.64, 25.82, 22.59, 18.62, 14.01, 11.26.

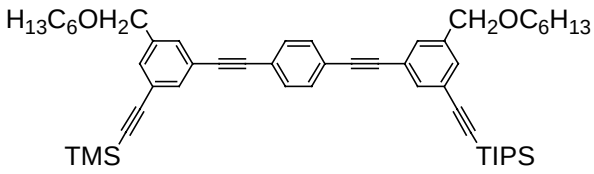
MS (**EI**, 80 eV, 160°C): m/z (%) = 498 (5.6), 497 (15.5), 496 (34.6) $[M]^+$, 455 (12.8), 454 (43.6), 453 (100.0), 452 (3.0) $[M\text{-}C_3H_7]^+$, 426 (3.6), 425 (10.5) $[M\text{-}C_5H_{11}]^+$, 412 (4.3), 411 (10.2) $[M\text{-}C_6H_{13}]^+$.

EA: Calc.: C:82.19 H:8.93

Found: C:81.99 H:9.04.

1-Hexoxymethyl-3-{[4-({3-hexoxymethyl-5-[(trimethylsilyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}-5-[(triisopropylsilyl)ethynyl]benzene ***101***

$C_{52}H_{70}O_2Si_2$, M = 783.29



The procedure was analogous to that described for **43b** (**42a**:[32] 8.85 g, 24.1 mmol; **100**: 11.97 g, 24.1 mmol; CuI: 138 mg, 0.723 mmol; $Pd[P(Ph_3)]_4$: 835 mg, 0.723 mmol; triethylamine: 150 ml; reaction time: 3 days; reaction temperature: 80°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **101** (13.38 g, 17.1 mmol, 71 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.41 (hexane/ethyl acetate 40:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.54 (d, 2 H, ^{4}J = 1.4 Hz, aryl-H), 7.47 (s, 4 H, aryl-H), 7.44 (s, 2 H, aryl-H), 7.39 (d, 2 H, ^{4}J = 1.0 Hz, aryl-H), 4.45 (s, 2 H, benzyl-H), 4.44 (s, 2 H, benzyl-H), 3.46 (t, 2 H, ^{3}J = 6.6 Hz, α-CH_2), 3.44 (t, 2 H, ^{3}J = 6.6 Hz, α-CH_2), 1.58-1.63 (m, 4 H, β-CH_2), 1.28-1.38 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, TIPS-H), 0.88 (t, 6 H, ^{3}J = 6.7 Hz, hexyl-CH_3), 0.24 (s, 9 H, TMS-H).

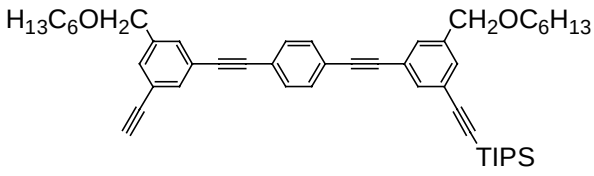
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.38, 134.04, 133.99, 131.55, 130.89, 130.81, 130.46, 130.58, 123.95, 123.55, 123.25, 123.00, 106.04, 104.05, 94.97, 91.39, 90.49, 90.45, 89.51, 71.87, 70.77, 31.65, 29.65, 25.83, 22.60, 18.64, 14.03, 11.28, -0.13.

MS (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 785 (8.1), 784 (12.7), 783 (22.9), 782 (50.3), 781 (73.8), 780 (40.4), 779 (13.3), 778 (8.7) $[M-2H]^+$, 741 (9.9), 740 (18.4), 739 (30.1), 738 (41.2) $[M-2H-C_3H_7]^+$, 696 (5.5) $[M-C_6H_{13}]^+$, 682 (41.7), 681 (67.1), 680 (100.0) $[M-CH_3-2C_3H_7]^+$.

EA: Calc.: C:79.74 H:9.00
Found: C:79.54 H:8.76.

1-Hexoxymethyl-3-({4-[(3-ethynyl-5-hexoxymethylphenyl)ethynyl]phenyl}ethynyl)-5-[(triisopropylsilyl)ethynyl]benzene ***102***

$C_{49}H_{62}O_2Si$, M = 711.11



The procedure was analogous to that described for **45b** (**101**: 12.59 g, 16.10 mmol; dichloromethane: 100 ml; methanol: 70 ml). The crude product was purified by chromatography over silica gel (hexane/toluene) to afford **102** (8.53 g, 12.0 mmol, 75 %) as a yellow sirup.

R_f = 0.26 (hexane/ethyl acetate 10:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.54-7.56 (m, 2 H, aryl-H), 7.48 (s, 5 H, aryl-H), 7.42-7.44 (m, 2 H, aryl-H), 7.40 (t, 1 H, ^4J = 1.4 Hz, aryl-H), 4.45 (s, 4 H, benzyl-H), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.08 (s, 1 H, ethynyl-H), 1.61 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.20-1.41 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 21 H, silyl-H), 0.88 (t, 6 H, ^3J =6.6 Hz, hexyl-CH_3).

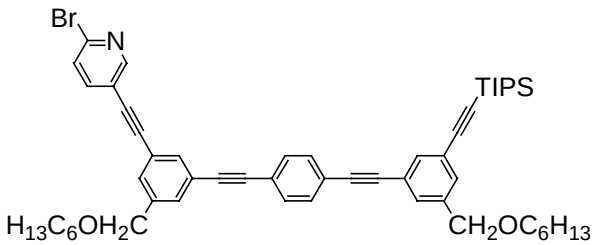
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.54, 139.36, 134.04, 131.55, 130.91, 130.77, 130.34, 123.93, 123.39, 123.20, 123.05, 122.90, 122.54, 106.02, 91.38, 90.52, 90.23, 89.65, 89.48, 82.68, 77.78, 71.86, 71.76, 70.79, 31.64, 29.65, 25.82, 22.60, 18.63, 14.02, 11.26.

MS (**EI**, 80 eV, 240°C): m/z (%) = 713 (9.1), 712 (27.2), 711 (61.7), 710 (95.6), 709 (83.5) $[M]^+$, 669 (23.3), 668 (58.5), 667 (100.0), 666 (89.7) $[M-C_3H_7]^+$.

EA: Calc.: C:82.76 H:8.79
Found: C:82.62 H:8.71.

2-Bromo-5-[(3-hexoxymethyl-5-{[4-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}-ethynyl)phenyl]ethynyl}phenyl)ethynyl]pyridine ***103***

$C_{54}H_{64}BrO_2NSi$, M = 867.09



The procedure was analogous to that described for **43b** (**59**:[31] 4.30 g, 15.2 mmol; **102**: 10.77 g, 15.15 mmol; CuI: 86 mg, 0.452 mmol; $Pd[P(Ph_3)]_4$: 520 mg, 0.452 mmol; triethylamine: 250 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **103** (11.10 g, 12.8 mmol, 84 %) as a brown sirup.

$\mathbf{R_f}$ = 0.60 (hexane/ethyl acetate 10:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.50 (d, 1 H, ^{4}J = 2.2 Hz, py-6-H), 7.62 (dd, 1 H, ^{3}J = 8.3 Hz, ^{4}J = 2.3 Hz, py-4-H), 7.61 (t, 1 H, ^{4}J = 1.5 Hz, phenyl-H), 7.54 (t, 1 H, ^{4}J = 1.4 Hz, phenyl-H), 7.46-7.48 (m, 7 H, 6 phenyl-H, py-2-H), 7.44 (s, 1 H, phenyl-H), 7.40 (s, 1 H, phenyl-H), 4.48 (s, 2 H, benzyl-H), 4.45 (s, 2 H, benzyl-H), 3.48 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 3.46 (t, 2 H, ^{3}J = 6.6 Hz, α-CH_2), 1.56-1.65 (m, 4 H, β-CH_2), 1.25-1.39 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.87 (t, 6 H, ^{3}J = 6.6 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 152.34, 141.23, 140.45, 139.77, 139.36, 134.03, 133.56, 131.55, 130.93, 130.34, 127.64, 123.93, 123.60, 123.16, 122.80, 122.59, 119.42, 106.00, 93.02, 91.40, 90.59, 90.15, 89.87, 89.44, 85.26, 71.85, 71.75, 70.89, 70.78, 31.63, 29.63, 25.81, 22.59, 18.62, 14.01, 11.25.

MS (**FAB(+)**, CH_2Cl_2 /DMSO/MNBA-Matrix)): m/z (%) = 870 (26.10), 869 (57.5), 868 (100.0), 867 (78.8), 866 (96.4) $[M+H]^+$.

EA:	Calc.:	C:74.80	H:7.44	N:1.55
	Found:	C:74.89	H:7.34	N:1.55.

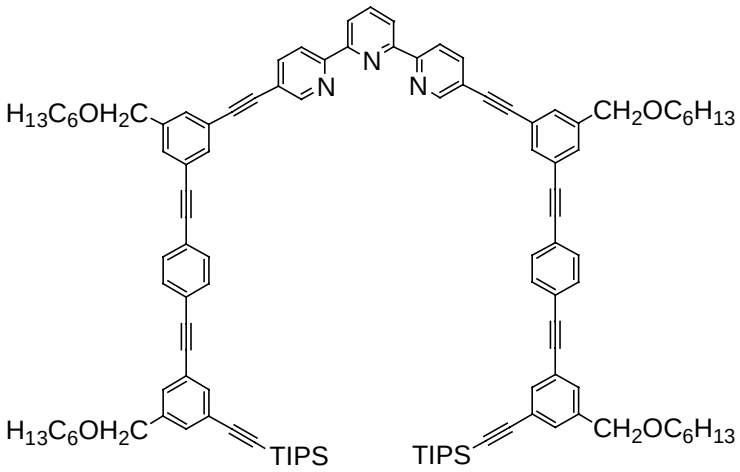
5,5‘‘-Bis[(3-hexoxymethyl-5-{[4-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}-ethynyl)phenyl]ethynyl}phenyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine ***104***

$C_{113}H_{131}N_3O_4Si_2$, M = 1651.47

The procedure is analogous to that described for **62** (**52**:[125] 2.54 g, 6.29 mmol; **103**: 10.90 g, 12.57 mmol; $Pd[P(Ph_3)]_4$: 436 mg, 0.377 mmol, toluene: 150 ml, reaction time: 48 hrs). The crude product was purified by repeated column chromatography (hexane/dichloromethane on

aluminium oxide, hexane/ethyl acetate on silica gel) to afford **104** (4.27 g, 2.59 mmol, 41 %) as a yellow resin.

R_f = 0.73 (hexane/ethyl acetate 4:1, aluminium oxide).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.82 (d, 2 H, ^{4}J = 1.6 Hz, tpy-6,6''-H), 8.62 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.98 (t, 1 H, ^{3}J = 7.8 Hz, tpy-4'-H), 7.96 (dd, 2 H, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, tpy-4,4''-H), 7.67 (s, 2 H, phenyl-H), 7.55 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.50 (s, 10 H, phenyl-H), 7.44 (s, 2 H, phenyl-H), 7.40 (s, 2 H, phenyl-H), 4.50 (s, 4 H, aryl-CH_2-O-), 4.45 (s, 4 H, aryl-CH_2-O-), 3.50 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 3.46 (t, 4 H, ^{3}J = 6.7 Hz, α-CH_2), 1.56-1.69 (m, 8 H, β-CH_2), 1.25-1.44 (m, 24 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.89 (t, 6 H, ^{3}J =6.5 Hz, hexyl-CH_3), 0.87 (t, 6 H, ^{3}J =6.8 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.84, 154.65, 151.62, 139.67, 139.35, 139.20, 137.87, 134.04, 133.63, 131.56, 130.90, 130.72, 130.33, 123.93, 123.54, 123.19, 123.06, 122.90, 121.52, 120.33, 120.06, 106.03, 92.66, 91.38, 90.56, 90.34, 89.79, 89.49, 87.02, 71.85, 70.88, 70.78, 31.65, 29.66, 25.83, 22.60, 18.63, 14.03, 11.26.

MS (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1655 (21.4), 1654 (31.4), 1653 (50.0), 1652 (52.8), 1651 (46.4) $[M+H]^+$, 1568 (20.5), 1567 (23.7), 1566 (22.9) $[M-C_6H_{12}]^+$.

EA:	Calc.:	C:82.18	H:7.99	N:2.54
	Found:	C:82.20	H:7.91	N:2.46.

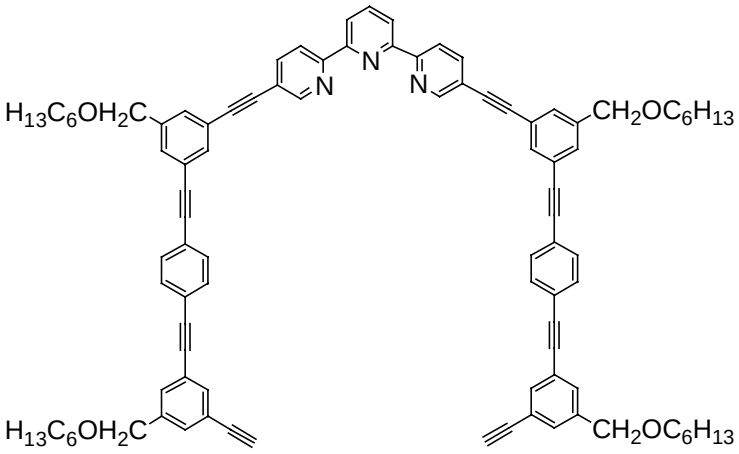
5,5''-Bis{[3-hexyloxymethyl-5-({4-[(3-ethynyl-5-hexoxymethylphenyl)ethynyl]phenyl}-ethynyl)phenyl]ethynyl}-2,2':6',2''-terpyridine ***105***

$C_{95}H_{91}N_3O_4$, M = 1338.78

The procedure was analogous to that described for **80a** (**104**: 4.08 g, 2.47 mmol; tetra-*n*-butylammonium fluoride trihydrate: 3.12 g, 9.88 mmol; THF: 50 ml). The crude product was purified by chromatography over aluminium oxide (hexane/ethyl acetate) to afford **105**

(2.04 g, 1.52 mmol, 62 %) as a yellow resin which could not be solidified even after freeze-drying from benzene.

R_f = 0.63 (hexane/ethyl acetate 4:1, aluminium oxide).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.82 (d, 2 H, ^{4}J = 1.9 Hz, tpy-6,6''-H), 8.61 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.96 (t, 1 H, ^{3}J ≈ 8 Hz, tpy-4'-H), 7.95 (dd, 2 H, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, tpy-4,4''-H), 7.66 (s, 2 H, phenyl-H), 7.59 (s, 2 H, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.49 (s, 10 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.42 (s, 2 H, phenyl-H), 4.50 (s, 4 H, aryl-CH_2-O-), 4.45 (s, 4 H, aryl-CH_2-O-), 3.48 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 3.46 (t, 4 H, ^{3}J = 6.7 Hz, α-CH_2), 3.08 (s, 2 H, ethynyl-H), 1.56-1.69 (m, 8 H, β-CH_2), 1.25-1.44 (m, 24 H γ-,δ-,ε-CH_2), 0.89 (t, 6 H, ^{3}J =6.7 Hz, hexyl-CH_3), 0.88 (t, 6 H, ^{3}J =6.7 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.73, 154.52, 151.54, 139.63, 139.49, 139.09, 137.74, 134.05, 133.97, 133.55, 131.51, 130.85, 130.67, 130.37, 123.44, 123.30, 122.91, 122.48, 121.44, 120.22, 119.97, 92.63, 90.37, 90.33, 89.73, 89.60, 87.02, 82.67, 77.82, 71.73, 71.68, 70.82, 70.76, 31.61, 29.62, 25.78, 22.57, 14.00.

MS (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1342 (0.07), 1341 (0.09), 1340 (0.18), 1339 (0.16) $[M+H]^+$.

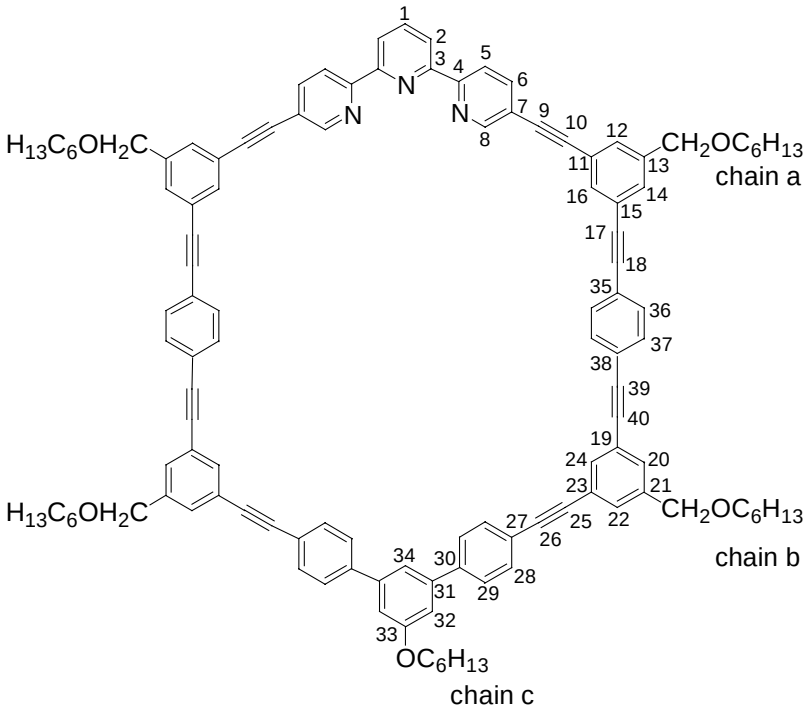
EA:	Calc.:	C:85.23	H:6.85	N:3.14
	Found:	C:85.35	H:6.88	N:3.03.

39-Hexoxy-15,28,50,63-tetrakis(hexoxymethyl)tridecacyclo[66.2.2.1^{2,6}.2^{7,10}.1^{13,17}.2^{20,23}.1^{26,30}.2^{33,36}.1^{37,41}.2^{42,45}.1^{48,52}.2^{55,58}.1^{61,65}]octaoctaconta-1(70),2,4,6(88),7,9,13,15,17(85),20,22,26,28,30(82),33,35,37,39,41(79),42,44,48,50,52(76),55,57,61,63,65(73),68,71,74,77,80,83,86-hexatriacontaen-11,18,24,31,46,53,59,66-octayne **106**

$C_{119}H_{113}N_3O_5$, M = 1665.22

The procedure was analogous to that described for **88**. **74a** (430 mg, 0.739 mmol), **105** (989 mg, 0.739 mmol), toluene/triethylamine (350 ml/350 ml), $Pd[P(Ph_3)]_4$ (68 mg, 0.059 mmol), CuI (11 mg, 0.059 mmol). From the brownish raw product (1.17 g), cycle **106**

and oligomer **[106]$_2$** were isolated by preparative GPC. These were dissolved in THF (ca. 5 ml), precipitated with methanol (ca. 8 ml), centrifuged, and the solvent layer taken off. This procedure was repeated once, to afford **106** (216 mg, 0.13 mmol, 18 %) and **[106]$_2$** (83 mg, 0.025 mmol, 7 %) as yellow, amorphous materials after freeze-drying.



^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.59 (s, 2 H, 8-H), 8.38 (d, 2 H, ^{3}J = 7.5 Hz, 5-H), 8.31 (d, 2 H, ^{3}J = 7.5 Hz, 2-H), 7.80 (t, 1 H, ^{3}J = 7.5 Hz, 1-H), 7.72 (d, 2 H, ^{3}J = 7.5 Hz, 6-H), 7.44 (d, 4 H, ^{3}J = 7.5 Hz, 29-H), 7.43, 7.39 (2 s, 4 H, H-16, H-24), 7.41 (d, 4 H, ^{3}J = 7.5 Hz, 28-H), 7.30 (s, 8 H, 36-H, 37-H), 7.21-7.30 (m, 9 H, 12-H, 14-H, 20-H, 22-H, 34-H), 6.95 (s, 2 H, 32-H), 4.38, 4.36 (2s, 8 H, aryl-CH_2 (a,b-chain)), 4.00 (t, 2 H, ^{3}J = 6.0 Hz, α-CH_2 (c-chain)), 3.49, 3.47 (2 t, 8 H, ^{3}J = 6.5 Hz, α-CH_2 (a,b-chain)), 1.84 (quintet, 2 H, ^{3}J = 7.0 Hz, β-CH_2 (c-chain)), 1.66 (m, 8 H, β-CH_2 (a,b-chain)), 1.52 (quintet, 2 H, ^{3}J ≈ 7 Hz, γ-CH_2 (c-chain)), 1.29-1.45 (m, 28 H, γ-CH_2 (a,b-chain), δ,ε-CH_2 (a,b,c-chain)), 0.91-0.99 (m, 15 H, -CH_3 (a,b,c-chain)).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 159.72 (33-C), 154.13 (3-C, 4-C), 151.00 (8-C), 141.07 (31-C), 139.65 (30-C), 139.16, 139.03 (13-C, 21-C), 138.83 (6-C), 137.05 (1-C), 133.67, 133.56 (16-C, 24-C), 131.85 (28-C), 131.30 (36,37), 129.93, 129.67 (2 signals), 129.58 (12-C, 14-C, 20-C, 22-C), 126.34 (29-C), 123.53, 123.38, 123.25, 122.88 (11-C, 15-C, 19-C, 23-C), 122.75, 122.60 (35-C, 38-C), 121.99 (27-C), 120.87 (2-C), 119.86 (5-C), 119.84 (7-C), 117.04 (34-C), 111.82 (32-C), 92.65, 90.59, 90.36, 89.78 (2 signals), 89.29 (10-C, 17-C, 18-C, 25-C, 39-C, 40-C), 89.57 (26-C), 87.07 (9-C), 71.91, 71.85 (aryl-CH_2 (a,b-chain)), 70.92, 70.82 (α-C (a,b-chain)), 68.06 (α-C (c-chain)), 31.74 (δ-C (a,b,c-chain)), 29.74 (β-C (a,b-chain)), 29.46 (β-C (c-chain)), 25.92 (γ-C (a,b-chain)), 25.85 (γ-C (c-chain)), 22.64 (ε-C (a,b,c-chain)), 14.03 (methyl-C (a,b,c-chain)).

MS (**MALDI**, THA): m/z (%) = 1692.79 $[M+C_2H_5]^+$, 1686.79 $[M+Na]^+$, 1678.80 $[M+CH_3]^+$, 1664.84 $[M+H]^+$, 1592.83 $[M-C_5H_{11}]^+$, 1578.73 $[M-C_6H_{13}]^+$.

Cyclic oligomer ***[106]$_2$***

$C_{238}H_{226}N_6O_{10}$, M = 3330.44

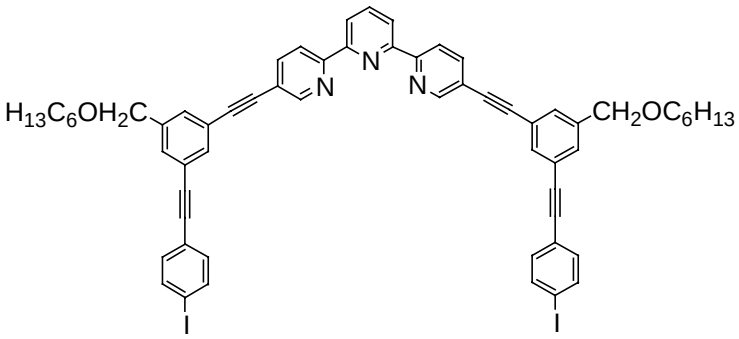
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.80 (dd, ^{4}J = 2.0 Hz, ^{5}J = 0.8 Hz, 4 H, 8-H), 8.60 (dd, 4 H, ^{3}J = 8.2 Hz, ^{4}J = 0.6 Hz, 5-H), 8.47 (d, 4 H, ^{3}J = 7.8 Hz, 2-H), 7.96 (t, 2 H, ^{3}J = 8.0 Hz, 1-H), 7.93 (d, 4 H, ^{3}J = 8.0 Hz, 6-H), 7.66 (t, 4 H, ^{4}J = 1.5 Hz), 7.64 (t, 4 H, ^{4}J = 1.5 Hz), 7.58-7.63 (m, 16 H), 7.48-7.52 (m, 28 H), 7.46 (t, 4 H, ^{4}J = 1.5 Hz), 7.38 (t, 2 H, ^{4}J = 1.5 Hz), 7.11 (d, 4 H, ^{4}J = 1.5 Hz), 4.50 (s, 8 H), 4.49 (s, 8 H), 4.06 (t, 4 H, ^{3}J = 6.5 Hz), 3.50 (t, 8 H, ^{3}J = 6.6 Hz), 3.49 (t, 8 H, ^{3}J = 6.5 Hz), 1.83 (quintet, 4 H, ^{3}J = 7.0 Hz), 1.61-1.65 (m, 16 H), 1.50 (m, 4 H), 1.27-1.42 (m, 56 H), 0.88-0.93 (m, 30 H).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 160.09, 154.94, 154.74, 151.61, 142.26, 140.99, 139.78, 139.63, 139.30, 137.91, 133.78, 132.10, 131.63, 130.68, 130.43, 130.25, 127.17, 123.76, 123.61, 123.46, 123.16, 123.10, 122.98, 122.26, 121.54, 120.40, 120.12, 118.38, 112.58, 92.72, 90.64, 90.41, 89.95, 89.86, 89.63, 89.40, 87.08, 71.95, 71.88, 70.95, 70.88, 68.33, 31.69, 31.60, 29.71, 29.33, 25.87, 25.77, 22.63, 14.03.

MS (**MALDI**, THA): m/z (%) = 3328.60 $[M+H]^+$ (signal with highest intensity); a number of signals with lower intensity at higher m/z values could not be assigned.

5,5‘-Bis({3-hexoxymethyl-5-[(4-iodophenyl)ethynyl]phenyl}ethynyl)-2,2‘:6‘,2‘‘-terpyridine ***109a***

$C_{61}H_{53}I_2N_3O_2$, M = 1113.92



The procedure was analogous to that described for **43b** (**80a**: 100 mg, 0.14 mmol; p-diiodobenzene: 0.924 mg, 2.80 mmol; CuI: 3 mg, 0.016 mmol; $Pd[P(Ph_3)]_4$: 16 mg, 0.016 mmol; triethylamine: 10 ml; toluene: 10 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford **109a** (100 mg, 0.089 mmol, 64 %) as a colorless amorphous material, m.p. 150-153°C.

R_f = 0.20 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.81 (d, 2 H, ^{4}J = 1.8 Hz, tpy-6,6‘‘-H), 8.61 (d, 2 H, ^{3}J = 8.3 , tpy-3,3‘‘-H), 8.47 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3’,5’-H), 7.96 (t, 1 H, ^{3}J ≈ 8 Hz, 4’-H), 7.95

(dd, 2 H, ^3J = 8.2 Hz , ^4J = 2.2 Hz, 4,4''-H), 7.67 (d, 4 H, ^3J = 8.3 Hz, iodophenyl-3,5-H), 7.64 (t, 2 H, ^3J = 1.4 Hz, phenyl-H), 7.51 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.22 (d, 4 H, ^3J = 8.3 Hz, iodophenyl-2,6-H), 4.49 (s, 4 H, benzyl-H), 3.49 (t, 4 H, ^3J = 6.6 Hz, α-CH_2), 1.64 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.23-1.43 (m, 12 H, γ-,δ-,ε-CH_2), 0.88 (t, 6 H, ^3J = 6.7 Hz, hexyl-CH_3).

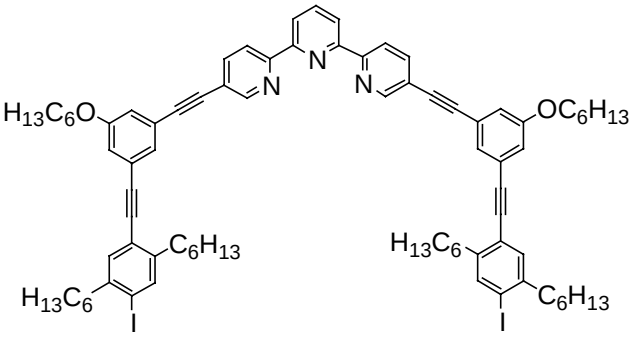
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.67, 154.46, 151.49, 139.60, 139.14, 137.79, 137.47, 133.52, 133.00, 130.60, 130.40, 123.34, 122.93, 122.33, 121.46, 120.26, 119.96, 94,41, 92.61, 89.76, 89.12, 86.98, 71.73, 70.82, 31.60, 29.61, 25.78, 22.57, 14.03.

MS (**FAB(+)**, CH_2Cl_2/DMSO/MNBA-Matrix): m/z (%) = 1118 (4.0), 1117 (9.10), 1116 (27.1), 1115 (67.5), 1114 (100.0) $[M+H]^+$, 1031 (4.7), 1030 (7.2), 1029 (11.3), 1028 (13.1) $[M-C_6H_{13}]^+$, 1016 (4.6), 1015 (6.4), 1014 (12.9), 1013 (16.3) $[M-C_6H_{12}O]^+$.

EA:	Calc.:	C:65.77	H:4.80	N:3.77
	Found:	C:65.84	H:4.71	N:3.60.

5,5'-Bis({3-hexoxymethyl-5-[(2,5-dihexyl-4-iodophenyl)ethynyl]phenyl}ethynyl)-2,2':6',2''-terpyridine ***109b***

$C_{85}H_{101}I_2N_3O_2$, M = 1450.56



The procedure was analogous to that described for **43b** (**80a**: 500 mg, 0.70 mmol; **108**:[70] 7.02 g, 14.1 mmol; CuI: 8 mg, 0.042 mmol; $Pd[P(Ph_3)]_4$: 50 mg, 0.042 mmol; triethylamine: 40 ml; toluene: 40 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by repeated column chromatography (silica gel, hexane / ethyl acetate and aluminium oxide, hexane/ethyl acetate) to afford **109b** (520 mg, 0.358 mmol, 51 %) as a colorless amorphous material. Most of **108** (6.28 g, 12.6 mmol, 89 %) was regained.

R_f = 0.35 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.83 (d, 2 H, ^4J = 1.7 Hz, tpy-6,6''-H), 8.63 (d, 2 H, ^3J = 8.3 , tpy-3,3''-H), 8.48 (d, 2 H, ^3J = 7.8 Hz, tpy-3',5'-H), 7.98 (t, 1 H, $^3J \approx 8$ Hz, 4'-H), 7.96 (dd, 2 H, ^3J = 8.3 Hz , ^4J = 2.0 Hz, 4,4''-H), 7.66 (s, 2 H, iodophenyl-3-H), 7.63 (t, 2 H, ^4J = 1.4 Hz, phenyl-H), 7.52 (t, 2 H, ^4J = 1.3 Hz, phenyl-H), 7.48 (t, 2 H, ^4J = 1.2 Hz, phenyl-H), 7.30 (s, 2 H, iodophenyl-6-H), 4.50 (s, 4 H, benzyl-H), 3.50 (t, 4 H, ^3J = 6.6 Hz, α-OCH_2),

2.74 (t, 4 H, ^3J = 8 Hz, α-CH_2), 2.64 (t, 4 H, ^3J = 8 Hz, α-CH_2), 1.52-1.67 (m, 8 H, β-CH_2), 1.23-1.41 (m, 40 H, γ-,δ-,ε-CH_2), 0.86-0.91 (m, 18 H, -CH_3).

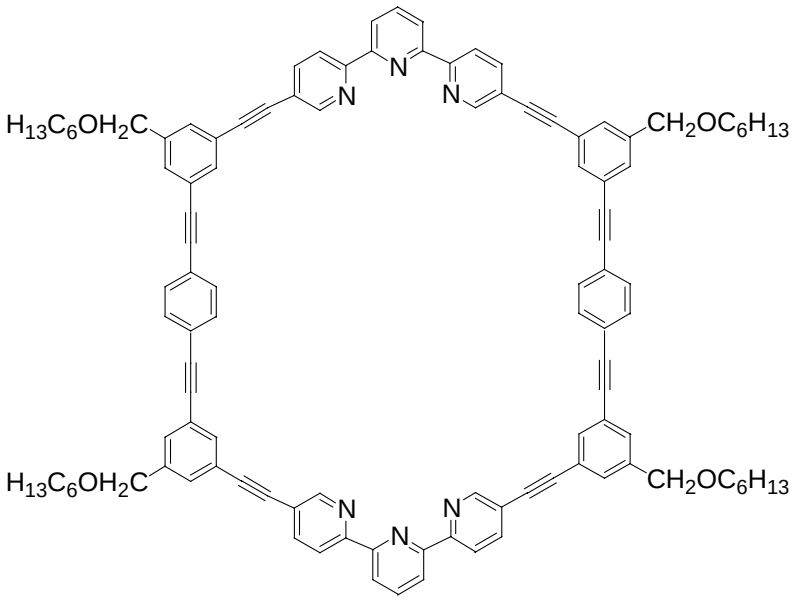
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.90, 154.72, 151.66, 144.12, 142.79, 139.70, 139.50, 139.26, 137.96, 133.45, 132.29, 130.61, 130.36, 123.91, 123.04, 122.36, 121.60, 120.38, 120.10, 101.23, 92.69, 92.42, 88.56, 86.97, 71.88, 70.91, 40.19, 33.79, 31.67, 30.60, 30.14, 29.68, 29.17, 29.01, 25.84, 22.62, 14.08.

MS (**EI**, 80 eV, 350°C): m/z (%) = 1451 (7.8), 1450 (9.0) $[M]^+$.

EA:	Calc.:	C:70.38	H:7.02	N:2.90
	Found:	C:70.43	H:6.81	N:2.76.

15,28,50,63-Tetrakis(hexyloxymethyl)-8,35,43,70,79,88-hexaaza-tridecacyclo[66.2.2.1^{2,6}.2^{7,10}.1^{13,17}.2^{20,23}.1^{26,30}.2^{33,36}.1^{37,41}.2^{42,45}.1^{48,52}.2^{55,58}.1^{61,65}]octaoctaconta-1(70),2,4,6(88),7,9,13,15,17(85),20,22,26,28,30(82),33,35,37,39,41(79),42,44,48,50,52(76),55,57,61,63,65(73),68,71,74,77,80,83,86-hexatriacontaen-11,18,24,31,46,53,59,66-octayne ***110a***

$C_{110}H_{98}N_6O_4$, M = 1568.02



The procedure was analogous to that described for **88** (**80a**: 727 mg, 1.02 mmol; **109a**: 1.14 g, 1.02 mmol; toluene/triethylamine: 350 ml/ 350 ml; $Pd[P(Ph_3)]_4$: 95 mg, 0.082 mmol; CuI: 16 mg, 0.082 mmol). Raw product: 1.15 g brownish solid after freeze-drying. During preparative GPC, a colorless material precipitated from the THF solution of the raw product, was collected, dissolved again and likewise separated by GPC. There, another precipitate formed and was treated the same way. As combined fractions from the three preparative GPC runs, cycle **110a** (181 mg, 0.115 mmol, 11 %) and oligomer **[110a]$_2$** (94 mg, 0.030 mmol, 6 %) were isolated as yellow, amorphous materials after freeze-drying. No interpretable solution NMR spectra of **110a** could be recorded. A solid state ^{13}C-NMR[187] did not show a resolution sufficient to prove **110a** to be cyclic rather than open-chain.

^{13}C-NMR (150.9 MHz, solid state):[187] δ = 152.4, 136.4, 130.4, 121.8 (arom. C), 89.8 (acetylenic C), 70.2 (aryl-$\underline{C}H_2$-O), 29.1, 25.1, 21.8 (-$\underline{C}H_2$-), 13.2 (-$\underline{C}H_3$).

MS (**FAB(+)**, MNBA/DMSO/CH_2Cl_2-Matrix): m/z (%) = 1566 (37.3), 1567 (52.9), 1568 (86.3), 1569 (80.4), 1570 (51.0), 1571 (33.3) $[M/M+H]^+$, 1636 (21.6), 1637 (62.8), 1638 (70.6), 1639 (100.0), 1640 (66.7), 1641 (62.8), 1642 (37.3), 1643 (21.6) $[M+C_5H_{11}]^+$

MS (**MALDI**, THA): m/z (%) = 1637.57 $[M+C_5H_{11}]^+$, 1581.60 $[M+CH_3]^+$, 1567.62 $[M+H]^+$, 1495.50 $[M-C_5H_{11}]^+$, 1481.53 $[M-C_6H_{13}]^+$.

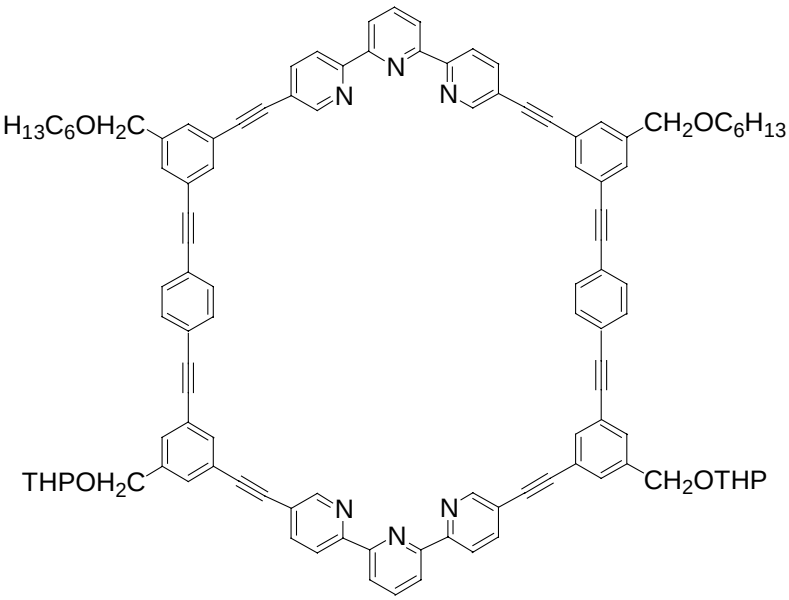
Cyclic oligomer ***[110a]$_2$***

$C_{220}H_{196}N_{12}O_8$, M = 3136.04

From analytical GPC, this material can be supposed to be a cyclic tetramer like those described for the other macrocycles here. However, neither NMR or MALDI showed any interpretatable results.

15,63-Bis(hexyloxymethyl)-28,50-bis(tetrahydro-pyran-2-yloxymethyl)-8,35,43,70,79,88-hexaazatridecacyclo[66.2.2.1^{2,6}.2^{7,10}.1^{13,17}.2^{20,23}.1^{26,30}.2^{33,36}.1^{37,41}.2^{42,45}.1^{48,52}.2^{55,58}.1^{61,65}] octaoctaconta-1(70),2,4,6(88),7,9,13,15,17(85),20,22,26,28,30(82),33,35,37,39,41(79),42,44,48,50,52(76),55,57,61,63,65(73),68,71,74,77,80,83,86-hexatriacontaen-11,18,24,31,46,53,59,66-octayne ***110b***

$C_{108}H_{90}N_6O_6$, M = 1567.93



The procedure was analogous to that described for **88** (**80c**: 108 mg, 0.153 mmol; **109a**: 170 mg, 0.153 mmol; toluene/triethyl-amine: 60 ml/ 60 ml; $Pd[P(Ph_3)]_4$: 14 mg, 0.012 mmol; CuI: 2.3 mg, 0.012 mmol). Raw product: 150 mg brownish solid after freeze-drying. By preparative GPC, cycle **110b** (46 mg, 0.030 mmol, 19 %) and oligomer **[110b]$_2$** (32 mg,

0.010 mmol, 13 %) were isolated as yellow, amorphous materials after freeze-drying. No interpretable solution NMR spectra of **110b** could be recorded.

MS (**MALDI**, THA): m/z (%) = 1637.57 $[M+C_5H_{11}]^+$, 1581.60 $[M+CH_3]^+$, 1567.88 $[M+H]^+$, 1494.50 $[M-C_5H_{11}]^+$, 1481.76 $[M-C_6H_{13}]^+$.

Cyclic oligomer ***[110b]$_2$***

$C_{216}H_{180}N_{12}O_{12}$, M = 3135.86

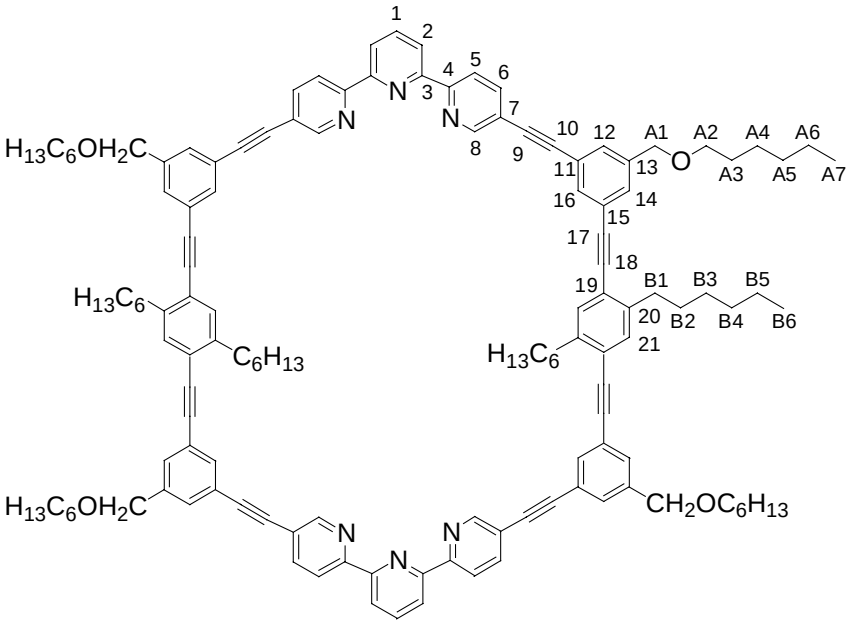
No interpretable solution NMR spectra of **110b** could be recorded.

MS (**MALDI**, THA): m/z (%) = 3196.78 $[M+Cu]^+$, 3156.82 $[M+Na]^+$.

21,56,83,74-Tetrahexyl-15,28,50,63-tetrakis(hexyloxymethyl)-8,35,43,70,79,88-hexaaza-tridecacyclo[66.2.2.1^{2,6}.2^{7,10}.1^{13,17}.2^{20,23}.1^{26,30}.2^{33,36}.1^{37,41}.2^{42,45}.1^{48,52}.2^{55,58}.1^{61,65}]octaoctaconta-1(70),2,4,6(88),7,9,13,15,17(85),20,22,26,28,30(82),33,35,37,39,41(79),42,44,48,50,52(76),55,57,61,63,65(73),68,71,74,77,80,83,86-hexatriacontaen-11,18,24,31,46,53,59,66-octayne

110c

$C_{134}H_{146}N_6O_4$, M = 1904.66



The procedure was analogous to that described for **88** (**80a**: 147 mg, 0.207 mmol; **109b**: 300 mg, 0.207 mmol; toluene/triethylamine: 80 ml/80 ml; $Pd[P(Ph_3)]_4$: 19 mg, 0.017 mmol; CuI: 3 mg, 0.02 mmol). Raw product: 420 mg brownish solid after freeze-drying. By preparative GPC, cycle **110c** (45 mg, 0.024 mmol, 11 %) and oligomer **[110c]$_2$** (24 mg, 0.006 mmol, 6 %) were isolated as yellow, amorphous materials. A relatively clean ^{1}H-NMR spectrum of **110c** was measured directly after the separation (see Fig. 25, p.72). The NMR analytical data stated below refer to solutions in $CDCl_3$/d-TFA (ref. p.73)

^{1}H-NMR (500 MHz, $CDCl_3$/d-TFA ca. 3:1, 300 K): δ = 9.28 (s, 4 H, ^{4}J = 1.5 Hz, 8-H), 8.77 (d, 4 H, ^{3}J = 8.0 Hz, ^{4}J = 1.5 Hz, 6-H), 8.70 (d, 4 H, ^{3}J = 8.5 Hz, 5-H), 8.54 (d, 4 H, ^{3}J = 7.5 Hz, 2-H), 8.47 (t, 2 H, ^{3}J = 7.0 Hz, 1-H), 7.81 (s br, 4 H, H-16), 7.62 (s br, 8 H, 12-H, 14-H), 7.44 (s br, 4 H, 21-H), 4.74 (s, 8 H, H-A1), 3.72 (t, 8 H, ^{3}J = 7.0 Hz, H-A2), 2.87 (s br, 8 H, B1-H), 1.75 (quintet, 8 H, ^{3}J = 7.0 Hz, B2-H), 1.72 (quintet, 8 H, ^{3}J = 7.5 Hz, A3-H), 1.31-1.46 (m, 48 H, A4-H, A5-H, A6-H, B3-H, B4-H, B5-H, 24 H), 0.87-0.92 (m, 30 H, A7-H, B6-H). The spectrum shows a number of impurities.

^{13}C-NMR (125.8 MHz, $CDCl_3$/d-TFA ca. 3:1, 300 K): δ = 149.41 (6-C), 146.64 (3-C), 144.79 (8-C), 144.65 (4-C), 142.90 (20-C), 142.38 (1-C), 137.58 (13-C), 134.89 (16-C), 135.58, 131.73 (12-C, 14-C), 132.94 (21-C), 126.23 (2-C), 125.98 (7-C), 125.41 (11-C or 15-C), 124.71 (5-C), 122.64 (19-C), 121.45 (11-C or 15-C), 100.40, 90.60 (10-C, 17-C), 91.98 (18-C), 82-01 (9-C), 71.75 (A1-C), 71.60 (A2-C), 34.18 (B1-C), 31.89, 31.60 (A5-C, B4-C), 30.76 (B2-C), 29.27 (B3-C), 28.77 (A3-C), 25.44 (A4-C), 22.69, 22.54 (A6-C, B5-C), 13.86, 13.63 (A7-C, B6-C).

MS (**MALDI**, THA): m/z (%) = 2044.11 $[M+C_5H_{10}+C_5H_{11}]^+$, 1974.16 $[M+C_5H_{11}]^+$, 1904.22 $[M+H]^+$.

Cyclic oligomer ***[110c]$_2$***

$C_{268}H_{252}N_{12}O_8$, M = 3809.32

By HETCOR spectra and comparison with similar substances, the NMR signals of **[110c]$_2$** were assigned; however, both spectra show a significant number of impurities.

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K): δ = 8.83 (s br, 8 H, ^{4}J = 1.5 Hz, 8-H), 8.63 (dd, 8 H, ^{3}J = 8.5 Hz, ^{5}J = 2.5 Hz, 5-H), 8.48 (d, 8 H, ^{3}J = 8.0 Hz, 2-H), 7.96-7.98 (m, 12 H, 1-H, 6-H), 7.63 (s br, 8 H, H-16), 7.52, 7.49 (2 s br, 16 H, 12-H, 14-H), 7.40 (s br, 8 H, 21-H), 4.51 (s, 16 H, H-A1), 3.51 (t, 16 H, ^{3}J = 7.0 Hz, H-A2), 2.81 (t, 16 H, ^{3}J = 7.5 Hz, H-B1), 1.72 (quintet, 16 H, ^{3}J = 7.0 Hz, B2-H), 1.64 (quintet, 16 H, ^{3}J = 7.0 Hz, A3-H), 1.31-1.42 (m, 96 H, A4-H, A5-H, A6-H, B3-H, B4-H, B5-H, 24 H), 0.90 (t, 60 H, ^{3}J = 6.5 Hz, A7-H, B6-H).

^{13}C-NMR (125.8 MHz, $CDCl_3$, 300 K): δ = 154.97 (4-C), 154.65 (3-C), 151.60 (8-C), 142.39 (20-C), 139.74 (13-C), 139.45 (6-C), 138.07 (1-C), 133.52 (16-C), 132.48 (21-C), 130.68, 130.41 (12-C, 14-C), 124.04, 123.04 (11-C, 15-C), 122.49 (19-C), 121.69 (2-C), 121.53 (5-C), 120.24 (7-C), 93.03, 92.86 (10-C, 17-C), 89.20 (18-C), 86.90 (9-C), 71.92 (A1-C), 70.94 (A2-C), 34.10 (B1-C), 31.77, 31.68 (A5-C, B4-C), 30.62 (B2-C), 29.70 (A3-C), 29.23 (B3-C), 25.86 (A4-C), 22.63 (A6-C, B5-C), 14.14, 14.05 (A7-C, B6-C).