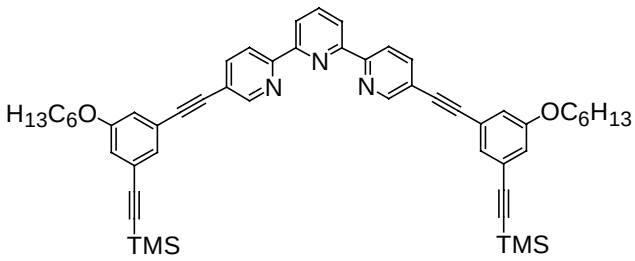
7.2.2 Compounds of Chapter 4.4

5,5‘‘-Bis({3-hexyloxy-5-[(trimethylsilyl)ethynyl]phenyl}ethynyl)-2,2‘:6‘,2‘‘-terpyridine ***79***

$C_{53}H_{59}N_3O_2Si_2$, M = 826.24



Method A:

The procedure was analogous to that described for **43b** (**63**: 513 mg, 1.83 mmol; **42b**: 1.29 g, 1.83 mmol; CuI: 21 mg, 0.11 mmol; $Pd[P(Ph_3)]_4$: 127 mg, 0.11 mmol; triethylamine/toluene: 40 ml/10 ml). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate) to afford **79** (490 mg, 0.59 mmol, 32 %) as a yellow resin.

Method B:

The procedure was analogous to Method A (**63**: 772 mg, 2.75 mmol; **46**: 2.20 g, 5.49 mmol; CuI: 3 mg, 0.2 mmol; $Pd[P(Ph_3)]_4$: 190 mg, 0.17 mmol; triethylamine/toluene: 40 ml/10 ml). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate) to afford **79** (1.90 g, 2.30 mmol, 84 %) as a yellow resin.

R_f = 0.87 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.79 (d, 2 H, ^4J = 1.8 Hz, tpy-6,6‘‘-H), 8.59 (d, 2 H, ^3J = 8.2 Hz, tpy-3,3‘‘-H), 8.46 (d, 2 H, ^3J = 7.8 Hz, tpy-3’,5’-H), 7.94 (t, 1 H, ^3J = 7.9 Hz, 4’-H), 7.93 (dd, 2 H, ^3J = 8.4 Hz , ^4J = 2.2 Hz, 4,4‘‘-H), 7.27 (s, 2 H, phenyl-H), 7.03 (dd, 2 H, ^4J = 1.3 Hz, ^4J = 2.3 Hz, phenyl-H), 6.98 (dd, 2 H, ^4J = 1.4 Hz, ^4J = 2.1 Hz, phenyl-H), 3.94 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 1.77 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.29-1.45 (m, 12 H, γ-,δ-,ε-CH_2), 0.90 (t, 6 H, ^3J = 6.7 Hz, hexyl-CH_3), 0.24 (s, 18 H, silyl-CH_3).

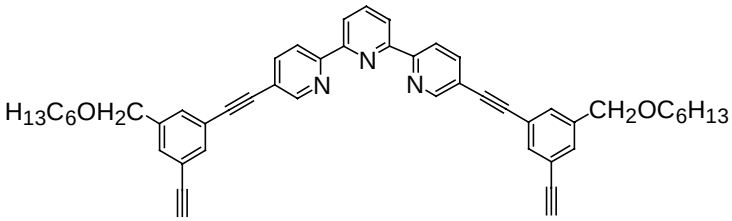
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.76, 154.81, 154.68, 151.60, 139.29, 137.97, 127.61, 124.43, 123.59, 121.55, 120.39, 120.13, 118.45, 118.09, 103.98, 94.82, 92.76, 86.52, 68.28, 31.50, 29.07, 25.63, 22.58, 14.02, -0.12.

MS (**EI**, 80 eV, 110°C): m/z (%) = 827 (2.2), 826 (5.2), 825 (6.7) $[M]^+$, 741 (1.7) $[M-C_6H_{12}]^+$.

EA:	Calc.:	C:77.05	H:7.20	N:5.09
	Found:	C:77.16	H:7.13	N:5.00.

5,5‘-Bis{[3-ethynyl-5-(hexoxymethyl)phenyl]ethynyl}-2,2‘:6‘,2‘‘-terpyridine ***80a***

$C_{99}H_{47}N_3O_2$, M = 709.93



85a (13.15 g, 12.86 mmol) was dissolved in THF (150 ml) and tetra-*n*-butylammonium fluoride trihydrate (12.2 g, 38.5 mmol) was added. After stirring overnight, the solvent was evaporated and the crude mixture purified by chromatography over aluminium oxide (hexane/ethyl acetate) to afford **80a** (6.87 g, 9.68 mmol, 75 %) as a slightly yellow solid, mp 97-98°C.

R_f = 0.50 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.80 (d, 2 H, ^{4}J = 1.7 Hz, tpy-6,6‘‘-H), 8.59 (d, 2 H, ^{3}J = 8.3 , tpy-3,3‘‘-H), 8.46 (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, ^{3}J = 8.4 Hz, ^{4}J = 1.8 Hz, 4,4‘‘-H), 7.60 (s, 2 H, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 4.47 (s, 4 H, benzyl-H), 3.48 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 3.09 (s, 2 H, ethynyl-H), 1.62 (quintet, 4 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.26-1.42 (m, 12 H, γ-,δ-,ε-CH_2), 0.88 (t, 6 H, ^{3}J = 6.7 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.81, 154.58, 151.58, 139.62, 139.17, 137.83, 134.09, 131.19, 130.77, 122.94, 122.60, 121.49, 120.27, 119.96, 92.46, 87.00, 82.59, 77.94, 71.69, 70.84, 31.61, 29.62, 25.79, 22.57, 14.00.

MS (**EI**, 80 eV, 180°C): m/z (%) = 711 (28.7), 710 (65.05), 709 (100.0) $[M]^+$, 624 (23.4) $[M\text{-}C_6H_{13}]^+$, 611 (20.2), 610 (42.3), 609 (64.9) $[M\text{-}OC_6H_{12}]^+$, 524 (24.5), 523 (19.8) $[M\text{-}C_6H_{13}\text{-}OC_6H_{12/13}]^+$, 510 (23.6), 509 (45.8), 508 (32.4), 507 (19.8), 506 (20.9), 505 (17.8) $[M–2OC_6H_{12/13}]^+$.

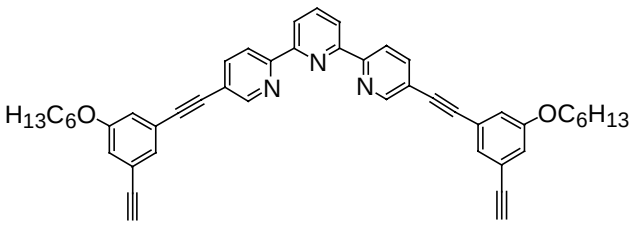
EA:	Calc.:	C:82.90	H:6.67	N:5.92
	Found:	C:82.87	H:6.39	N:5.74.

5,5‘‘-Bis[(3-ethynyl-5-hexoxyphenyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine ***80b***

$C_{47}H_{43}N_3O_2$, M = 681.88

Method A:

79 (460 mg, 0.56 mmol) was dissolved in a mixture of THF (30 ml) and MeOH (60 ml), and a few drops of 2 N NaOH were added. After stirring overnight, the solvent was evaporated and the crude mixture purified by chromatography over silica gel (hexane/ethyl acetate) to afford **80b** (380 mg, 0.56 mmol, quant.) as a slightly yellow sirup.



Method B:

The procedure was analogous to that described for **80a** (**85b**: 270 mg, 0.27 mmol; tetra-*n*-butylammonium fluoride trihydrate: 260 mg, 0.82 mmol; THF :10 ml. The crude mixture was purified by chromatography over silica gel (hexane/ethyl acetate) to afford **80b** (150 mg, 0.22 mmol, 81 %) as a slightly yellow sirup.

R_f = 0.50 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.79 (dd, 2 H, ^{4}J = 1.9 Hz, ^{4}J = 0.7 Hz, tpy-6,6''-H), 8.58 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.45 (d, 2 H, ^{3}J = 7.9 Hz, tpy-3',5'-H), 7.93 (t, 1 H, ^{3}J ≈ 8 Hz, tpy-4'-H), 7.91 (dd, 2 H, ^{3}J = 8.1 Hz, ^{4}J = 2.0 Hz, tpy-4,4''-H), 7.27 (t, 2 H, ^{4}J = 1.1 Hz, phenyl-H), 7.06 (dd, 2 H, ^{4}J = 1.4 Hz, ^{4}J = 2.2 Hz, phenyl-H), 7.00 (dd, 2 H, ^{4}J = 1.3 Hz, ^{4}J = 2.3 Hz, phenyl-H),3.94 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 3.01 (s, 2 H, ethynyl-H), 1.76 (quintet, 4 H, ^{3}J ≈ 8 Hz, β-CH_2), 1.23-1.46 (m, 12 H, γ-,δ-,ε-CH_2), 0.90 (t, 3 H, ^{3}J = 6.8 Hz, -CH_3).

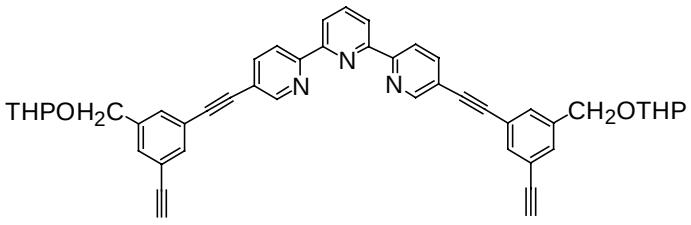
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.81, 154.86, 154.66, 151.62, 139.28, 137.94, 127.64, 123.77, 123.42, 121.55, 120.35, 120.03, 118.85, 118.24, 92.59, 86.70, 82.67, 77.62, 68.32, 31.51, 29.06, 25.63, 22.58, 14.01.

MS (**EI**, 80 eV, 300°C): m/z (%) = 684 (5.5), 683 (8.7), 682 (55.2), 681 (100.0) $[M]^+$, 598 (21.5), 597 (30.6) $[M-C_6H_{12}]^+$, 514 (21.8), 513 (50.3) $[M-2C_6H_{12}]^+$.

EA:	Calc.:	C:82.79	H:6.36	N:6.16
	Found:	C:82.97	H:6.33	N:5.88.

5,5'-Bis{[3-ethynyl-5-(tetrahydropyran-2-yloxymethyl)phenyl]ethynyl}-2,2':6',2''-terpyridine ***80c***

$C_{47}H_{39}N_3O_4$, M = 709.84



The procedure was analogous to that described for **80a** (**85c**: 2.26 g, 2.20 mmol; tetra-n-butylammonium fluoride trihydrate: 2.3 g, 7.1 mmol; THF: 60 ml). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate) to afford **80c** (1.22 g, 1.72 mmol, 78 %) as a yellow resin which could not be solidified by freeze-drying from benzene.

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

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.80 (dd, 2 H, ^{4}J = 1.7 Hz, ^{5}J = 0.6 Hz, tpy-6,6''-H), 8.61 (d, 2 H, ^{3}J = 8.2 , tpy-3,3''-H), 8.46 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.95 (t, 1 H, ^{3}J ≈ 8 Hz, 4'-H), 7.94 (dd, 2 H, ^{3}J = 8.2 Hz , ^{4}J = 2.0 Hz, 4,4''-H), 7.61 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.54 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 4.70-4.78 (m, 4 H, benzyl-H, THP-2-H), 4.47 (d, 2 H, ^{2}J = 12.3 Hz, benzyl-H'), 3.85-3.93 (m, 2 H, THP-6-H), 3.51-3.59 (m, 2 H, THP-6'-H), 3.10 (s, 2 H, ethynyl-H), 1.52-1.92 (m, 12 H, THP-3,3',4,4',5,5'-H).

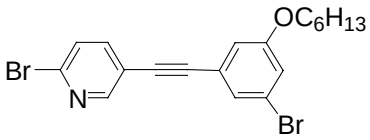
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.74, 154.51, 151.52, 139.16, 137.78, 134.08, 131.31, 130.88, 122.90, 122.56, 121.44, 120.22, 119.88, 97.84, 92.41, 87.00, 82.56, 77.99, 67.63, 62.01, 30.37, 25.31, 19.17.

MS (**FAB(+)**, DMSO/CH_2Cl_2-Matrix): m/z (%) = 713 (6.5), 712 (20.3), 711 (55.8), 710 (100.0) $[M+H]^+$, 628 (7.3), 627 (12.2), 626 (9.6), 625 (13.8) $[M-C_5H_8O]^+$, 612 (5.8), 611 (14.4), 610 (21.1), 609 (7.8) $[M-C_5H_7O_2]^+/[M-C_5H_8O_2]^+$.

EA:	Calc.:	C:79.53	H:5.54	N:5.92
	Found:	C:79.33	H:5.67	N:5.76.

*2-Bromo-5-[(3-bromo-5-hexoxyphenyl)ethynyl]pyridine **81***

$C_{19}H_{19}Br_2NO$, M = 437.17



The procedure was analogous to that described for **43b** (**34b**: 13.0 g, 33.9 mmol; **60**: 6.17 g, 33.9 mmol; CuI: 194 mg, 1.02 mmol; $Pd[P(Ph_3)]_4$: 1.18 g, 1.02 mmol; triethylamine/toluene: 200 ml/50 ml). The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford **81** (12.16 g, 27.8 mmol, 82 %) as a yellow sirup which, in the course of weeks, slowly started to crystallize.

R_f = 0.50 (hexane/ethyl acetate 20:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.45 (d, 1 H, ^{4}J = 2.3 Hz, py-6-H), 7.57 (dd, 1 H, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, py-4-H), 7.43 (d, 1 H, ^{3}J = 8.3 Hz, py-3-H), 7.20 (t, 1 H, ^{4}J = 1.3, phenyl-H), 7.02 (t, 1 H, ^{4}J = 1.9, phenyl-H), 6.92-6.93 (dd, 1 H, ^{4}J = 1.3, ^{4}J = 2.2, phenyl-H), 3.89 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.68-1.76 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.26-1.43 (m, 6 H, γ-, δ-, ε-CH_2), 0.87 (t, 3 H, ^{3}J = 6.5, -CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 159.52, 152.29, 141.32, 140.44, 127.61, 126.44, 124.33, 122.55, 119.08, 116.14, 92.33, 85.44, 68.41, 31.41, 28.92, 25.53, 22.51, 13.97.

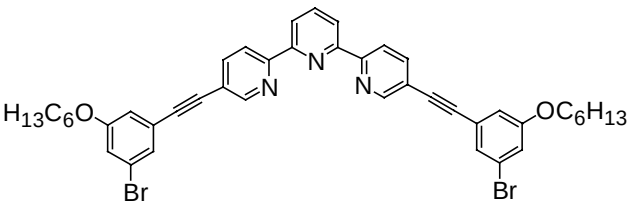
MS (**EI**, 80 eV, 185°C): m/z (%) = 440 (2.20), 439 (25.4), 438 (11.6), 437 (50.8), 436 (7.0), 435 (25.2) $[M]^+$, 356 (8.6), 355 (49.6), 354 (20.0), 353 (100.0), 352 (10.1), 351 (50.6), 350

(1.5) $[M\text{-}C_6H_{12}]^+$, 327 (1.9), 326 (6.1), 325 (3.6), 324 (11.3), 323 (2.0), 322 (5.8) $[M\text{-}C_5H_{11}\text{–}CH_2O]^+$, 275 (2.1), 274 (8.3), 273 (5.2), 272 (8.1), 271 (3.4) $[M\text{-}Br\text{-}C_6H_{12}]^+$, 257 (3.3), 256 (1.3), 255 (2.9) $[M\text{-}C_5H_{11}\text{–}CH_2O\text{-}Br]^+$, 246 (4.2), 245 (2.7), 244 (5.2), 243 (2.1) $[M\text{-}Br\text{-}COC_6H_{12}]^+$, 194 (4.9), 193 (26.9) $[M\text{-}2Br\text{-}C_6H_{12}]^+$, 167 (1.3), 166 (2.3), 165 (9.3), 164 (38.2), 163 (4.0) $[M\text{-}C_5H_{11}\text{–}CH_2O\text{-}2Br]^+$.

EA:	Calc.:	C: 52.20	H: 4.38	N: 3.20
	Found:	C: 52.29	H: 4.37	N: 3.10.

5,5‘‘-Bis[(3-bromo-5-hexoxyphenyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine ***82***

$C_{43}H_{41}Br_2N_3O_2$, M = 791.62



The procedure was analogous to that described for **62** (**81**: 2.06 g, 4.71 mmol; **52**[125]: 0.95 g, 2.35 mmol; $Pd[P(Ph_3)]_4$: 112 mg, 0.097 mmol; toluene : 50 ml). The crude product was purified by column chromatography (hexane/ethyl acetate) to afford **82** (1.07 g, 1.35 mmol, 58 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.55 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.75 (s, 2 H, tpy-6,6’’-H), 8.53 (d, 2 H, ^3J = 8.2 Hz, tpy-3,3’’-H), 8.41 (d, 2 H, ^3J = 7.8 Hz, tpy-3’,5’-H), 7.88 (t, 1 H, $^3J \approx 9$ Hz, tpy-4’-H), 7.86 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 2.0 Hz, tpy-4,4’’-H), 7.24 (s, 2 H, phenyl-H), 7.01 (s, 2 H, phenyl-H), 6.96 (s, 2 H, phenyl-H), 3.89 (t, 4 H, ^3J = 6.4 Hz, α-CH_2), 1.69 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.23-1.43 (m, 12 H, γ-,δ-,ε-CH_2), 0.89 (t, 6 H, ^3J = 6.3 Hz, -CH_3).

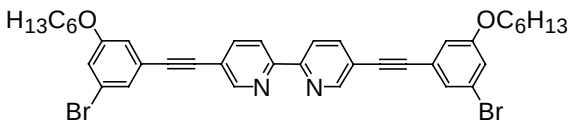
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 159.52, 154.82, 154.48, 151.57, 139.19, 137.84, 126.53, 124.79, 122.54, 121.50, 120.26, 119.77, 118.86, 116.16, 92.01, 87.19, 68.40, 31.48, 28.99, 25.59, 22.56, 14.02.

MS (**EI**, 80 eV, 260°C): m/z (%) = 794 (0.8), 793 (1.5), 792 (1.0), 790 (0.6), 789 (1.2) $[M]^+$, 707 (0.7) $[M\text{-}C_6H_{12}]^+$, 623 (0.7) $[M\text{-}2C_6H_{12}]^+$.

EA:	Calc.:	C:65.24	H:5.22	N:5.31
	Found:	C:65.42	H:5.39	N:5.04.

5,5''-Bis[(3-bromo-5-hexoxyphenyl)ethynyl]-2,2'-bipyridine ***82x***

$C_{38}H_{38}Br_2N_2O_2$, M = 714.54



This compound was isolated as a side product from the column chromatography of **82** (110 mg **82x**, 0.15 mmol, 6.5 %, pure enough for characterisation). Further purification by chromatography over aluminium oxide (hexane/ethyl acetate) afforded **82x** as an analytically pure, yellow colored, crystalline solid, m.p. = 124°C.

$\mathbf{R_f}$ = 0.39 (hexane/ethyl acetate 20:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.78 (d, 2 H, ^{4}J = 1.5 Hz, bpy-6,6'-H), 8.45 (d, 2 H, ^{3}J = 8.3 Hz, bpy-3,3'-H), 7.92 (dd, 2 H, ^{3}J = 8.3 Hz, ^{4}J = 2.2 Hz, bpy-4,4'-H), 7.27 (t, 2 H, ^{4}J = 1.4 Hz, phenyl-H), 7.06 (t, 2 H, ^{4}J = 2.0 Hz, phenyl-H), 7.00 (dd, 2 H, ^{4}J = 2.3 Hz, ^{4}J = 1.4 Hz, phenyl-H), 3.94 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 1.77 (quintet, 4 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.29-1.46 (m, 12 H, γ-,δ-,ε-CH_2), 0.90 (t, 6 H, ^{3}J = 6.9 Hz, -CH_3).

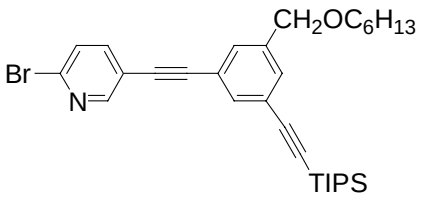
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 159.55, 154.17, 151.67, 139.36, 126.54, 124.73, 122.54, 120.58, 119.99, 118.97, 116.17, 92.24, 87.07, 68.43, 31.45, 28.97, 25.57, 22.54, 13.99.

MS (**EI**, 80 eV, 240°C): m/z (%) = 718 (5.0), 717 (20.4), 716 (56.6), 715 (40.6), 714 (100.0), 713 (20.2), 712 (48.1) $[M]^+$, 632 (1.4), 631 (4.0), 630 (1.7), 629 (6.8), 628 (3.1), 627 (3.6) $[M-C_6H_{13}]^+$.

EA:	Calc.:	C:63.87	H:5.36	N:3.92
	Found:	C:63.58	H:5.36	N:3.86.

2-Bromo-5-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)pyridine ***84a***

$C_{31}H_{42}BrNOSi$, M = 552.66



The procedure was analogous to that described for **43b** (**59**:[31] 15.64 g, 55.09 mmol; **45a**:[32] 22.21 g, 56.00 mmol; CuI: 314 mg, 1.65 mmol; $Pd[P(Ph_3)]_4$: 1.91 g, 1.65 mmol; triethylamine: 160 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **84a** (25.88 g, 46.83 mmol, 85 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.70 (hexane/ethyl acetate 10:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.48 (d, 1 H, ^{4}J = 2.3 Hz, py-6-H), 7.62 (dd, 1 H, ^{3}J = 8.3 Hz, ^{4}J = 2.4 Hz, py-4-H), 7.54 (t, 1 H, ^{4}J = 1.4 Hz, phenyl-H), 7.46 (d, 1 H, ^{3}J = 8.5 Hz,

py-3-H), 7.44 (s, 1 H, phenyl-H), 7.42 (s, 1 H, phenyl-H), 4.45 (s, 2 H, benzyl-H), 3.46 (t, 2 H, ^{3}J = 6.6 Hz, α-CH_2), 1.61 (quintet, 2 H, ^{3}H ≈ 7 Hz, β-CH_2), 1.27-1.30 (m, 6 H, γ-, δ-, ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.87 (t, 3 H, ^{3}J = 6.8, -CH_3).

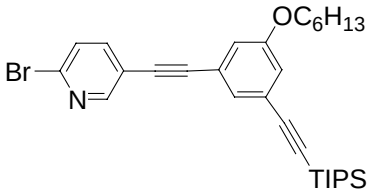
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 152.29, 141.16, 140.43, 139.51, 134.00, 131.36, 130.26, 127.60, 124.04, 122.34, 119.42, 105.72, 93.05, 91.69, 85.10, 71.73, 70.81, 31.59, 29.59, 25.78, 22.55, 18.59, 13.98, 11.21.

MS (**EI**, 80 eV, 150°C): m/z (%) = 554 (3.4), 553 (9.7), 552 (19.8), 551 (9.7) $[M]^+$, 550 (18.3) $[M-H]^+$, 512 (3.7), 511 (11.5), 510 (37.0), 509 (100.0), 508 (38.14) $[M^+-C_3H_7]$, 507 (93.9) $[M-H-C_3H_7]^+$.

EA:	Calc.:	C:67.37	H:7.66	N:2.53
	Found:	C:67.42	H:7.86	N:2.46.

2-Bromo-5-({3-hexoxy-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)pyridine ***84b***

$C_{30}H_{40}BrNOSi$, M = 538.64



The procedure was analogous to that described for **43b** (**59**[31]: 556 mg, 1.96 mmol; **45b**: 750 mg, 1.96 mmol; CuI: 37 mg, 0.20 mmol; $Pd[P(Ph_3)]_4$: 226 mg, 0.20 mmol; triethylamine/toluene: 30 ml/20 ml). The crude product was purified by chromatography over aluminium oxide (hexane/ethyl acetate) to afford **84b** (690 mg, 1.28 mmol, 65 %) as a slightly yellow oil.

R_f = 0.13 (hexane, aluminium oxide).

^{1}H-NMR (270 MHz, DMSO): δ = 8.48 (d, 1 H, ^{4}J = 2.3 Hz, tpy-6-H), 7.61 (dd, 2 H, ^{3}J = 8.2 Hz, ^{4}J = 2.3 Hz, tpy-4-H), 7.45 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3-H), 7.22 (t, 1 H, ^{4}J = 1.1 Hz, phenyl-2-H), 6.98 (d, 2 H, ^{3}J = 0.8 Hz, phenyl-4,6-H), 3.94 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2), 1.76 (quintett,2 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.28-1.46 (m, 6 H, γ-, δ-, ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.87 (t, 3 H, ^{3}J = 6.9 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, DMSO): δ = 158.79, 152.38, 141.20, 140.51, 127.61, 124.91, 123.13, 119,47, 119.06, 117.53, 105.81, 93.17, 91.43, 84.82, 68.28, 31.50, 29.09, 25.64, 22.57, 18.63, 14.00, 11.68, 11.25.

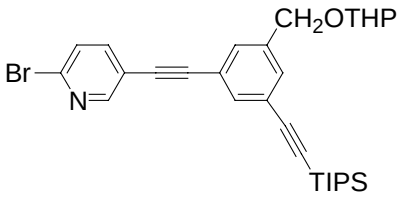
MS (**EI**, 80 eV, 150°C): m/z (%) = 540 (4.5), 539 (11.8), 538 (4.0), 537 (10.8) $[M]^+$, 499 (1.4), 498 (8.2), 497 (30.1), 496 (100.0), 495 (33.4), 494 (86.1) $[M-C_3H_7]^+$, 470 (1.5), 469

(5.8), 468 (19.3), 467 (7.3), 466 (18.5) $[M-C_5H_{11}]^+$, 456 (2.4), 455 (7.5), 454 (25.1), 453 (9.8), 452 (24.7), $[M-C_6H_{13}]^+$.

EA: Calc.: C:66.90 H:7.48 N:2.60
Found: C:66.88 H:7.25 N:2.45.

2-Bromo-5-({3-[(triisopropylsilyl)ethynyl]-5-(tetrahydropyran-2-yloxymethyl)phenyl}ethynyl) -pyridine ***84c***

$C_{30}H_{38}BrNO_2Si$, M = 552.66



The procedure was analogous to that described for **43b** (**59**:[31] 5.00 g, 17.6 mmol; **45c**: 7.00 g, 17.6 mmol; CuI: 101 mg, 0.530 mmol; $Pd[P(Ph_3)]_4$: 611 mg, 0.530 mmol; triethylamine: 150 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **84c** (12.14 g, 21.97 mmol, 87 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.16 (hexane/ethyl acetate 30:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.48 (d, 1 H, ^{4}J = 2.2 Hz, py-6-H), 7.62 (dd, 1 H, ^{3}J = 8.2 Hz, ^{4}J = 2.3 Hz, py-4-H), 7.55 (t, 1 H, ^{4}J = 1.2, phenyl-H), 7.48 (s, 1 H, phenyl-H), 7.45 (d, 1 H, ^{3}J = 8.6 Hz, py-3-H), 7.44 (s, 1 H, phenyl-H), 4.68-4.75 (m, 2 H, benzyl-H, THP-2-H), 4.45 (d, 1 H, ^{2}J = 12.4 Hz, benzyl-H'), 3.84-3.92 (m, 1 H, THP-6-H), 3.50-3.58 (m, 1 H, THP-6'-H), 1.51-1.84 (m, 6 H, THP-3,3',4,4',5,5'-H), 1.11 (s, 21 H, TIPS-H).

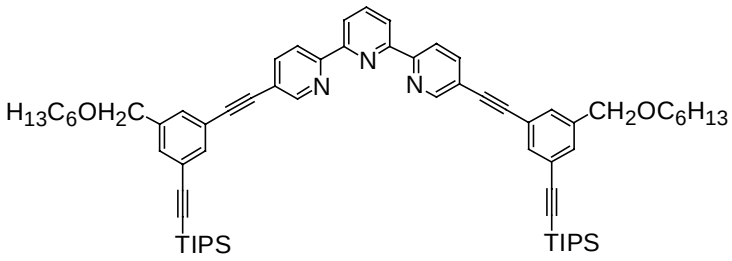
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 152.30, 141.17, 140.44, 139.07, 134.06, 131.58, 130.50, 127.60, 124.04, 122.37, 119.40, 105.70, 97.85, 93.03, 91.75, 85.13, 67.71, 62.09, 30.40, 25.34, 19.22, 18.58, 11.20.

MS (**EI**, 80 eV, 80 - 100°C): m/z (%) = 554 (1.3), 553 (3.4), 552 (3.4), 551 (3.2), 550 (3.3) $[M]^+/[M-H]^+$, 513 (2.0), 512 (8.2), 511 (28.6), 510 (82.3), 509 (100.0), 508 (76.5), 507 (94.8) $[M-C_3H_7]^+/[M-H-C_3H_7]^+$, 454 (30.5), 453 (83.2), 452 (79.9), 451 (72.9), 450 (89.9) $[M-C_5H_8O_2]^+/[M-H-C_5H_8O_2]^+$, 426 (18.1), 425 (21.3), 424 (17.1), 423 (21.4) $[M-C_7H_{11}O_2]^+/[M-H-C_7H_{11}O_2]^+$, 410 (15.8), 408 (16.9), 407 (16.3) $[M-C_5H_8O_2-C_3H_7]^+/[M-H-C_5H_8O_2-C_3H_7]^+$, 382 (15.9), 380 (16.2) $[M-C_7H_{11}O_2-C_3H_7]^+/[M-H-C_7H_{11}O_2-C_3H_7]^+$, 368 (17.4), 367 (19.0), 366 (17.7), 365 (23.3) $[M-C_5H_8O_2-C_3H_7-C_3H_6]^+/[M-C_5H_8O_2-2C_3H_7]^+$.

EA: Calc.: C:65.20 H:6.93 N:2.53
Found: C:65.40 H:7.03 N:2.40.

5,5‘-Bis({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-2,2‘:6‘,2‘‘-terpyridine ***85a***

$C_{67}H_{87}N_3O_2Si_2$, M = 1022.61



The procedure was analogous to that described for **62** (**52**:[125] 9.48 g, 23.5 mmol; **84a**: 25.88 g, 46.83 mmol; $Pd[P(Ph_3)]_4$: 1.62 g, 1.40 mmol; toluene: 500 ml; reaction time: 36 hrs). The crude product was purified by repeated column chromatography (hexane/dichloromethane on aluminium oxide, hexane/ethyl acetate on silica gel) to afford **85a** (13.15 g, 12.86 mmol, 55 %) as a yellow resin which could not be solidified even after freeze-drying from benzene.

$\mathbf{R_f}$ = 0.78 (hexane/ethyl acetate 10:1, aluminium oxide).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.81 (d, 2 H, ^{4}J = 1.7 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, ^{3}J = 8.3 Hz , ^{4}J = 2.0 Hz, 4,4‘‘-H), 7.60 (t, 2 H, ^{4}J = 1.4 Hz, phenyl-H), 7.49 (s, 2 H, phenyl-H), 7.43 (s, 2 H, phenyl-H), 4.47 (s, 4 H, benzyl-H), 3.48 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 1.62 (quintet, 4 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.26-1.42 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.88 (t, 6 H, ^{3}J = 6.7 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.90, 154.76, 151.66, 139.48, 139.28, 137.97, 134.11, 131.27, 130.44, 124.07, 122.84, 121.56, 120.39, 120.14, 105.91, 92.72, 91.62, 86.87, 71.88, 70.86, 31.66, 29.66, 25.84, 22.61, 18.65, 14.03, 11.28.

MS (**EI**, 80 eV, 250 - 300°C): m/z (%) = 1024 (3.2), 1023 (7.9), 1022 (14.1), 1021 (16.3) $[M]^+$, 982 (4.6), 981 (14.0), 980 (36.3), 979 (74.7), 978 (100.0) $[M\text{-}C_3H_7]^+$, 951 (1.7), 950 (2.4) $[M\text{-}C_5H_{11}]^+$, 939 (2.6), 938 (6.6), 937 (14.5), 936 (23.5), 935 (23.0) $[M\text{-}C_6H_{13}]^+$/$[M\text{-}C_5H_{11}\text{-}CH_3]^+$.

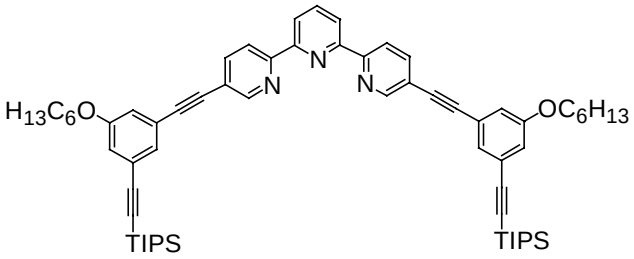
EA:	Calc.:	C:78.69	H:8.57	N:4.11
	Found:	C:78.82	H:8.77	N:3.88.

5,5‘-Bis({3-hexoxy-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-2,2‘:6‘,2‘‘-terpyridine ***85a***

$C_{65}H_{83}N_3O_2Si_2$, M = 994.56

The procedure was analogous to that described for **62** (**52**[125]: 225 mg, 0.56 mmol; **84b**: 600 mg, 1.1 mmol; $Pd[P(Ph_3)]_4$: 39 mg, 0.033 mmol; toluene: 25 ml; reaction time: 5 days).

The crude product was purified by column chromatography (hexane/ethyl acetate, silica gel) to afford **85b** (280 mg, 0.28 mmol, 50 %) as a yellow foam.



R_f = 0.20 (hexane/ethyl acetate 30:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.81 (d, 2 H, ^4J = 1.6 Hz, tpy-6,6''-H), 8.60 (dd, 2 H, ^3J = 8.3 , ^5J = 0.6 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^3J = 7.8 Hz, tpy-3',5'-H), 7.96 (t, 1 H, $^3J \approx 8$ Hz, 4'-H), 7.94 (dd, 2 H, ^3J = 8.2 Hz , ^4J = 2.0 Hz, 4,4''-H), 7.27 (t, 2 H, ^4J = 1.3 Hz, phenyl-H), 7.03 (dd, 2 H, ^4J = 0.9 Hz, ^4J = 1.3 Hz, phenyl-H), 7.00 (dd, 2 H, ^4J = 1.1 Hz, phenyl-H), 3.96 (t, 4 H, ^3J = 6.4 Hz, α-CH_2), 1.77 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.33-1.35 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.90 (t, 6 H, ^3J = 6.8 Hz, hexyl-CH_3).

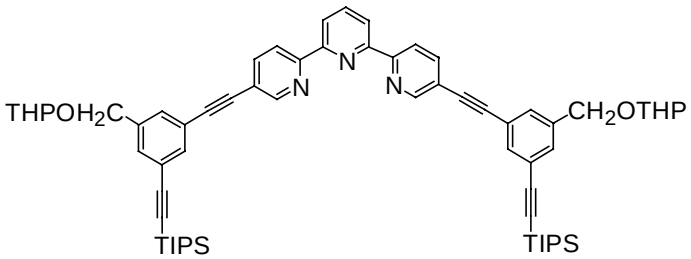
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.79, 154.84, 154.72, 151.63, 139.32, 137.98, 127.66, 124,86, 123.57, 121.57, 120.40, 120.14, 118.92, 117.58, 105.96, 92.83, 91.29, 86.52, 68.28, 31.52, 29.12, 25.66, 22.58, 18.65, 14.01, 11.28.

MS (**FAB(+)**, DMSO/CH_2Cl_2-Matrix): m/z (%) = 997 (26.0), 996 (50.6), 995 (82.0), 994 (100.0) $[M+H]^+$.

EA:	Calc.:	C:78.50	H:8.41	N:4.22
	Found:	C:78.22	H:8.24	N:4.08.

5,5'-Bis({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-2,2':6',2''-terpyridine ***85c***

$C_{65}H_{79}N_3O_4Si_2$, M = 1022.53



The procedure was analogous to that described for **62** (**52**:[125] 2.12 g, 5.23 mmol; **84c**: 5.78 g, 10.5 mmol; $Pd[P(Ph_3)]_4$: 363 mg, 0.314 mmol; toluene: 120 ml; reaction time: 48 hrs). The crude product was purified by repeated column chromatography (ethyl acetate + triethylamine, silica gel) to afford **85c** (2.41 g, 2.36 mmol, 45 %) as a colorless foam.

R_f = 0.60 (hexane/ethyl acetate 4:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.81 (dd, 2 H, ^{4}J = 1.6 Hz, ^{5}J = 0.6 Hz, tpy-6,6''-H), 8.61 (d, 2 H, ^{3}J = 8.2 , 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, ^{3}J = 8.2 Hz , ^{4}J = 2.1 Hz, 4,4''-H), 7.60 (t, 2 H, ^{4}J = 1.2 Hz, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 4.70-4.78 (m, 4 H, benzyl-H, THP-2-H), 4.47 (d, 2 H, ^{2}J = 12.3 Hz, benzyl-H'), 3.86-3.95 (m, 2 H, THP-6-H), 3.52-3.60 (m, 2 H, THP-6'-H), 1.52-1.89 (m, 12 H, THP-3,3',4,4',5,5'-H), 1.12 (s, 42 H, silyl-H).

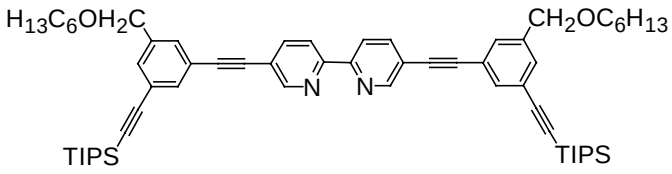
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.85, 154.69, 151.62, 139.21, 139.01, 137.89, 134.13, 131.43, 130.63, 124.02, 122.84, 121.52, 120.32, 120.06, 105.88, 97.85, 92.67, 91.63, 86.89, 67.80, 62.12, 30.44, 25.38, 19.26, 18.62, 11.25.

MS (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1025 (10.0), 1024 (21.6), 1023 (46.9), 1022 (83.9), 1021 (100.0), 1020 (12.4), 1019 (13.9) $[M]^+$, 979 (10.5), 978 (11.4), 977 (10.8) $[M\text{-}C_3H_7]^+$, 965 (11.0) $[M\text{-}C_3H_7 \text{–} CH_3]^+$, 938 (14.8), 937 (20.3), 936 (21.9), 935 (26.4), 934 (9.9), 933 (9.7) $[M\text{-}2C_3H_7]^+$, 923 (11.1), 922 (15.8), 921 (23.3), 920 (23.7), 919 (10.6) $[M\text{-}2C_3H_7\text{-}CH_3]^+$.

EA:	Calc.:	C:76.35	H:7.79	N:4.11
	Found:	C:76.36	H:7.69	N:4.02.

5,5'-Bis({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-2,2'bipyridine ***85x***

$C_{62}H_{84}N_2O_2Si_2$, M = 945.53



This compound was isolated as a side product from the column chromatography of **85a** (1.49 g, 1.58 mmol, 15 %) as a yellow crystaline material pure enough for characterisation.

R_f = 0.15 (hexane/ethyl acetate 30:1).

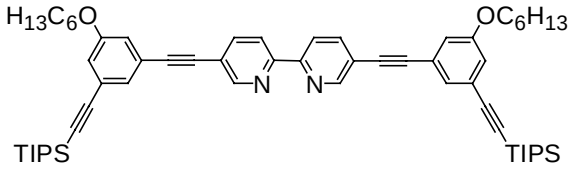
^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.79 (s br, 2 H, bpy-6,6'-H), 8.42 (d, 2 H, ^{3}J = 8.2 Hz, bpy-3,3'-H), 7.91 (dd, 2 H, ^{3}J = 8.3 Hz, ^{4}J = 1.8 Hz, bpy-4,4'-H), 7.59 (s, 2 H, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.43 (s, 2 H, phenyl-H), 4.46 (s, 4 H, benzyl-H), 3.47 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 1.62 (quintet, 4 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.26-1.42 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.88 (t, 6 H, ^{3}J = 6.6 Hz, -CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.15, 151.67, 139.48, 139.32, 134.10, 131.23, 130.39, 124.05, 122.77, 120.59, 120.26, 105.90, 92.95, 91.59, 86.79, 71.83, 70.83, 31.64, 29.65, 25.83, 22.60, 18.63, 14.02, 11.27.

MS (**EI**, 80 eV, 200°C): m/z (%) = 948 (2.6), 947 (9.1), 946 (22.6), 945 (44.2), 944 (56.9), 943 (2.5) $[M]^+$, 905 (4.0), 904 (13.1), 903 (36.3), 902 (77.1), 901 (100.0) $[M\text{-}C_3H_7]^+$, 875 (4.2), 874 (8.0), 873 (10.2) $[M\text{-}C_5H_{11}]^+$, 862 (2.2), 861 (5.3), 860 (9.1), 859 (12.4) $[M\text{-}C_6H_{13}]^+$, 846 (3.4), 845 (6.3), 844 (6.7), 843 (5.6) $[M\text{-}C_6H_{12}O]^+/[M\text{-}C_6H_{13}O]^+$, 832 (4.9), 831 (7.3) $[M\text{-}C_5H_{11}\text{-}C_3H_7]^+$.

5,5'-Bis({3-hexoxy-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-2,2'-bipyridine ***85y***

$C_{60}H_{80}N_2O_2Si_2$, M = 917.48



This compound was isolated as a side product from the column chromatography of **85b** (110 mg, 0.12 mmol, 22 %) as a yellow crystalline material pure enough for characterisation.

$\mathbf{R_f}$ = 0.51 (hexane/ethyl acetate 30:1).

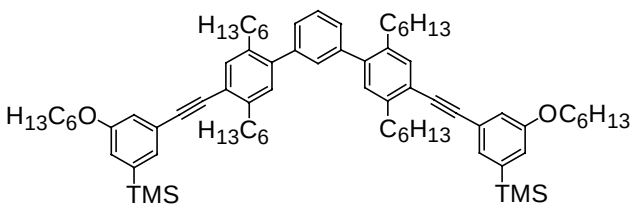
^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.78 (d, 2 H, ^4J = 1.7 Hz, bpy-6,6'-H), 8.41 (d, 2 H, ^3J = 8.3 Hz, bpy-3,3'-H), 7.90 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 2.0 Hz, bpy-4,4'-H), 7.26 (t, 2 H, ^4J = 1.0 Hz, phenyl-H), 7.02 (t, 2 H, ^4J = 1.1 Hz, phenyl-H), 7.00 (t, 2 H, ^4J = 1.0 Hz, phenyl-H), 3.95 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 1.76 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.29-1.47 (m, 12 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.90 (t, 6 H, ^3J = 6.8 Hz, -CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.78, 154.15, 151.70, 139.38, 133.85, 133.56, 128.67, 128.40, 127.67, 124.86, 123.53, 120.61, 118.94, 117.55, 105.95, 93.05, 91.29, 86.47, 68.27, 31.52, 29.12, 25.66, 22.59, 18.65, 14.02, 11.28, 10.86.

MS (**EI**, 80 eV, 300°C): m/z (%) = 919 (4.7), 918 (14.9), 917 (27.1), 916 (34.4) $[M]^+$, 878 (2.2), 877 (3.6), 876 (12.3), 875 (35.2), 874 (73.7), 873 (100) $[M\text{-}C_3H_7]^+$.

2,5,2'',5''-Tetrahexyl-4,4''-bis{[3-hexoxy-5-(trimethylsilyl)phenyl]ethynyl}-1,1':3',1''-terphenyl ***86***

$C_{76}H_{110}O_2Si_2$, M = 1111.87



The procedure was analogous to that described for **43b** (**74b**: 2.31 g, 2.82 mmol; **48**: 1.86 g, 6.77 mmol; CuI: 32 mg, 0.17 mmol; $Pd[P(Ph_3)]_4$: 196 mg, 0.17 mmol; triethylamine: 50 ml; toluene: 30 ml; reaction time: 48 hrs). The crude product was purified by chromatography

over silica gel (hexane) to afford **86** (840 mg, 0.76 mmol, 27 %) as a nearly colorless sirup. The side products **86x** (400 mg, 0.41 mmol, 15 %, nearly colorless sirup) and **86y** (320 mg, 0.59 mmol, 9 %, yellow fluorescent oil) were isolated as well.

$\mathbf{R_f}$ = 0.29 (hexane/ethyl acetate 50:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.44-7.49 (m, 3 H, aryl-H), 7.29-7.33 (m, 5 H, aryl-H), 7.13 (s, 2 H, aryl-H), 7.05 (m, 4 H, aryl-H), 4.01 (t, 4 H, ^{3}J = 6.5 Hz, O-CH_2-), 2.86 (t, 4 H, ^{3}J = 7.5 Hz, aryl-CH_2-), 2.62 (t, 4 H, ^{3}J = 7.5 Hz, aryl-CH_2-), 1.72-1.85 (m, 8 H, alkyl-H), 1.21-1.55 (m, 40 H, alkyl-H), 0.82-0.96 (m, 18 H, -CH_3), 0.30 (s, 18 H, silyl-H).

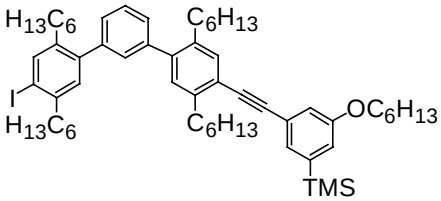
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.34, 142.31, 142.26, 141.80, 141.44, 137.71, 132.88, 130.47, 129.89, 128.65, 127.65, 124.24, 121.53, 120.23, 116.60, 92.91, 88.17, 67.94, 34.52, 32.59, 31.75, 31.59, 31.25, 30.92, 29.45, 29.29, 29.18, 25.75, 22.66, 22.62, 22.52, 14.05, -1.24.

MS (**EI**, 80 eV, 100°C): m/z (%) = 1116 (2.2), 1115 (8.3), 1114 (17.3), 1113 (58.5), 1112 (92.1), 1111 (100.0), 1110 (2.2) $[M]^+$, 1042 (0.9), 1041 (1.5) $[M-C_5H_{10}]^+$, 1028 (1.1), 1027 (1.2), 1026 (1.0) $[M-C_6H_{12}]^+$.

HRMS: calc.: 1110.80444
found: 1110.80850.

2,5,2‘‘,5‘‘-Tetrahexyl-4‘‘-{[3-hexoxy-5-(trimethylsilyl)phenyl]ethynyl}-4-iodo-1,1‘:3‘,1‘‘-terphenyl ***86x***

$C_{59}H_{85}ISiO$, M = 965.31



86x was isolated as a side product from the synthesis of **86**.

$\mathbf{R_f}$ = 0.48 (hexane/ethyl acetate 50:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.74 (s, 1 H), 7.42-7.47 (m, 2 H), 7.24-7.33 (m, 4 H), 7.05-7.11 (m, 4 H), 4.01 (t, 2 H, J = 6.5 Hz), 2.86 (t, 2 H, J = 7.5 Hz), 2.70 (t, 2 H, J = 7.6 Hz), 2.52-2.63 (m, 6 H), 1.20-1.85 (m, 40 H), 0.82-0.96 (m, 15 H), 0.31 (s, 9 H).

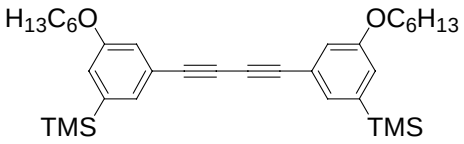
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.34, 142.59, 142.29, 141.82, 141.68, 141.52, 140.89, 139.94, 139.84, 137.67, 132.89, 130.63, 130.45, 129.81, 128.65, 127.78, 127.55, 124.23, 121.58, 120.24, 116.62, 99.45, 92.96, 88.13, 67.94, 40.36, 34.52, 32.57, 32.32, 31.75, 31.61, 31.22, 30.92, 30.39, 29.48, 29.30, 29.13, 25.76, 22.62, 22.51, 14.06, -1.23.

MS (**EI**, 80 eV, 30-60°C): m/z (%) = 968 (2.2), 967 (7.3), 966 (26.6), 965 (70.9), 964 (100.0), 963 (0.9) $[M^+]$, 841 (1.6), 840 (4.2), 839 (8.6), 838 (12.9), 837 (1.4), 836 (2.2) $[M\text{-}HI]^+/[M\text{-}I+H]^+$.

HRMS: calc.: 964.54145
found: 964.54620

1,4-Bis{1-[3-hexoxy-5-(trimethylsilyl)phenyl]}-buta-1,3-diyne ***86y***

$C_{34}H_{50}O_2Si_2$, M = 546.94



86y was isolated as a side product from the synthesis of **86**.

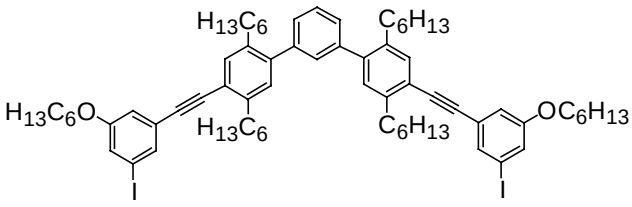
^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.26 (s, 2 H), 7.05 (d, 2 H, ^4J = 2.1 Hz), 6.99 (dd, 2 H, ^4J = 1.4 Hz, ^4J = 2.3 Hz), 3.94 (t, 4 H, J = 6.5 Hz), 1.77 (quintet, 4 H), 1.31-1.48 (m, 12 H), 0.91 (t, 3 H, ^3J = 6.8 Hz), 0.27 Hz (s, 18 H).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.20, 142.61, 129.75, 122.34, 121.54, 117.17, 81.91, 73.56, 67.98, 31.56, 29.18, 25.69, 22.58, 14.02, -1.32.

MS (**EI**, 80 eV, 220°C): m/z (%) = 550 (1.1), 549 (4.8), 548 (18.4), 547 (47.2), 546 (100.0) $[M]^+$, 532 (2.3), 531 (5.0) $[M\text{-}CH_3]^+$, 463 (1.1), 462 (2.5) $[M\text{-}C_6H_{12}]$,$^+$ 448 (1.2), 447 (2.9) $[M\text{-}C_6H_{12}\text{-}CH_3]^+$, 365 (1.3), 364 (3.2), 363 (9.5) $[M\text{-}2C_6H_{12}\text{-}CH_3]^+$.

2,5,2‘‘,5‘‘-Tetrahexyl-4,4‘‘-bis[(3-hexoxy-5-iodophenyl)ethynyl]-1,1‘:3‘,1‘‘-terphenyl ***87***

$C_{70}H_{92}O_2I_2$, M = 1219.30



The procedure was analogous to that described for **34b** (**86**: 500 mg, 0.45 mmol; iodine chloride: 160 mg, 0.99 mmol; chloroform: 50 ml/20 ml). The crude product (yellow sirup, 740 mg) was purified by chromatography (silica gel; hexane/toluene) to afford **87** (210 mg, 0.17 mmol, 43 %) as a yellow sirup. The NMR spectra were sufficiently pure, while the MS revealed traces of chlorinated side products (see explanation in General Part).

$\mathbf{R_f}$ = 0.25 (hexane/ethyl acetate 100:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.46 (t, 1 H, $^3J \approx 8$ Hz, 5’-H), 7.38 (d, 1 H, ^4J = 1.3 Hz, 2’-H), 7.36 (dd, 2 H, ^3J = 7 Hz, ^4J = 1.4 Hz, 4’,6’-H), 7.33 (s, 2 H, phenyl-H), 7.20 (dd, ^4J = 2.2 Hz, ^4J = 1.5 Hz, phenyl-H), 7.17, 716 (2 s, 2 × 2 H, 3,6,3‘‘,6‘‘-H), 6.95 (dd, 2 H, ^4J = 2.0

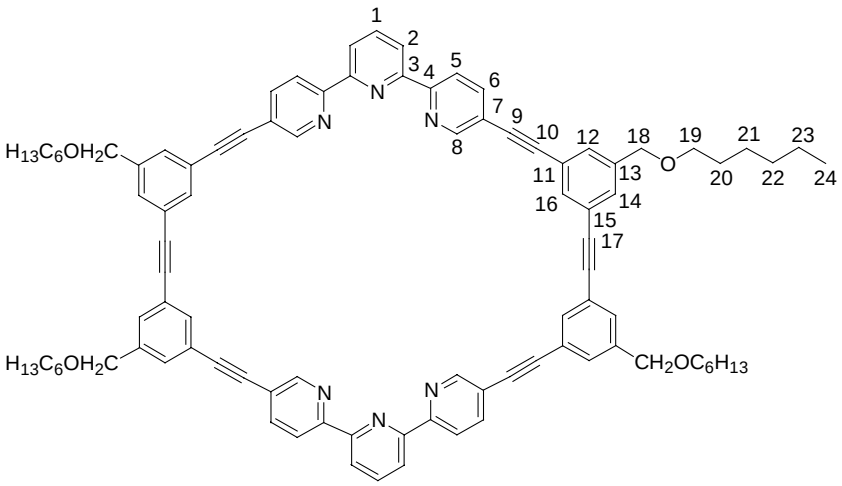
Hz, ^4J = 1.6 Hz, phenyl-H), 3.97 (t, 4 H, ^3J = 6.5 Hz, O-CH_2-), 2.58-2.74 (m, 8 H, aryl-CH_2-), 1.71-1.84 (m, 8 H, alkyl-H), 1.20-1.53 (m, 44 H, alkyl-H), 0.80-0.94 (m, 18 H, -CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 159.29, 144.55, 142.70, 141.31, 139.69, 138.27, 137.15, 131.58, 131.08, 130.14, 129.87, 129.64, 127.74, 123.58, 114.93, 93.75, 93.69, 68.39, 32.68, 31.71, 31.59, 31.54, 31.07, 30.44, 29.57, 29.09, 29.04, 25.66, 22.64, 22.57, 14.16, 14.10, 14.04.

MS (**EI**, 80 eV, 200°C): m/z (%) = 1221 (9.3), 1220 (32.4), 1219 (76.5), 1218 (100.0), 1217 (7.1) $[M]^+$; signals at m/z (%) = 1253 (14.7) and 1286 (26.8; main peaks) were assigned as the mono- and dichlorinated side products.

15,22,44,51-Tetrakis(hexoxymethyl)-8,29,37,58,65,72-hexaazaundecacyclo[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 ***88***

$C_{94}H_{90}N_6O_4$, M = 1367.78



A solution of **97** (100 mg, 0.109 mmol) and **80a** (78 mg, 0.109 mmol) in dried toluene/ triethylamine (100 ml, 1:1) was freeze-degassed twice. $Pd[P(Ph_3)]_4$ (10 mg, 0.0087 mmol) and CuI (1.7 mg, 0.0087 mmol) were added, the mixture degassed again and stirred at 60°C in a sealed flask for 4 days, and at 80°C for one more day. The mixture was allowed to cool down and stirred with an aqueous solution of KCN (50 mg KCN, 50 ml H_2O) for 30 mins. The phases were separated, the aqueous phase was extracted with toluene (50 ml), the combined organic phases with water (100 ml), and dried over $MgSO_4$. The solvent was evaporated in vacuo to yield a brownish raw product (120 mg, solid after freeze-drying). From this, cycle **88** was isolated as a yellow, amorphous material (40 mg, 0.029 mmol, 27 %) by preparative GPC, and likewise **[88]$_2$** (9 mg, 0.0032 mmol, 6 %).

^{1}H-NMR (500 MHz, $CDCl_3$, 293 K): δ = 8.48 (s, 4 H, 8-H), 8.40 (d, 4 H, ^{3}J = 8.5 Hz, 5-H), 8.19 (d, 4 H, ^{3}J = 7.5 Hz, 2-H), 7.72 (d, 8 H, ^{3}J = 8.0 Hz, 6-H), 7.71 (t, 2 H, ^{3}J = 8.0 Hz, 1-H), 7.38, 7.28, 7.24 (3 s, 18 H, 12-H, 14-H, 16-H), 4.41 (s, 8 H, 18-H), 3.52 (t, 8 H, ^{3}J = 6.5 Hz, 19-H), 1.68 (quintet, 8 H, ^{3}J = 7.0 Hz, 20-H), 1.43 (quintet, 8 H, ^{3}J = 7.0 Hz, 21-H), 1.24-1.39 (m, 16 H, 22-H, 23-H), 0.93 (t, 12 H, ^{3}J = 7.0 Hz, 24-H).

MS (**MALDI**, THA): m/z (%) = 1465.85 $[M+CH_3+C_6H_{12}]^+$, 1389.94 $[M+Na]^+$, 1367.95 $[M+H]^+$.

*Cyclic compound **[88]$_2$***

$C_{188}H_{180}N_{12}O_8$, M = 2735.56

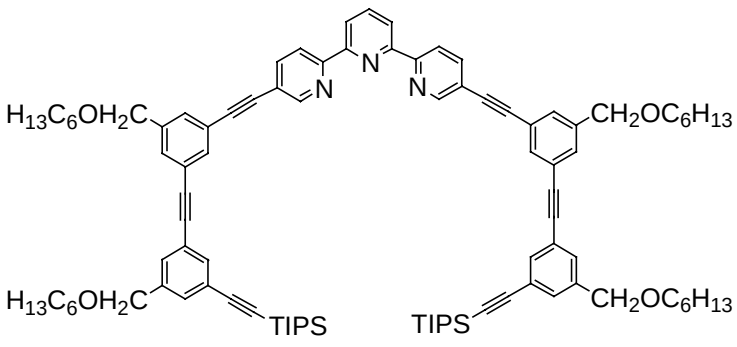
^{1}H-NMR (500 MHz, $CDCl_3$, 293 K): δ = 8.81 (d, 8 H, ^{4}J = 2.0 Hz, 8-H), 8.60 (d, 8 H, ^{3}J = 8.0 Hz, 5-H), 8.44 (d, 8 H, ^{3}J = 8.0 Hz, 2-H), 7.95 (dd, 8 H, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, 6-H), 7.92 (t, 4 H, ^{3}J = 8.0 Hz, 1-H), 7.65 (s, 8 H, 16-H), 7.48 and 7.50 (2 s, 16 H, 12-H, 14-H), 4.49 (s, 16 H, 18-H), 3.50 (t, 16 H, ^{3}J = 7.0 Hz, 19-H), 1.64 (t, 16 H, ^{3}J = 7.0 Hz, 20-H), 1.36-1.42 (m, 16 H, 21-H), 1.27-1.35 (m, 32 H, 22-H, 23-H), 0.89 (t, 24 H, ^{3}J = 7.0 Hz, 24-H).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.93 (4-C), 154.71 (3-C), 151.63 (8-C), 141.82 (13-C), 139.34 (6-C), 137.94 (1-C), 133.93 (16-C), 131.88 (28-C), 130.45 and 130.70 (12-C, 14-C), 123.09 and 123.52 (11-C, 15-C), 120.54 (2-C), 120.43 (5-C), 120.13 (7-C), 89.21 and 92.72 (10-C, 17-C), 87.09 (9-C), 71.90 (C-18), 69.18 (C-19), 31.70 (C-22), 29.73 (C-20), 25.98 (C-21); 19.87 (C-23); 14.06 (C-24).

MS (**MALDI**, THA): m/z (%) = 2756.7 $[M+Na]^+$, 2748.8 $[M+CH_3]^+$, 2734.8 $[M+H]^+$.

*5,5‘‘-Bis{[3-hexoxymethyl-5-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-phenyl]ethynyl}-2,2‘:6‘,2‘‘-terpyridine **89a***

$C_{97}H_{123}N_3O_4Si_2$, M = 1451.23



The procedure was analogous to that described for **62** (**52**:[125] 847 mg, 2.09 mmol; **94a**: 3.21 g, 4.19 mmol; $Pd[P(Ph_3)]_4$: 150 mg, 0.130 mmol, toluene: 50 ml, reaction time: 60 hrs). For the chromatographic purification, dichloromethane was used as eluent to afford **89a** (1.67 g, 1.15 mmol, 55 %) as a yellow sirup.

R_f = 0.50 (hexane/ethyl acetate 10:1, aluminium oxide).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.81 (dd, 2 H, ^{4}J = 1.8 Hz, ^{5}J = 0.6 Hz, tpy-6,6''-H), 8.60 (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), 7.95 (t, 1 H, ^{3}J = 7.8 Hz, tpy-4'-H), 7.95 (dd, 2 H, ^{3}J = 8.2 Hz, ^{4}J = 2.2 Hz, tpy-4,4''-H), 7.64 (s, 2 H, phenyl-H), 7.55 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.50 (d, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.44 (s, 2 H, phenyl-H), 7.40 (s, 2 H, phenyl-H), 4.49 (s, 4 H, aryl-CH_2-O-), 4.45 (s, 4 H, aryl-CH_2-O-), 3.49 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 3.46 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 1.59-1.66 (m, 8 H, β-CH_2), 1.29-1.38 (m, 24 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.89 (t, 6 H, ^{3}J =6.6 Hz, hexyl-CH_3), 0.88 (t, 6 H, ^{3}J =6.5 Hz, hexyl-CH_3).

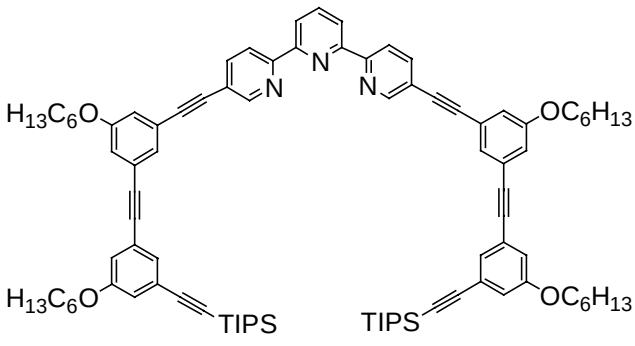
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.89, 154.71, 151.66, 139.68, 139.37, 139.24, 137.92, 134.13, 133.69, 130.91, 130.78, 130.38, 123.95, 123.56, 123.15, 123.02, 121.54, 120.36, 120.10, 106.02, 92.67, 91.42, 89.30, 88.86, 86.98, 71.87, 70.87, 70.80, 31.66, 29.67, 25.83, 22.61, 18.64, 14.03, 11.27.

MS (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1453 (7.2), 1452 (8.5), 1451 (7.6) $[M+H]^+$, 1367 (4.1), 1366 (4.0), 1365 (4.3) $[M-C_6H_{12}]^+$/$[M-C_6H_{14}]^+$.

EA:	Calc.:	C:80.28	H:8.54	N:2.90
	Found:	C:80.39	H:8.26	N:2.68.

5,5''-Bis{[3-({3-[(triisopropylsilyl)ethynyl]-5-hexoxyphenyl}ethynyl)-5-hexoxyphenyl]-ethynyl}-2,2':6',2''-terpyridine ***89b***

$C_{93}H_{115}N_3O_4Si_2$, M = 1395.12



The procedure was analogous to that described for **62** (**52**[125]: 2.00 g, 4.95 mmol; **94b**: 7.32 g, 9.91 mmol; $Pd[P(Ph_3)]_4$: 344 mg, 0.30 mmol; toluene: 125 ml). The crude product was purified by column chromatography (dichloromethane) to afford **89b** (3.00 g, 2.15 mmol, 43 %) as a yellow resin.

R_f = 0.53 (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), 8.60 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.46 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.97 (t, 1 H, ^{3}J ≈ 9 Hz, tpy-4'-H), 7.95 (dd, 2 H, ^{3}J = 8.3 Hz, ^{4}J = 2.0 Hz, tpy-4,4''-H), 7.33 (s, 2 H, phenyl-H), 7.23 (d, 2 H, ^{4}J = 2.4 Hz, phenyl-H), 7.05 (dd, 4 H, ^{4}J = 1.0 Hz, ^{4}J = 4.7 Hz, phenyl-H), 6.98 (dd, 4 H, ^{4}J =

1.0 Hz, ^4J = 3.9 Hz, phenyl-H), 3.98 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 3.95 (t, 4 H, ^3J = 6.6 Hz, α-CH_2), 1.76 (quintet, 8 H, $^3J \approx 7$ Hz, β-CH_2), 1.31-1.45 (m, 24 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.90 (m, 12 H, hexyl-CH_3).

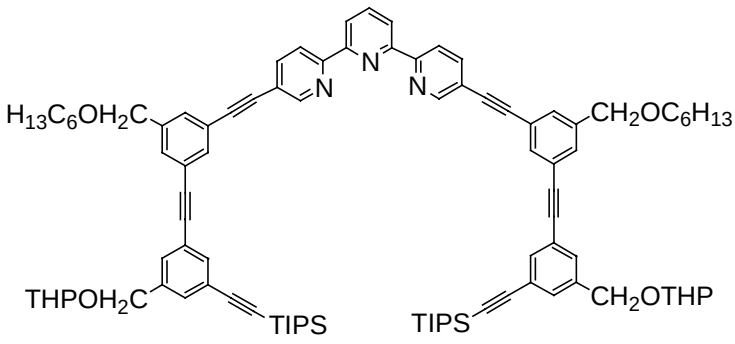
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.93, 158.76, 154.92, 154.77, 151.68, 139.35, 138.01, 127.72, 127.30, 124.77, 124.37, 123.94, 123.79, 121.59, 120.48, 120.17, 118.62, 118.27, 118.01, 117.60, 106.10, 92.81, 91.14, 89.10, 88.63, 86.63, 68.37, 68.28, 31.53, 29.12, 25.66, 22.59, 18.66, 14.01, 11.30.

MS (**EI**, 80 eV, 320°C): m/z (%) = 1397 (0.2), 1396 (0.3), 1395 (0.5), 1394 (0.4), 1393 (0.4) $[M]^+$, 1355 (0.4), 1354 (0.9), 1353 (2.0), 1352 (3.8), 1351 (3.5), 1350 (2.5) $[M\text{-}C_3H_7]^+$, 1314 (0.2), 1313 (0.4), 1312 (1.1), 1311 (2.5), 1310 (4.6), 1309 (10.9), 1308 (6.4), 1307 (5.8), 1306 (0.2) $[M\text{-}2C_3H_7]^+$, 1271 (0.3), 1270 (0.9), 1269 (1.7), 1268 (2.5), 1267 (2.8), 1266 (3.4), 1265 (0.3) $[M\text{-}3C_3H_7]^+$.

EA:	Calc.:	C:80.07	H:8.31	N:3.01
	Found:	C:79.82	H:8.26	N:2.93.

5,5‘‘-Bis{[3-hexyloxymethyl-5-({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)-ethynyl]phenyl}ethynyl)phenyl]ethynyl} -2,2‘:6‘,2‘‘-terpyridine ***89c***

$C_{95}H_{115}N_3O_6Si_2$, M = 1451.14



The procedure was analogous to that described for **62** (**52**:[125] 1.61 g, 3.98 mmol; **94c**: 6.10 g, 7.95 mmol; $Pd[P(Ph_3)]_4$: 276 mg, 0.23 mmol, toluene: 120 ml, reaction time: 72 hrs). The crude product was purified by column chromatography (aluminium oxide, hexane/ethyl acetate 15:1) to afford **89c** (1.80 g, 1.24 mmol, 31 %) as a colorless resin.

R_f = 0.29 (hexane/ethyl acetate 20:1, aluminium oxide).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.82 (dd, 2 H, ^4J = 1.7 Hz, ^5J = 0.7 Hz, tpy-6,6‘‘-H), 8.62 (d, 2 H, ^3J = 8.3 Hz, tpy-3,3‘‘-H), 8.47 (d, 2 H, ^3J = 7.8 Hz, tpy-3’,5’-H), 7.97 (t, 1 H, ^3J = 7.7 Hz, tpy-4’-H), 7.95 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 2.3 Hz, tpy-4,4‘‘-H), 7.66 (t, 2 H, ^4J = 1.4 Hz, phenyl-H), 7.56 (t, 2 H, ^4J = 1.4 Hz, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7. t, 2 H, ^4J = 1.2 Hz, phenyl-H), 7.48 (s, 2 H, phenyl-H), 7.42 (s, 2 H, phenyl-H), 4.69-4.76 (m, 4 H, benzyl (THP)-H, THP-2-H), 4.50 (s, 4 H, benzyl (hexyl)-H), 4.45 (d, 2 H, $^2J \approx 12$ Hz, benzyl (THP)-

H'), 3.85-3.94 (m, 2 H, THP-6-H), 3.51-3.59 (m, 2 H, THP-6'-H), 3.49 (t, 4 H, ^3J = 6.6 Hz, hexyl-α-CH_2), 1.52-1.85 (m, 16 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.29-1.41 (m, 12 H, hexyl-γ-, δ-, ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.89 (t, 3 H, ^3J = 6.8 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.86, 154.68, 151.64, 139.66, 139.23, 138.92, 137.92, 134.18, 133.68, 131.10, 130.77, 130.57, 130.44, 123.93, 123.52, 123.17, 123.00, 121.52, 120.35, 120.08, 105.98, 97.83, 92.66, 91.47, 89.27, 88.87, 86.97, 71.83, 70.85, 67.82, 62.09, 31.65, 30.44, 29.66, 25.82, 25.39, 22.61, 19.25, 18.63, 14.03, 11.25.

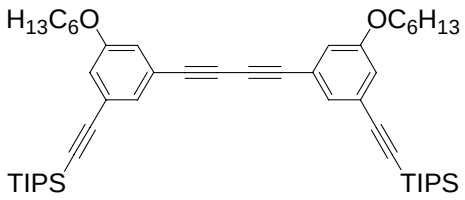
MS (**EI**, 80 eV, 350°C, decomposition): m/z (%) = 1452 (20.4), 1451 (25.4) $[M]^+$, 1410 (25.8), 1409 (28.2), 1408 (35.9), 1407 (34.0) $[M-C_3H_7]^+$, 1369 (27.1), 1368 (43.5), 1367 (59.7), 1366 (94.3), 1365 (100.0), 1364 (80.7) $[M-C_6H_{13}]^+$, 1327 (17.9), 1326 (26.0), 1325 (57.4), 1324 (48.5), 1323 (52.6) $[M-C_6H_{13}-C_3H_7]^+$, 1282 (26.5), 1280 (47.2) $[M-C_6H_{13}-C_6H_{12}]^+$.

MS (**FAB(+)**, CH_2Cl_2/MNBA-Matrix): m/z (%) = 1455 (4.8), 1454 (9.5), 1453 (10.6), 1452 (13.5) $[M+H]^+$, 1370 (2.8), 1369 (3.8), 1368 (6.3) $[M+H-C_6H_{12}]^+$.

EA:	Calc.:	C:78.63	H:7.99	N:2.90
	Found:	C:78.78	H:7.87	N:3.00.

1,4-Bis{3-hexoxy-5-[(triisopropylsilyl)ethynyl]}buta-1,3-diyne ***89n***

$C_{50}H_{74}O_2Si_2$, M = 762.50



This compound was isolated as a side product from the synthesis of **89b** according to a different protocol. This was analogous to that described for **79** (**82**: 140 mg, 0.177 mmol; **45b**: 405 mg, 1.06 mmol; CuI: 10 mg, 0.05 mmol; $Pd[P(Ph_3)]_4$: 61 mg, 0.05 mmol; triethylamine: 25 ml; toluene: 25 ml; reaction temperature: 70°C; reaction time: 72 hrs). The crude product was purified by chromatography over silica gel (hexane) to afford the desired product (**89b**) as impure material (130 mg) and **89n** (260 mg, 0.34 mmol, 64 %).

R_f = 0.16 (hexane).

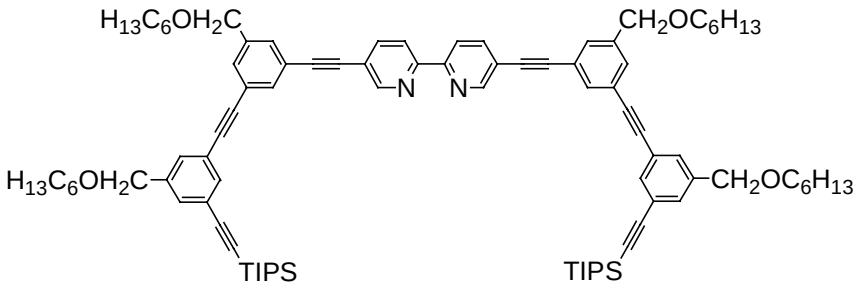
^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.22 (t, 2 H, ^4J = 1.2 Hz, aryl-H), 6.97-7.00 (m, 4 H, aryl-H), 3.92 (t, 4 H, ^3J = 6.4 Hz, α-CH_2), 1.75 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.28-1.44 (m, 12 H, γ-, δ-, ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.91 (t, 3 H, ^3J = 6.3 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.71, 128.50, 124.91, 122.68, 119.46, 118.12, 105.76, 91.15, 80.92, 73.90, 68.28, 31.52, 29.08, 25.65, 22.59, 18.63, 14.01, 11.28.

MS (**EI**, 80 eV, 270°C): m/z (%) = 765 (5.4), 764 (13.9), 763 (26.7), 762 (39.6) $[M]^+$, 723 (5.7), 722 (13.1), 721 (30.1), 720 (64.0), 719 (100.0) $[M\text{-}C_3H_7]^+$, 679 (8.0), 678 (13.4), 677 (15.7) $[M\text{-}C_6H_{13}]^+$, 639 (7.6), 638 (9.6), 637 (11.2), 636 (11.5), 635 (16.0) $[M^+\text{-}C_3H_7\text{-}C_6H_{12}]^+$.

5,5‘‘-Bis{[3-hexoxymethyl-5-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-phenyl]ethynyl}-2,2‘-bipyridine ***89x***

$C_{92}H_{120}N_2O_4Si_2$, M = 1374.14



This compound was isolated as a side product from one batch of **89a** (**52**:[125] 140 mg, 0.35 mmol; **94a**: 530 mg, 0.69 mmol; $Pd[P(Ph_3)]_4$: 24 mg, 0.02 mmol, toluene: 20 ml, reaction time: 48 hrs) via column chromatography to yield **89x** (170 mg, 0.12 mmol, 36 %, pure enough for characterisation) as a yellow film next to **89a** (170 mg, 0.11 mmol, 24 %).

$\mathbf{R_f}$ = 0.89 (hexane/ethyl acetate 4:1).

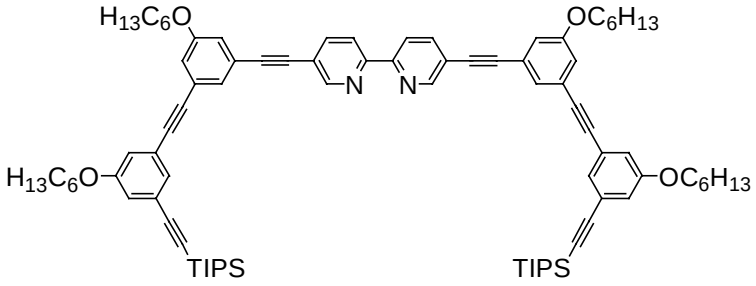
^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.79 (d, 2 H, ^4J = 1.6 Hz, bpy-6,6’-H), 8.42 (d, 2 H, ^3J = 8.3 Hz, bpy-3,3’-H), 7.90 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 2.1 Hz, bpy-4,4’-H), 7.63 (s, 2 H, phenyl-H), 7.56 (s, 2 H, phenyl-H), 7.49 (s, 4 H, phenyl-H), 7.44 (s, 2 H, phenyl-H), 7.40 (s, 2 H, phenyl-H), 4.48 (s, 4 H, aryl-CH_2-O-), 4.45 (s, 4 H, aryl-CH_2-O-), 3.48 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 3.45 (t, 4 H, ^3J = 6.6 Hz, α-CH_2), 1.59-1.66 (m, 8 H, β-CH_2), 1.20-1.36 (m, 24 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.88 (2 t, 12 H, $^3J \approx 7$ Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.17, 151.70, 139.68, 139.35, 134.10, 133.65, 130.88, 130.35, 123.93, 123.54, 123.13, 122.95, 120.57, 120.22, 106.01, 92.89, 91.38, 89.29, 88.83, 86.90, 71.84, 70.85, 70.78, 31.64, 29.65, 25.82, 22.59, 18.62, 14.01, 11.25.

MS (**EI**, 80 eV, 320°C): m/z (%) = 1376 (0.1), 1374 (0.2), 1373 (0.2) $[M]^+$, 1335 (0.1), 1334 (0.4), 1333 (0.9), 1332 (2.1), 1331 (2.5), 1330 (2.2) $[M\text{-}C_3H_7]^+$, 1290 (0.09), 1289 (0.11), 1288 (0.09) $[M\text{-}C_6H_{13}]^+$.

5,5‘‘-Bis{[3-({3-[(triisopropylsilyl)ethynyl]-5-hexoxyphenyl}ethynyl)-5-hexoxyphenyl]-ethynyl}-2,2‘-bipyridine ***89y***

$C_{98}H_{112}N_2O_4Si_2$, M = 1318.03



This compound was isolated as a side product from the synthesis of **89b** (**52**:[125] 195 mg, 0.482 mmol; **94b**: 750 mg, 1.01 mmol; $Pd[P(Ph_3)]_4$: 33 mg, 0.029 mmol; toluene: 20 ml; reaction time: 72 hrs). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate). Beside of the product **89b** (330 mg, 0.24 mmol, 49 %), the side product **89y** (70 mg, 0.053 mmol, 11 %) was isolated as a yellow resin.

$\mathbf{R_f}$ = 0.40 (hexane/ethyl acetate 50:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.78 (d, 2 H, ^{4}J = 1.5 Hz, bpy-6,6’-H), 8.40 (d, 2 H, ^{3}J = 8.3 Hz, bpy-3,3’-H), 7.92 (dd, 2 H, ^{3}J = 8.3 Hz, ^{4}J = 1.4 Hz, bpy-4,4’-H), 7.31 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.23 (t, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.04 (t, 4 H, ^{4}J = 1.5 Hz, phenyl-H), 6.98 (d, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 6.97 (d, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 3.97 (t, 4 H, ^{3}J = 6.7 Hz, α-CH_2), 3.95 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 1.76 (quintet, 8 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.32-1.49 (m, 24 H, γ-,δ-,ε-CH_2), 1.12 (s, 42 H, silyl-H), 0.90 (t, 12 H, ^{3}J = 6.7 Hz, -CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.88, 158.72, 154.14, 151.68, 139.31, 127.68, 127.25, 124.73, 124.33, 123.91, 123.73, 120.59, 120.20, 118.57, 118.23, 117.94, 117.54, 106.08, 92.99, 91.07, 89.08, 88.63, 86.61, 68.30, 68.21, 31.52, 29.10, 25.65, 22.59, 18.64, 14.01, 11.28.

MS (**EI**, 80 eV, 320°C): m/z (%) = 1321 (0.3), 1320 (0.3), 1319 (0.6), 1318 (0.9), 1317 (0.8) $[M]^+$, 1279 (0.7), 1278 (1.1), 1277 (2.4), 1276 (8.1), 1275 (9.8), 1274 (9.6) $[M-C_3H_7]^+$, 1234 (0.3), 1233 (0.3) $[M-C_6H_{12}]^+$.

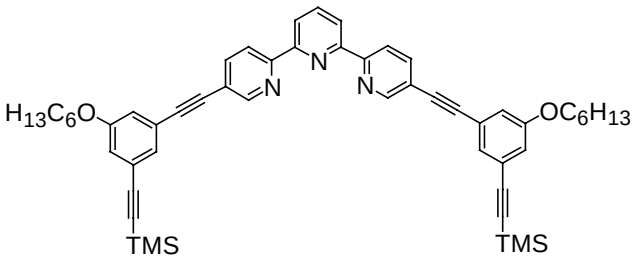
5,5‘‘-Bis[(3-{[3-(trimethylsilyl)ethynyl-5-hexoxyphenyl]ethynyl}-5-hexoxyphenyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine ***90***

$C_{81}H_{91}N_3O_4Si_2$, M = 1226.80

The procedure was analogous to that described for **43b** (**46**: 493 mg, 1.23 mmol; **80b**: 140 mg, 0.205 mmol; $Pd[P(Ph_3)]_4$: 43 mg, 0.037 mmol; CuI: 7 mg, 0.037 mmol; toluene/triethylamine: 10 ml/20 ml). The crude product was purified by column

chromatography (hexane /ethyl acetate) to afford **90** (150 mg, 0.12 mmol, 60 %) as a yellow sirup. The spectra showed small impurities, but **90** was deprotected to **91b** without further purification.

R_f = 0.39 (hexane/ethyl acetate 4:1).



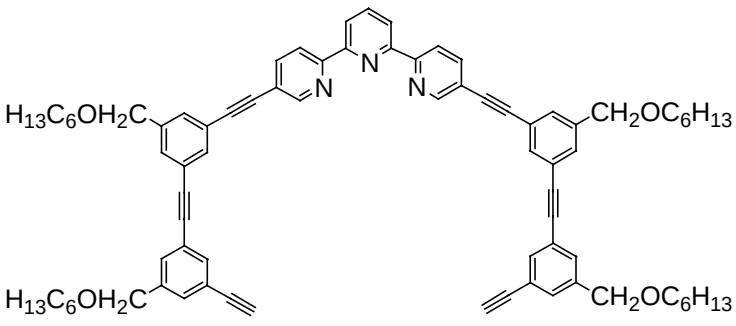
^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.82 (d, 2 H, ^{4}J = 1.9 Hz, tpy-6,6''-H), 8.62 (d, 2 H, ^{3}J = 8.3 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.8 Hz, tpy-3',5'-H), 7.95-8.00 (m, 3 H, 5,4',5"-H), 7.31 (s, 2 H, phenyl-H), 7.23 (d, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 7.06 (d, 2 H, ^{4}J = 1.2 Hz, phenyl-H), 7.03 (s, 2 H, phenyl-H), 6.99 (d, 2 H, ^{4}J = 1.3 Hz, phenyl-H), 6.96 (d, 2 H, ^{4}J = 1.0 Hz, phenyl-H), 3.98 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 3.94 (t, 4 H, ^{3}J = 6.6 Hz, α-CH_2), 1.76 (quintet, 8 H, ^{3}J ≈ 7 Hz, β-CH_2), 1.23-1.46 (m, 24 H, γ-,δ-,ε-CH_2), 0.89-0.93 (m, 12 H, hexyl-CH_3), 0.23 (18 H, silyl-H).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.83, 158.69, 154.78, 154.59, 151.60, 139.16, 137.80, 127.58, 127.21, 124.30, 123.96, 123.77, 121.47, 120.28, 120.03, 118.08, 117.90, 104.15, 94.61, 92.74, 89.00, 88.68, 86.69, 68.26, 68.20, 31.51, 29.08, 25.63, 22.58, 14.01, -0.12.

MS (**EI**, 80 eV, 300°C): m/z (%) = 1231 (0.2), 1230 (0.4), 1229 (0.8), 1228 (1.2), 1227 (1.9), 1226 (1.8), 1225 (0.1), 1224 (0.1) $[M]^+$.

5,5''-Bis({3-[(3-ethynyl-5-hexoxymethylphenyl)ethynyl]-5-hexoxymethylphenyl}ethynyl)-2,2':6',2''-terpyridine ***91a***

$C_{79}H_{83}N_3O_4$, M = 1138.54



The procedure was analogous to that described for **80a** (**89a**: 1.66 g, 1.14 mmol; tetra-*n*-butylammonium fluoride trihydrate: 1.18 g, 3.70 mmol; THF: 50 ml). The crude product was purified by chromatography over silica gel (dichloromethane/methanol) to afford **91a** (1.09 g, 0.957 mmol, 84 %) as a yellow resin which could not be solidified even after freeze-drying from benzene.

R_f = 0.27 (hexane/ethyl acetate 10:1, aluminium oxide).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.82 (d, 2 H, ^{4}J = 1.7 Hz, tpy-6,6''-H), 8.61 (d, 2 H, ^{3}J = 8.2 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^{3}J = 7.9 Hz, tpy-3',5'-H), 7.97 (t, 1 H, ^{3}J ≈ 8 Hz, tpy-4'-H), 7.95 (dd, 2 H, ^{3}J = 8.2 Hz, ^{4}J = 2.3 Hz, tpy-4,4''-H), 7.65 (s, 2 H, phenyl-H), 7.55 (s, 2 H, phenyl-H), 7.52 (s, 2 H, phenyl-H), 7.48 (d, 4 H, ^{4}J = 1.3 Hz, phenyl-H), 7.43 Hz (s, 2 H, phenyl-H), 4.50 (s, 4 H, aryl-CH_2-O-), 4.46 (s, 4 H, aryl-CH_2-O-), 3.49 (t, 4 H, ^{3}J = 6.8 Hz, α-CH_2), 3.46 (t, 4 H, ^{3}J = 6.7 Hz, α-CH_2), 3.08 (s, 2 H, ethynyl-H), 1.59-1.66 (m, 8 H, β-CH_2), 1.29-1.39 (m, 24 H γ-,δ-,ε-CH_2), 0.89 (t, 6 H, ^{3}J =6.5 Hz, hexyl-CH_3), 0.88 (t, 6 H, ^{3}J =6.5 Hz, hexyl-CH_3).

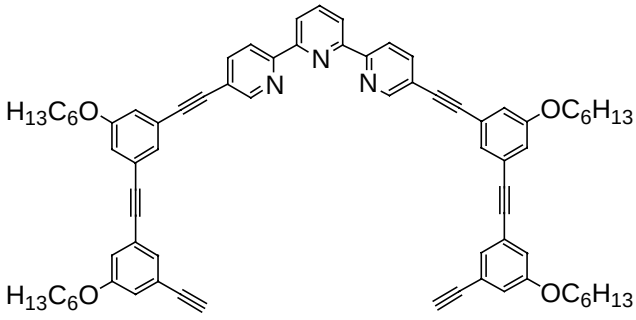
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.81, 154.62, 151.60, 139.65, 139.51, 139.20, 137.87, 134.05, 133.63, 130.93, 130.78, 130.44, 123.42, 123.28, 122.98, 122.51, 121.49, 120.31, 120.03, 92.62, 89.06, 88.99, 86.99, 82.66, 77.80, 71.74, 70.81, 31.63, 29.63, 25.80, 22.58, 14.01.

MS (**FAB(+)**, MNBA/DMSO-Matrix): m/z (%) = 1160 (0.5) $[M+Na]^+$, 1140 (0.4), 1139 (1.8), 1138 (2.3), 1137 (1.6) $[M+H]^+$.

EA:	Calc.:	C:83.34	H:7.35	N:3.69
	Found:	C:83.31	H:7.18	N:3.63.

5,5''-Bis({3-[(3-ethynyl-5-hexoxyphenyl)ethynyl]-5-hexoxyphenyl}ethynyl)-2,2':6',2''-terpyridine ***91b***

$C_{75}H_{75}N_3O_4$, M = 1082.43



Method A:

The procedure was analogous to that described for **45b** (**90**: 150 mg, 0.12 mmol; methanol: 12 ml; dichloromethane: 10 ml). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate) to afford **91b** (20 mg, 0.02 mmol, 15 %) as a colorless oil. The yield is subject to improvement; the reaction was only done once, and the low yield was presumably due to impure reagents.

Method B:

The procedure was analogous to that described for **80a** (**89b**: 300 mg, 0.215 mmol; tetra-*n*-butylammonium fluoride trihydrate: 220 mg, 0.70 mmol; THF: 10 ml). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate) to afford **91b** as a yellow sirup (190 mg, 82 % after freeze-drying).

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

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.81 (dd, 2 H, ^4J = 2.4 Hz, ^5J = 0.7 Hz, tpy-6,6''-H), 8.61 (d, 2 H, ^3J = 8.3 Hz, tpy-3,3''-H), 8.47 (d, 2 H, ^3J = 7.8 Hz, tpy-3',5'-H), 7.97 (t, 1 H, $^3J \approx$ 9 Hz, tpy-4'-H), 7.95 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 1.9 Hz, tpy-4,4''-H), 7.32 (t, 2 H, ^4J = 1.3 Hz, phenyl-H), 7.23 (m, 2 H, phenyl-H), 6.98-7.08 (m, 8 H, phenyl-H), 3.98 (t, 4 H, ^3J = 6.5 Hz, α-CH_2), 3.94 (t, 4 H, ^3J = 6.6 Hz, α-CH_2), 3.06 (s, 2 H, ethynyl-H), 1.78 (quintet, 8 H, $^3J \approx$ 7 Hz, β-CH_2), 1.23-1.46 (m, 24 H, γ-,δ-,ε-CH_2), 0.81-0.96 (m, 12 H, hexyl-CH_3).

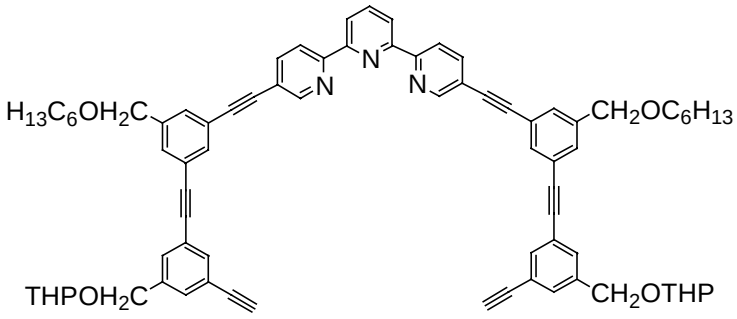
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.95, 158.82, 154.96, 154.79, 151.71, 139.34, 138.01, 127.66, 127.31, 124.31, 124.16, 123.84, 123.36, 121.60, 120.43, 120.15, 118.65, 118.32, 118.05, 92.76, 88.88, 86.70, 82.79, 77.21, 68.35, 31.54, 29.11, 25.67, 22.60, 14.02.

MS (**FAB(+)**, DMSO/MNBA-Matrix): m/z (%) = 1105 (0.4), 1104 (0.4) $[M+Na]^+$, 1085 (0.7), 1084 (1.8), 1083 (3.0), 1082 (3.1), 1081 (2.4), 1080 (1.0) $[M+H]^+$.

EA:	Calc.:	C:83.22	H:6.98	N:3.88
	Found:	C:83.14	H:7.28	N:3.74.

5,5''-Bis[(3-{[3-ethynyl-5-(tetrahydropyran-2-yloxymethyl)phenyl]ethynyl}-5-hexoxymethylphenyl)ethynyl]-2,2':6',2''-terpyridine ***91c***

$C_{77}H_{75}N_3O_6Si_2$, M = 1138.45



The procedure was analogous to that described for **80a** (**89c**: 1.56 g, 1.08 mmol; tetra-*n*-butylammonium fluoride trihydrate: 1.02 g, 3.23 mmol; THF: 50 ml). The crude product was purified by chromatography over aluminium oxide (hexane/ethyl acetate) to afford **91c** (1.14 g, 1.00 mmol, 93 %) as a yellow resin which could not be solidified even after freeze-drying from benzene.

R_f = 0.52 (hexane/ethyl acetate 4:1, aluminium oxide).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.80 (d, 2 H, ^4J = 1.9 Hz, tpy-6,6''-H), 8.60 (d, 2 H, ^3J = 8.3 Hz, tpy-3,3''-H), 8.45 (d, 2 H, ^3J = 7.9 Hz, tpy-3',5'-H), 7.94 (t, 1 H, ^3J = 7.8 Hz, tpy-4'-H), 7.94 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 2.0 Hz, tpy-4,4''-H), 7.64 (t, 2 H, ^4J = 1.3 Hz, phenyl-H), 7.55 (t, 2 H, ^4J = 1.2 Hz, phenyl-H), 7.48-7.50 (m, 6 H, phenyl-H), 7.45 (s, 2 H, phenyl-H), 4.69-4.76 (m, 4 H, benzyl (THP)-H, THP-2-H), 4.48 (s, 4 H, benzyl (hexyl)-H), 4.45 (d, 2 H, $^2J \approx$ 12 Hz, benzyl (THP)-H'), 3.84-3.93 (m, 2 H, THP-6-H), 3.52-3.59 (m, 2 H, THP-6'-H),

3.48 (t, 4 H, ^{3}J = 6.7 Hz, hexyl-α-CH_2), 3.09 (s, 1 H, ethynyl-H), 1.52-1.85 (m, 16 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.26-1.43 (m, 12 H, hexyl-γ-, δ-, ε-CH_2), 0.88 (t, 3 H, ^{3}J = 6.8 Hz, hexyl-CH_3).

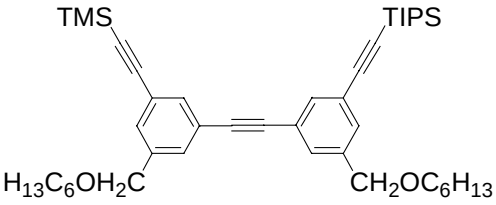
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.70, 154.49, 151.51, 139.59, 139.08, 137.74, 134.01, 133.56, 130.99, 130.84, 130.64, 130.36, 123.33, 123.23, 122.91, 122.47, 121.41, 120.21, 119.94, 97.80, 92.57, 88.99, 86.97, 82.63, 77.86, 71.70, 70.78, 67.62, 61.95, 31.57, 30.35, 29.59, 25.76, 25.30, 22.54, 19.14, 13.98.

MS (**FAB(+)**, DMSO/MNBA-Matrix): m/z (%) = 1141 (0.6), 1140 (0.9), 1139 (1.3), 1138 (1.4) $[M+H]^+$.

EA:	Calc.:	C:81.24	H:6.64	N:3.69
	Found:	C:81.32	H:6.73	N:3.68.

1-Hexoxymethyl-3-({3-hexoxymethyl-5-[(trimethylsilyl)ethynyl]phenyl}ethynyl)-5-[(triisopropylsilyl)ethynyl]benzene ***92a***

$C_{44}H_{66}O_2Si_2$, M = 683.17



The procedure was analogous to that described for **43b** (**42a**[32]: 13.11 g, 35.7 mmol; **45a**[32]: 14.16 g, 35.7 mmol; CuI: 204 mg, 1.07 mmol; $Pd[P(Ph_3)]_4$: 1.24 g, 1.07 mmol; triethylamine: 500 ml; reaction time: 3 days; reaction temperature: 70°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **92a** (18.50 g, 27.1 mmol, 76 %) as a yellow oil.

R_f = 0.36 (hexane/ethyl acetate 50:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.53 (d, 2 H, ^{4}J = 1.7 Hz, aryl-H), 7.42 (d, 2 H, ^{4}J = 1.4 Hz, aryl-H), 7.39 (s, 2 H, aryl-H), 4.44 (2 s, 4 H, benzyl-H), 3.45 (t, 2 H, ^{3}J = 6.6 Hz, α-CH_2), 3.44 (t, 2 H, ^{3}J = 6.6 Hz, α-CH_2), 1.58-1.60 (m, 4 H, β-CH_2), 1.28-1.35 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.88 (t, 6 H, ^{3}J =6.8 Hz, hexyl-CH_3), 0.22 (s, 9 H, TMS-H).

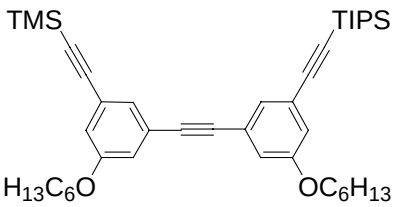
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.34, 134.10, 134.02, 130.75, 130.47, 130.34, 123.92, 123.52, 123.24, 106.04, 104.05, 94.91, 91.34, 89.00, 88.95, 71.86, 70.76, 31.65, 29.65, 25.82, 22.60, 18.63, 14.02, 11.27, -0.14.

MS (**EI**, 80 eV, 180°C): m/z (%) = 685 (7.7), 684 (23.6), 683 (54.9), 682 (100.0) $[M]^+$, 641 (16.3), 640 (37.7), 639 (70.4) $[M-C_3H_7]^+$, 583 (10.9), 582 (20.9) $[M-OC_6H_{13}]^+$, 540 (8.1), 539 (16.3) $[M-C_3H_7-OC_6H_{13}]^+$.

EA: Calc.: C:77.36 H:9.74
Found: C:77.13 H:9.51.

1-Hexoxy-3-({3-hexoxy-5-[(trimethylsilyl)ethynyl]phenyl}ethynyl)-5-[(triisopropylsilyl)ethynyl]benzene ***92b***

$C_{42}H_{62}O_2Si_2$, M = 655.12



The procedure was analogous to that described for **43b** (**42b**: 7.43 g, 20.9 mmol; **45b**: 8.00 g, 20.9 mmol; CuI: 119 mg, 0.63 mmol; $Pd[P(Ph_3)]_4$: 725 mg, 0.63 mmol; triethylamine: 150 ml; reaction temperature: 70°C; reaction time: 4 days). The crude product was purified by chromatography over silica gel (hexane/toluene) to afford **92b** (10.22 g, 15.6 mmol, 75 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.79 (hexane/ethyl acetate 100:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.19-7.20 (m, 2 H, aryl-H), 6.94-7.00 (m, 4 H, aryl-H), 3.90-3.96 (2 t, 4 H, ^3J = 6.5 Hz, α-CH_2), 1.70-1.78 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.31-1.43 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.89 (t, 6 H, ^3J = 6.6 Hz, hexyl-CH_3), 0.23 (s, 9 H, TMS-H).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.72, 127.66, 124.71, 124.32, 124.03, 118.55, 118.15, 118.03, 117.50, 106.12, 104.15, 94.58, 91.03, 88.80, 88.74, 68.22, 31.53, 29.11, 25.66, 22.59, 18.65, 14.01, 11.29, -0.12.

MS (**EI**, 80 eV, 180°C): m/z (%) = 657 (2.4), 656 (7.8), 655 (16.5), 654 (33.0) $[M]^+$, 639 (1.6) $[M\text{-}CH_3]^+$, 615 (2.2), 614 (6.3), 613 (22.3), 612 (54.1), 611 (100.0) $[M\text{-}C_3H_7]^+$, 585 (2.1), 584 (5.3), 583 (11.5) $[M\text{-}C_5H_{11}]^+$, 571 (3.6), 570 (8.0), 569 (15.5) $[M\text{-}C_6H_{13}]^+$.

EA: Calc.: C:77.00 H:9.54
Found: C:77.00 H:9.58.

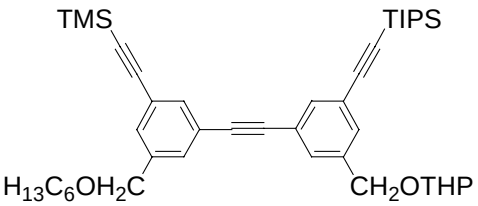
1-Hexoxymethyl-3-({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]phenyl}-ethynyl)-5-[(trimethylsilyl)ethynyl]benzene ***92c***

$C_{43}H_{62}O_3Si_2$, M = 683.13

The procedure was analogous to that described for **43b** (**42a**:[32] 6.50 g, 17.6 mmol; **45c**: 7.00 g, 17.6 mmol; CuI: 100 mg, 0.530 mmol; $Pd[P(Ph_3)]_4$: 610 mg, 0.530 mmol; triethylamine: 150 ml; reaction time: 3 days; reaction temperature: 70°C). The crude product

was purified by column chromatography (silica gel, hexane/toluene) to afford **92c** (7.38 g, 10.8 mmol, 61 %) as a brownish foam.

R_f = 0.24 (hexane/ethyl acetate 20:1).



^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.53 (d, 2 H, ^{4}J = 1.6 Hz, aryl-H), 7.38-7.44 (m, 4 H, aryl-H), 4.68-4.75 (m, 2 H, benzyl (THP)-H, THP-2-H), 4.42-4.47 (m, 3 H, benzyl (THP)-H', benzyl (hexyl)-H), 3.85-3.93 (m, 1 H, THP-6-H), 3.50-3.58 (m, 1 H, THP-6'-H), 3.44 (t, 2 H, ^{3}J = 6.6 Hz, hexyl-α-CH_2), 1.52-1.85 (m, 8 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.24-1.38 (m, 6 H, hexyl-γ-, δ-, ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.88 (t, 3 H, ^{3}J = 6.7 Hz, hexyl-CH_3), 0.23 (s, 9 H, TMS-H).

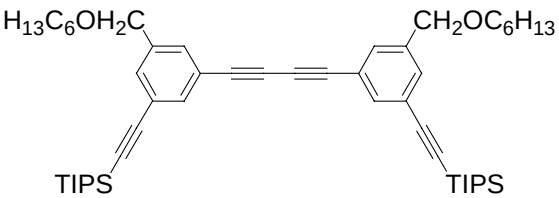
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.36, 138.90, 134.18, 134.04, 131.03, 130.78, 130.52, 123.92, 123.52, 123.26, 106.02, 104.05, 97.83, 94.94, 91.44, 88.99, 71.86, 70.74, 67.85, 62.11, 31.65, 30.46, 29.66, 25.82, 25.41, 22.61, 19.26, 18.64, 14.03, 11.28, -0.13.

MS (**EI**, 80 eV, 220°C): m/z (%) = 683 (5.9), 682 (10.4), 681 (9.0) $[M]^+$, 642 (5.5), 641 (18.9), 640 (44.8), 639 (77.9), 638 (42.5) $[M-C_3H_7]^+$, 598 (8.2), 597 (8.8) $[M-C_3H_7-C_3H_6]^+$, 585 (7.7), 584 (23.6), 583 (56.9), 582 (100.0), 581 (4.9) $[M-C_5H_8O_2]^+$, 540 (4.9), 539 (8.9) $[M-C_5H_8O_2-C_3H_7]^+$.

EA: Calc.: C:75.60 H:9.15
Found: C:75.59 H:9.35.

1,4-Bis{3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]}buta-1,3-diyne ***92m***

$C_{52}H_{78}O_2Si_2$, M = 791.36



This compound was isolated as a side product from one rather unsuccessful preparation of **92a** (**42a**[32]: 11.21 g, 30.5 mmol; **45a**[32]: 12.10 g, 35.5 mmol; CuI: 174 mg, 0.91 mmol; $Pd[P(Ph_3)]_4$: 1.06 g, 0.91 mmol; triethylamine: 500 ml; reaction time: 3 days; reaction temperature: 70°C). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **92m** (1.77 g, 2.23 mmol, 15 %, slightly colored amorphous material) next to **92a** (9.75 g, 14.3 mmol, 47 %, brownish oil).

R_f = 0.25 (hexane/ethyl acetate 40:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.52 (t, 2 H, ^{4}J = 1.4 Hz, aryl-H), 7.41 (d, 4 H, ^{4}J = 1.2 Hz, aryl-H), 4.24 (s, 4 H, benzyl-H), 3.44 (t, 4 H, ^{3}J = 6.5 Hz, α-CH_2), 1.75 (quintet, 4 H, ^{3}J ≈

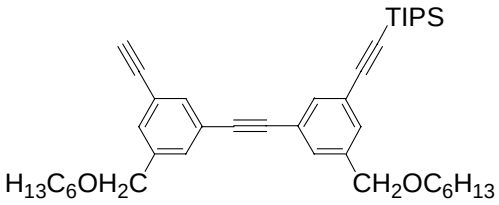
7 Hz, β-CH_2), 1.27-1.32 (m, 12 H, γ-, δ-, ε-CH_2), 1.10 (s, 42 H, silyl-H), 0.87 (t, 3 H, ^3J = 6.6 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.72, 135.13, 131.81, 131.24, 124.28, 122.13, 105.88, 92.04, 81.07, 74.40, 71.93, 71.05, 31.85, 29.84, 26.02, 22.80, 18.82, 14.22, 11.46.

MS (**EI**, 80 eV, 250°C): m/z (%) = 795 (2.2), 794 (10.7), 793 (33.0), 792 (40.4), 791 (100.0) $[M]^+$, 761 (3.0), 750 (14.3), 749 (17.5), 748 (34.6), 747 (55.9) $[M\text{-}C_3H_7]^+$, 708 (2.2), 707 (3.6), 706 (6.1) $[M\text{-}C_6H_{13}]^+$, 692 (2.8), 691 (4.8), 690 (10.3) $[M^+\text{-}OC_6H_{13}]^+$, 649 (4.3), 648 (8.7), 647 (14.5) $[M^+\text{-}C_3H_7\text{–}OC_6H_{13}]^+$.

1-Hexoxymethyl-3-[1-(3-hexoxymethyl-5-ethynylphenyl)ethynyl]-5-[(triisopropylsilyl)ethynyl] -benzene ***93a***

$C_{41}H_{58}O_2Si$, M = 610.99



The procedure was analogous to that described for **45b** (**92a**: 18.50 g, 27.08 mmol; dichloromethane: 250 ml; methanol: 250 ml). The solvent was evaporated and the crude product dissolved in dichloromethane (200 ml) and washed with aqueous NaCl (200 ml). The aqueous phase was extracted with dichloromethane (100/50 ml), the combined organic phases are dried over $MgSO_4$ and the solvent was evaporated to afford **93a** (16.08 g, 26.32 mmol, 97 %) as a brownish oil. Alternatively, the crude product was purified by chromatography over silica gel (hexane/toluene).

R_f = 0.67 (hexane/ethyl acetate 40:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.54 (d, 2 H, ^4J = 1.4 Hz, aryl-H), 7.46 (s, 1 H, aryl-H), 7.40-7.43 (m, 3 H, aryl-H), 4.45 (s, 4 H, aryl-CH_2-O-), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.45 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.07 (s, 1 H, ethynyl-H), 1.59 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.26-1.39 (m, 12 H, γ-,δ-,ε-CH_2), 1.21 (s, 21 H, silyl-H), 0.88 (t, 6 H, ^3J =6.8 Hz, hexyl-CH_3).

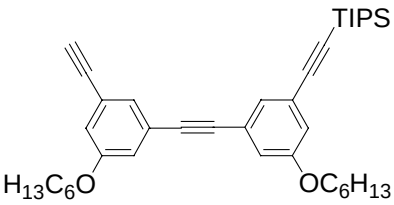
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.51, 139.34, 134.09, 130.89, 130.36, 123.93, 123.39, 123.14, 122.52, 106.01, 91.38, 89.15, 88.80, 82.69, 77.72, 71.87, 71.78, 70.79, 31.65, 29.65, 25.82, 22.60, 18.63, 14.02, 11.26.

MS (**EI**, 80 eV, 160°C): m/z (%) = 612 (12.7), 611 (44.3), 610 (100.0) $[M]^+$, 569 (8.1), 568 (29.6), 567 (75.1) $[M\text{-}C_3H_7]^+$, 525 (9.4) $[M\text{-}C_6H_{13}]^+$, 511 (7.3), 510 (20.7) $[M\text{-}OC_6H_{13}]^+$, 468 (6.7), 467 (20.3) $[M\text{-}C_3H_7\text{-}OC_6H_{13}]^+$.

EA: Calc.: C:80.60 H:9.57
Found: C:80.51 H:9.45.

1-Hexoxy-3-[1-(3-hexoxy-5-ethynylphenyl)ethynyl]-5-[(triisopropylsilyl)ethynyl]benzene ***93b***

$C_{39}H_{54}O_2Si$, M = 582.94



The procedure was analogous to that described for **45b**, (**92b**: 10.2 g, 15.6 mmol; methanol: 70 ml; dichloromethane: 70 ml). The crude product was dissolved in dichloromethane (100 ml), washed with water (100 ml) and the aqueous phase extracted with dichloromethane (2 × 100 ml). The combined organic phases were dried over $MgSO_4$, and the solvent was evaporated to afford **93b** (8.87 g, 15.2 mmol, 98 %) as a brownish sirup, which crystallized to a slightly colored amorphous material.

$\mathbf{R_f}$ = 0.21 (hexane).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.21 (m, 2 H, aryl-H), 6.97-7.01 (m, 4 H, aryl-H), 3.91-3.96 (2 t, 4 H, $^3J \approx 7$ Hz, α-CH_2), 3.04 (s, 1 H, ethynyl-H), 1.75 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.32-1.43 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.89 (t, 6 H, ^3J = 6.8 Hz, hexyl-CH_3).

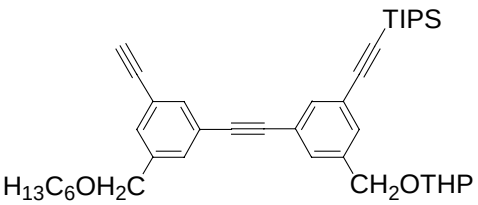
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.74, 127.64, 124.73, 124.20, 123.92, 123.30, 118.60, 118.21, 117.56, 106.08, 91.10, 88.95, 88.58, 82.77, 68.28, 31.52, 29.12, 25.65, 22.58, 18.65, 14.01, 11.29.

MS (**EI**, 80 eV, 150°C): m/z (%) = 583 (8.0), 582 (13.6) $[M]^+$, 541 (22.2), 540 (55.4), 539 (100.0) $[M\text{-}C_3H_7]^+$, 512 (6.9), 511 (15.0) $[M\text{-}C_5H_{11}]^+$, 498 (9.8), 497 (21.7) $[M\text{-}C_6H_{13}]^+$, 484 (6.7), 483 (11.8) $[M\text{-}C_5H_{11}\text{-}C_2H_4]^+$, 469 (15.3) $[M\text{-}C_6H_{13}\text{-}C_2H_4]^+$.

EA: Calc.: C:80.36 H:9.34
Found: C:80.08 H:9.12.

1-Hexoxymethyl-3-({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)-5-ethynylbenzene ***93c***

$C_{40}H_{54}O_3Si$, M = 610.95



The procedure was analogous to that described for **45b** (**92c**: 7.38 g, 10.80 mmol; dichloromethane: 125 ml; methanol: 125 ml). The solvent was evaporated, the crude product dissolved in

dichloromethane (200 ml) and washed with aqueous NaCl (200 ml). The crude product was purified by chromatography over silica gel (hexane/ethyl acetate + a few drops of triethylamine) to afford **93c** (5.69 g, 9.33 mmol, 86 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.63 (hexane/ethyl acetate 10:1).

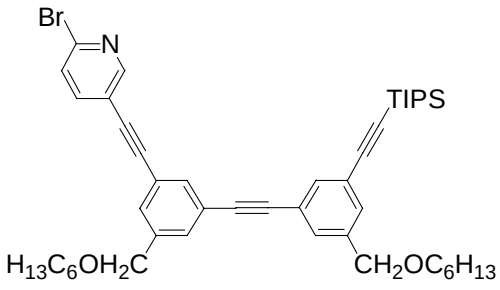
^{1}H-NMR (270 MHz, $CDCl_3$): δ = 7.54 (d, 2 H, ^{4}J = 1.3 Hz, aryl-H), 7.45 (s, 2 H, aryl-H), 7.40 (m, 2 H, aryl-H), 4.68-4.75 (m, 2 H, benzyl (THP)-H, THP-2-H), 4.43-4.52 (m, 3 H, benzyl (THP)-H', benzyl (hexyl)-H), 3.85-3.93 (m, 1 H, THP-6-H), 3.51-3.57 (m, 1 H, THP-6'-H), 3.45 (t, 2 H, ^{3}J = 6.7 Hz, hexyl-α-CH_2), 3.07 (s, 1 H, ethynyl-H), 1.58-1.84 (m, 8 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.29-1.40 (m, 6 H, hexyl-γ-, δ-, ε-CH_2), 1.11 (s, 21 H, TIPS-H), 0.88 (t, 3 H, ^{3}J = 6.6 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 139.52, 138.92, 134.15, 134.08, 131.08, 130.89, 130.82, 130.57, 123.92, 123.37, 123.17, 122.52, 105.99, 97.83, 91.45, 89.14, 88.82, 82.68, 77.74, 71.77, 70.80, 67.82, 62.08, 31.64, 30.45, 29.65, 25.81, 25.40, 22.59, 19.25, 18.63, 14.01, 11.26.

MS (**EI**, 80 eV, 230°C): m/z (%) = 610 (3.7), 609 (5.7) $[M-H]^+$, 569 (13.0), 568 (39.5), 567 (84.7), 566 (32.2), 565 (1.9) $[M-C_3H_7]^+$, 512 (5.4), 511 (14.2), 510 (45.2), 509 (100.0), 508 (2.3) $[M-C_5H_9O_2]^+$.

EA: Calc.: C:78.64 H:8.91
Found: C:78.81 H:8.67.

2-Bromo-5-{[3-hexoxymethyl-5-({3-hexoxymethyl-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}pyridine ***94a***



$C_{46}H_{60}BrNO_2Si$, M = 766.97

The procedure was analogous to that described for **43b** (**59**:[31] 7.47 g, 26.32 mmol; 74: 16.08 g, 26.32 mmol; CuI: 150 mg, 0.79 mmol; $Pd[P(Ph_3)]_4$: 912 mg, 0.79 mmol, triethylamine: 270 ml; reaction time: 3 days). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **94a** (14.79 g, 19.28 mmol, 73 %) as a yellow sirup, which slowly crystallized.

$\mathbf{R_f}$ = 0.13 (hexane/ethyl acetate 50:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.49 (d, 1 H, ^{4}J = 2.1 Hz, py-6-H), 7.62 (dd, 1 H, ^{3}J = 8.3 Hz, ^{4}J = 2.3 Hz, py-4-H), 7.59 (t, 1 H, ^{4}J = 1.2 Hz, phenyl-H), 7.53 (s, 1 H, phenyl-H),

7.45-7.48 (m, 3 H, py-2-H, 2 phenyl-H), 7.43 (s, 1 H, phenyl-H), 7.40 (s, 1 H, phenyl-H) 4.47 (s, 2 H, aryl-CH_2-O-), 4.44 (s, 2 H, aryl-CH_2-O-), 3.47 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 3.46 (t, 2 H, ^3J = 6.6 Hz, α-CH_2), 1.58-1.64 (m, 4 H, β-CH_2), 1.28-1.39 (m, 12 H, γ-,δ-,ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.87 (t, 6 H, ^3J =6.8 Hz, hexyl-CH_3).

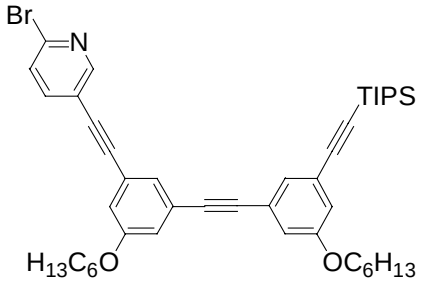
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 152.34, 141.21, 120.46, 139.74, 139.36, 134.08, 133.59, 130.94, 130.32, 127.64, 123.93, 123.59, 123.06, 122.56, 119.43, 105.96, 93.03, 91.42, 89.38, 88.68, 85.21, 71.84, 71.75, 70.87, 70.78, 31.62, 29.63, 25.80, 22.58, 18.61, 14.00, 11.24.

MS (**EI**, 80 eV, 155°C): m/z (%) = 769 (1.5), 768 (4.7), 767 (9.1), 766 (4.3), 765 (7.1) $[M]^+$, 727 (3.6), 726 (14.5), 725 (44.3), 724 (100.0), 723 (47.6), 723 (83.6) $[M\text{-}C_3H_7]^+$, 696 (1.6), 694 (1.5) $[M\text{-}C_5H_{11}]^+$, 683 (1.8), 682 (3.9), 681 (2.1), 680 (4.1) $[M\text{-}C_6H_{13}]^+$, 668 (1.0), 667 (1.7), 666 (1.1), 665 (1.2) $[M\text{-}OC_6H_{13}]^+$.

EA:	Calc.:	C:72.04	H:7.88	N:1.83
	Found:	C:72.00	H:7.63	N:1.72.

2-Bromo-5-{[3-hexoxy-5-({3-hexoxy-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)phenyl]-ethynyl}pyridine ***94b***

$C_{44}H_{56}BrNO_2Si$, M = 738.92



The procedure was analogous to that described for **43b** (**59**:[31] 4.32 g, 15.2 mmol; **93b**: 8.87 g, 15.2 mmol; CuI: 87 mg, 0.46 mmol; $Pd[P(Ph_3)]_4$: 527 mg, 0.46 mmol; triehtylamine: 150 ml; reaction time: 3 days). The crude product was purified by column chromatography (silica gel, hexane/toluene) to afford **94b** (9.88 g, 13.88 mmol, 88 %) as a yellow sirup, which crystallized to an amorphous material.

R_f = 0.48 (hexane/ethyl acetate 30:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.48 (d, 1 H, ^4J = 2.3 Hz, py-6-H), 7.62 (dd, 1 H, ^3J = 8.3 Hz, ^4J = 2.4 Hz, py-4-H), 7.45 (d, 1 H, ^3J = 8.3 Hz, py-3-H), 7.27 (s, 1 H, phenyl-H), 7.21 (s, 1 H, phenyl-H), 6.97-7.04 (m, 4 H, phenyl-H), 3.96 (t, 2 H, ^3J = 6.3 Hz, α-CH_2), 3.94 (t, 2 H, ^3J = 6.3 Hz, α-CH_2), 1.77 (m, 4 H, β-CH_2), 1.32-1.46 (m, 12 H, γ-, δ-, ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.89 (t, 6 H, ^3J = 6.7, -CH_3).

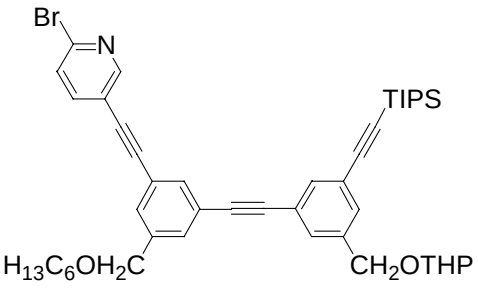
^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 158.90, 158.74, 152.39, 141.23, 140.52, 127.68, 127.19, 124.75, 124.42, 123.85, 119.47, 118.60, 118.40, 117.95, 117.58, 106.05, 92.12, 91.14, 89.17, 88.48, 84.92, 68.34, 68.25, 31.51, 29.10, 25.64, 22.58, 18.64, 14.01, 11.27.

MS (**EI**, 80 eV, 100°C): m/z (%) = 741 (2.6), 740 (6.3), 739 (13.1), 738 (7.3), 737 (12.5) $[M]^+$, 699 (3.8), 698 (17.9), 697 (48.7), 696 (100.0), 695 (43.1), 694 (84.8) $[M\text{-}C_3H_7]^+$, 668 (3.9), 666 (4.0) $[M\text{-}C_5H_{11}]^+$, 655 (2.9), 654 (8.2), 653 (3.9), 652 (6.5) $[M\text{-}C_6H_{13}]^+$, 640 (3.9), 638 (3.5) $[M\text{-}C_6H_{13}\text{-}C_2H_4]^+$.

EA:	Calc.:	C:71.52	H:7.64	N:1.90
	Found:	C:71.34	H:7.74	N:1.65.

2-Bromo-5-{[3-hexoxymethyl-5-({3-(tetrahydropyran-2-yloxymethyl)-5-[(triisopropylsilyl)ethynyl]phenyl}ethynyl)phenyl]ethynyl}pyridine ***94c***

$C_{45}H_{56}BrO_3NSi$, M = 766.93



The procedure was analogous to that described for **43b** (**59**:[31] 2.54 g, 8.94 mmol; **93c**: 5.46 g, 8.94 mmol; CuI: 51 mg, 0.27 mmol; $Pd[P(Ph_3)]_4$: 310 mg, 0.27 mmol; triethylamine: 100 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (silica gel, hexane/ethyl acetate) to afford **94c** (6.37 g, 8.31 mmol, 93 %) as a yellow sirup.

$\mathbf{R_f}$ = 0.42 (hexane/ethyl acetate 10:1).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.49 (d, 1 H, ^{4}J = 2.4 Hz, py-6-H), 7.62 (dd, 1 H, ^{3}J = 8.3 Hz, ^{4}J = 2.4 Hz, py-4-H), 7.60 (t, 1 H, ^{4}J = 1.4 Hz, phenyl-H), 7.54 (t, 1 H, J = 1.3 Hz, phenyl-H), 7.46-7.49 (m, 4 H, py-3-H, phenyl-H), 7.41 (s, 1 H, phenyl-H), 4.68-4.75 (m, 2 H, benzyl (THP)-H, THP-2-H), 4.47 (s, 2 H, benzyl (hexyl)-H), 4.45 (d, 1 H, ^{2}J ≈ 13 Hz, benzyl (THP)-H'), 3.85-3.94 (m, 1 H, THP-6-H), 3.51-3.59 (m, 1 H, THP-6'-H), 3.47 (t, 2 H, ^{3}J = 6.6 Hz, hexyl-α-CH_2), 1.52-1.84 (m, 8 H, THP-3,3',4,4',5,5'-H, hexyl-β-CH_2), 1.29-1.39 (m, 6 H, hexyl-γ-, δ-, ε-CH_2), 1.11 (s, 21 H, silyl-H), 0.87 (t, 3 H, ^{3}J = 6.8 Hz, hexyl-CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 152.29, 141.17, 140.41, 139.71, 138.90, 134.10, 133.55, 131.07, 130.91, 130.50, 130.28, 127.59, 123.89, 123.53, 123.05, 122.52, 119.38, 105.91, 97.79, 92.99, 91.45, 89.33, 88.68, 85.19, 71.70, 70.83, 67.76, 62.04, 31.58, 30.49, 29.59, 25.76, 25.23, 22.55, 19.21, 18.58, 13.97, 11.21.

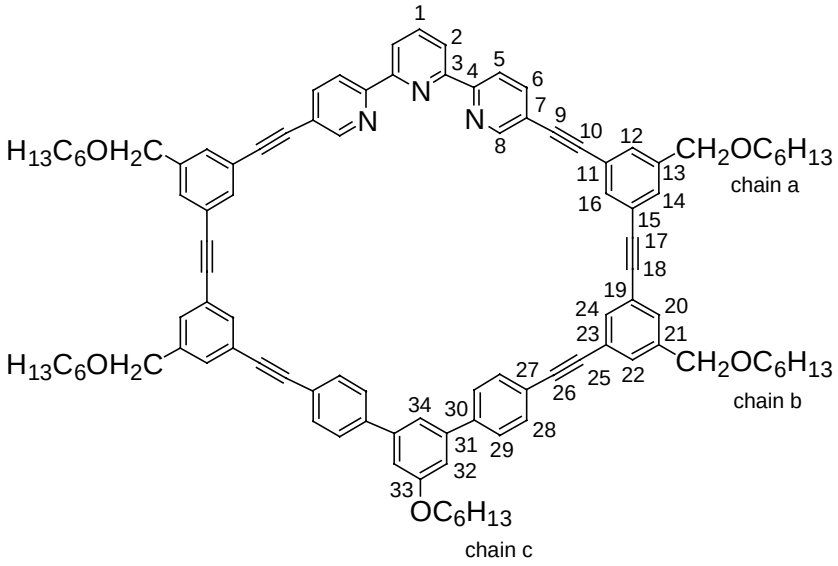
MS (**EI**, 80 eV, 120°C): m/z (%) = 767 (0.2), 766 (0.5), 765 (0.3), 764 (0.4) $[M]^+/[M\text{-}H]^+$, 727 (0.4), 726 (2.1), 725 (6.6), 724 (21.5), 723 (42.3), 722 (20.9), 721 (43.9) $[M\text{-}C_3H_7]^+/[M\text{-}H\text{-}C_3H_7]^+$, 682 (10.2), 681 (6.4), 680 (10.1) $[M\text{-}C_6H_{13}]^+$, 667 (11.2), 666 (24.6), 665 (12.5),

664 (22.3) $[M\text{-}C_5H_8O_2]^+/[M\text{-}H\text{-}C_5H_8O_2]^+$, 641 (13.1), 640 (42.3), 639 (99.2), 638 (45.0), 637 (100.0) $[M\text{-}C_7H_{11}O_2]^+/[M\text{-}H\text{-}C_7H_{11}O_2]^+$.

EA:	Calc.:	C:70.48	H:7.35	N:1.83
	Found:	C:70.35	H:7.30	N:1.72.

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 ***95a***

$C_{103}H_{105}N_3O_5$, M = 1464.98



The procedure was analogous to that described for **88** (**74a**: 549 mg, 0.944 mmol; **91a**: 1.08 g, 0.944 mmol; $Pd[P(Ph_3)]_4$: 87 mg, 0.076 mmol; CuI: 14 mg, 0.076 mmol; toluene/triethylamine: 700 ml, 1:1). The raw product (1.48 g, solid after freeze-drying) was worked up by preparative GPC to give cycle **95a** (290 mg, 0.20 mmol, 21 %) and cyclic oligomer **[95a]$_2$** (132 mg, 0.043 mmol, 9 %) as yellow, amorphous materials after freeze-drying.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.64 (s, 2 H, 8-H), 8.48 (d, 2 H, ^{3}J = 7.5 Hz, 5-H), 8.33 (d, 2 H, ^{3}J = 7.5 Hz, 2-H), 7.82 (t, 1 H, ^{3}J = 8.0 Hz, 1-H), 7.79 (d, 2 H, ^{3}J = 7.0 Hz, 6-H), 7.53 (d, 4 H, ^{3}J = 7.5 Hz, 29-H), 7.50 (s, 4 H, H-16, H-24), 7.45 (d, 4 H, ^{3}J = 7.5 Hz, 28-H), 7.37 (s, 1 H, 34-H, overlayed with H-12 etc.), 7.37, 7.31, 7.26 (3 s, 8 H, 12-H, 14-H, 20-H, 22-H), 6.95 (s, 2 H, 32-H), 4.47, 4.37 (2s, 8 H, aryl-CH_2 (a,b-chain)), 3.97 (t, 2 H, ^{3}J = 6.5 Hz, α-CH_2 (c-chain)), 3.54, 3.51 (2 t, 8 H, ^{3}J = 6.5 Hz, α-CH_2 (a,b-chain)), 1.82 (quintet, 2 H, ^{3}J =

7.0 Hz, β-CH_2 (c-chain)), 1.69 (sextet, 8 H, $^3J \approx 6$ Hz, β-CH_2 (a,b-chain)), 1.48 (quintet, 2 H, $^3J \approx 7$ Hz, γ-CH_2 (c-chain)), 1.36-1.48 (m, 28 H, γ-CH_2 (a,b-chain), δ,ε-CH_2 (a,b,c-chain)), 0.93-0.98 (m, 15 H, -CH_3 (a,b,c-chain)).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 159.89 (33-C), 154.42, 154.24 (3-C, 4-C), 151.16 (8-C), 141.38 (31-C), 140.14 (30-C), 139.41, 139.25 (13-C, 21-C), 139.18 (6-C), 137.52 (1-C), 134.18, 134.09 (16-C, 24-C), 131.97 (28-C), 130.19, 129.95 (2 signals), 129.76 (12-C, 14-C, 20-C, 22-C), 126.67 (29-C), 123.61, 123.46, 123.21, 122.98 (11-C, 15-C, 19-C, 23-C), 122.10 (27-C), 121.15 (2-C), 120.18 (5-C), 119.98 (7-C), 117.50 (34-C), 111.98 (32-C), 92.70, 89.40, 89.29, 89.01 (10-C, 17-C, 18-C, 25-C), 89.80 (26-C), 87.06 (9-C), 71.94, 71.89 (aryl-CH_2 (a,b-chain)), 70.92, 70.84 (α-C (a,b-chain)), 68.06 (α-C (c-chain)), 31.70 (δ-C (a,b-chain)), 31.66 (δ-C (c-chain)), 29.72 (β-C (a,b-chain)), 29.36 (β-C (c-chain)), 25.88 (γ-C (a,b-chain)), 25.80 (γ-C (c-chain)), 22.63 (ε-C (a,b,c-chain)), 14.04 (methyl-C (a,b,c-chain)).

MS (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1465 $[M+H]^+$.

MS (**MALDI**, THA): m/z (%) = 1478.86 $[M+CH_3]^+$, 1464.90 $[M+H]^+$, 1392.77 $[M-C_5H_{11}]^+$, 1378.78 $[M-C_6H_{13}]^+$.

Cyclic oligomer ***[95a]$_2$***

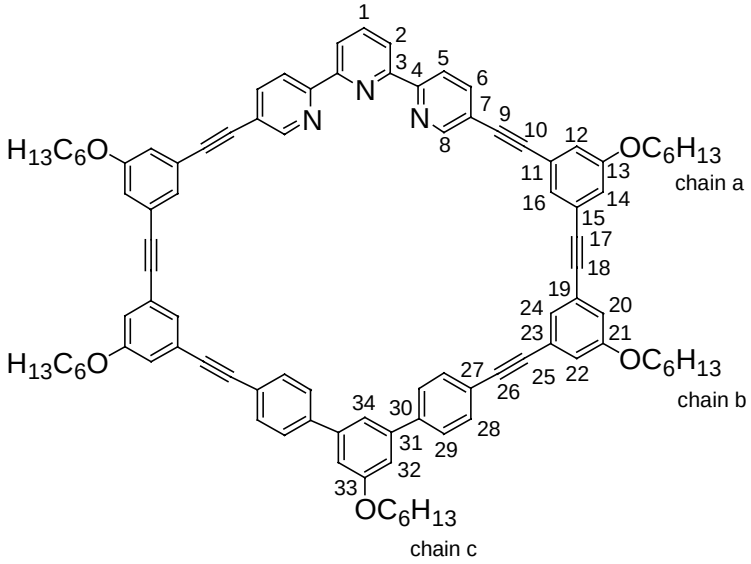
$C_{206}H_{210}N_6O_{10}$, M = 2929.96

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.79 (s, 4 H), 8.61 (d, 4 H, ^3J = 8.0 Hz), 8.45 (d, 4 H, ^3J = 7.5 Hz), 7.92-7.95 (m, 6 H), 7.61-7.65 (m, 24 H), 7.46-7.49 (m, 8 H), 7.38 (s, 4 H), 7.10 (s, 6 H), 4.50 (s, 8 H), 4.49 (s, 8 H), 4.05 (t, 4 H, ^3J = 6.0 Hz), 3.50 (t, 8 H, ^3J = 6.5 Hz), 3.49 (t, 8 H, ^3J = 6.5 Hz), 1.82 (quintett, 4 H, ^3J = 7.0 Hz), 1.63-1.68 (m, 16 H), 1.47-1.49 (m, 4 H), 1.27-1.47 (m, 56 H), 0.87-0.91 (m, 30 H).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 160.04, 154.85, 154.66, 151.58, 142.22, 140.95, 139.68, 139.57, 139.27, 137.89, 133.83, 132.08, 130.67, 130.42, 130.25, 127.15, 123.71, 123.54, 123.37, 123.03, 122.21, 121.49, 120.38, 120.11, 118.35, 112.51, 92.70, 89.92, 89.34, 88.98, 87.01, 71.91, 71.86, 70.90, 70.85, 68.25, 31.66, 31.57, 29.68, 29.29, 25.84, 25.74, 22.61, 14.03.

MS (**MALDI**, THA): m/z (%) = 2952.60 $[M+Na]^+$, 2944.66 $[M+CH_3]^+$, 2930.77 $[M+H]^+$, 2844.89 $[M-C_6H_{13}]^+$.

15,22,33,44,51-Pentakis(hexyloxy)-8,58,72-triaza-undecacyclo[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 ***95b***



$C_{99}H_{97}N_3O_5$, M = 1408.87

The procedure was analogous to that described for **88** (**74a**: 48 mg, 0.083 mmol; **91b**: 90 mg, 0.083 mmol; Pd[P(Ph_3)]$_4$: 8 mg, 0.007 mmol; CuI:1.3 mg, 0.007 mmol; toluene/triethylamine: 60 ml, 1:1) From the brownish raw product (110 mg, solid after freeze-drying), cycle **95b** (25 mg, 0.018 mmol, 21 %) and oligomer **[95b]$_2$** (14 mg, 0.005 mmol, 12 %) were isolated as yellow, amorphous materials by preparative GPC.

^{1}H-NMR (500 MHz, d^8-THF, 320 K): δ = 8.95 (d, 2 H, ^{4}J = 1.5 Hz, 8-H), 8.90 (d, 2 H, ^{3}J = 8.0 Hz, 5-H), 8.70 (d, 2 H, ^{3}J = 7.5 Hz, 2-H), 8.18 (dd, 2 H, ^{3}J = 8.0 Hz, ^{4}J = 2.0 Hz, 6-H), 8.15 (t, 1 H, ^{3}J = 7.5 Hz, 1-H), 7.94 (d, 4 H, ^{3}J = 8.5 Hz, 29-H), 7.77 (d, 4 H, ^{3}J = 8.5 Hz, 28-H), 7.75 (m, 1 H, 34-H), 7.53 and 7.50 (2 s, 4 H, H-16, H-24), 7.38 (s, 2 H, 32-H), 7.29, 7.25, 7.24 and 7.20 (4 s, 8 H, 12-H, 14-H, 20-H, 22-H), 4.29 (t, 2 H, ^{3}J = 6.0 Hz, α-CH_2 (c-chain)), 4.23 and 4.21 (2 t, 8 H, ^{3}J = 6.5 Hz, α-CH_2 (a,b-chain)), 1.97-2.01 (m, 10 H, β-CH_2 (a,b,c-chain)), 1.70 (s br, 10 H, γ-CH_2 (a,b,c-chain)), 1.57 (s br, 20 H, δ,ε-CH_2 (a,b,c-chain)), 1.11 (t, 15 H, ^{3}J = 7.0 Hz, -CH_3 (a,b,c-chain)).

^{13}C-NMR (125.8 MHz, d^8-THF, 320 K): δ = 161.31 (33-C), 160.15 (13-C, 21-C), 155.79 (4-C), 155.57 (3-C), 152.06 (8-C), 142.59 (31-C), 141.67 (30-C), 140.04 (6-C), 138.43 (1-C), 132.69 (28-C), 128.52 and 128.39 (16-C, 24-C), 127.73 (29-C), 125.59, 125.33, 125.10 and 124.93 (11-C, 15-C, 19-C, 23-C), 123.06 (27-C), 122.10 (2-C), 120.94 (5-C), 118.57, 118.30 and 118.13 (12-C, 14-C, 20-C, 22-C, 34-C), 113.06 (32-C), 93.32, 89.91, 89.79 and 89.48

(10-C, 17-C, 18-C, 25-C), 90.33 (26-C), 87.50 (9-C), 69.11 (α-C (a,b-hexyl)), 68.83 (α-C (c-hexyl)), 32.40 (δ-C (a,b,c-hexyl)), 30.25 (β-C (c-hexyl)), 30.01 (β-C (a,b-hexyl)), 26.62 (γ-C (c-hexyl)), 26.49 (γ-C (a,b-hexyl)), 23.35 (ε-C (a,b,c-hexyl)), 14.17 (methyl-C (a,b,c-hexyl)); 7-C could not be assigned.

MS (**FAB(+)**, MNBA/CH_2Cl_2-Matrix): m/z (%) = 1409 $[M+H]^+$.

Cyclic oligomer ***[95b]$_2$***

$C_{198}H_{194}N_6O_{10}$, M = 2817.74

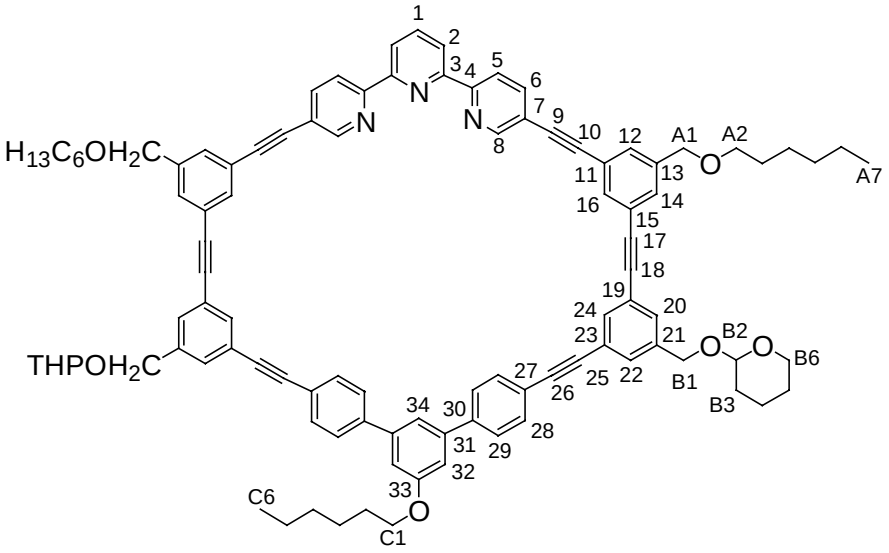
^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.75 (s, 4 H), 8.57 (d, 4 H, ^{3}J = 8.2 Hz), 8.42 (d, 4 H, ^{3}J = 8.0 Hz), 7.91-7.93 (m, 6 H), 7.60 (s br, 16 H), 7.33 (m, 6 H), 7.27 (s br, 4 H), 7.24 (s, 4 H), 7.00-7.07 (m, 16 H), 3.96 (m, 20 H), 1.78 (s br, 20 H), 1.46 (s br, 20 H), 1.23-1.34 (m, 40 H), 0.90 (s br, 30 H).

^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 159.98, 158.81, 154.73, 154.57, 151.54, 142.19, 140.89, 139.31, 137.88, 132.12, 127.44, 127.15, 124.43, 124.24, 124.09, 123.72, 122.15, 121.44, 120.36, 120.07, 118.36, 118.09, 117.72, 112.40, 92.78, 89.48, 89.08, 88.77, 86.68, 68.25, 31.55, 29.69, 29.11, 25.68, 22.62, 22.00, 14.07.

MS (**MALDI**, THA): m/z (%) = 2943.81 $[M+CH_3]^+$, 2929.02 $[M+H]^+$.

15,51-Bis(hexoxymethyl)-22,24-di-(tetrahydropyran-2-yloxymethyl)-8,58,72-triaza-undecacyclo[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 ***95c***

$C_{101}H_{97}N_3O_7$, M = 1464.89



The procedure was analogous to that described for **88** (**74a**: 307 mg, 0.527 mmol; **91c**: 600 mg, 0.527 mmol; toluene/triethylamine: 260 ml/260 ml; $Pd[P(Ph_3)]_4$: 49 mg, 0.042 mmol; CuI: 8 mg, 0.042 mmol). From the brownish raw product (850 mg, solid after freeze-drying), cycle **95c** and oligomer **[95c]$_2$** were isolated by preparative GPC. These were dissolved in THF (ca. 5 ml), precipitated with methanol (ca. 8 ml), centrifugated, and the solvent layer taken off. This procedure was repeated once, to afford **95c** (135 mg, 0.092 mmol, 18 %) and **[95c]$_2$** (38 mg, 0.013 mmol, 5 %) as yellow, amorphous materials after freeze-drying.

^{1}H-NMR (500 MHz, $CDCl_3$, 293 K): δ = 8.53 (s, 2 H, 8-H), 8.37 (d, 2 H, ^{3}J = 7.5 Hz, 5-H), 8.24 (d, 2 H, ^{3}J = 7.5 Hz, 2-H), 7.74 (t, 1 H, ^{3}J = 7.5 Hz, 1-H), 7.67 (d, 2 H, ^{3}J = 7.5 Hz, 6-H), 7.45 (d, 4 H, ^{3}J = 7.2 Hz, 29-H), 7.38 (s, 4 H, H-16, H-24), 7.35 (d, 4 H, ^{3}J = 7.2 Hz, 28-H), 7.31 (s, 3 H, 34-H and 12-H or 14-H), 7.28 and 7.29 (2 s, 4 H, 12-H or 14-H, and 20-H or 22-H), 7.23 (s, 2 H, 20-H or 22-H), 6.85 (s, 2 H, 32-H), 4.73 (t, 2 H, ^{3}J = 2.5 Hz, B2-H), 4.68 (d, 2 H, ^{2}J = 12.0 Hz, B1-H), 4.38 (d, 2 H, ^{2}J = 12.0 Hz, B1'-H), 4.42 (s, 4 H, A1-H), 3.94 (dt, 2 H, ^{2}J = 10.0 Hz, ^{3}J = 2.2 Hz, B6-H), 3.58-3.61 (m, 2 H, B6'-H), 3.89 (t, 2 H, ^{3}J = 5.5 Hz, C1-H), 3.51 (t, 4 H, ^{3}J = 6.5 Hz, A2-H), 1.92-1.94 (m, 2 H, B3-H), 1.72-1.82 (m, 6 H, B3'-H, C2-H, B4-H,), 1.65-1.74 (m, 6 H, A3-H, B5-H), 1.60-1.65 (m, 6 H, B4'-H, B5'-H, C3-H), 1.45-1.49 (m, 2 H, C4-H), 1.34-1.45 (m, 14 H, A4-H, A5-H, A6-H, C5-H), 0.90-0.97 (m, 9 H, A7-H, C6-H).

^{13}C-NMR (125.8 MHz, $CDCl_3$, 293 K): δ = 159.75 (33-C), 154.07 and 154.24 (3-C, 4-C), 151.04 (8-C), 141.10 (27-C or 31-C), 139.90 (30-C), 139.23 (13-C), 138.97 (6-C), 138.64 (21-C), 137.31 (1-C), 133.98 and 134.04 (16-C, 24-C), 131.88 (28-C), 129.81 and 130.06 (12-C, 14-C, 20-C, 22-C), 126.48 (29-C), 122.91, 123.10, 123.33 and 123.53 (11-C, 15-C, 19-C, 23-C), 121.97 (27-C or 31-C), 120.97 (2-C), 120.00 (5-C), 119.84 (7-C), 117.18 (34-C), 111.80 (32-C), 97.81 (B2-C), 88.95 and 92.59 (10-C, 17-C), 89.74 (26-C), 89.21 and 89.30 (18-C, 25-C), 87.04 (9-C), 71.85 (A1-C), 70.86 (A2-C), 67.85 (B1-C, C1-C), 62.02 (B6-C), 31.66 (A5-C, C5-C), 30.48 (B3-C), 29.67 (A3-C), 29.33 (C2-C), 25.83 (A4-C), 25.76 (C3-C), 25.42 (B5-C), 22.60 (A6-C, C4-C), 19.27 (B4-C), 14.01 (A7-C, C6-C).

MS (**MALDI**, THA): m/z (%) = 1562.58 $[M+C_5H_7O_2]^+$, 1486.68 $[M+Na]^+$, 1464.51 $[M+H]^+$.

*Cyclic oligomer **[95c]$_2$***

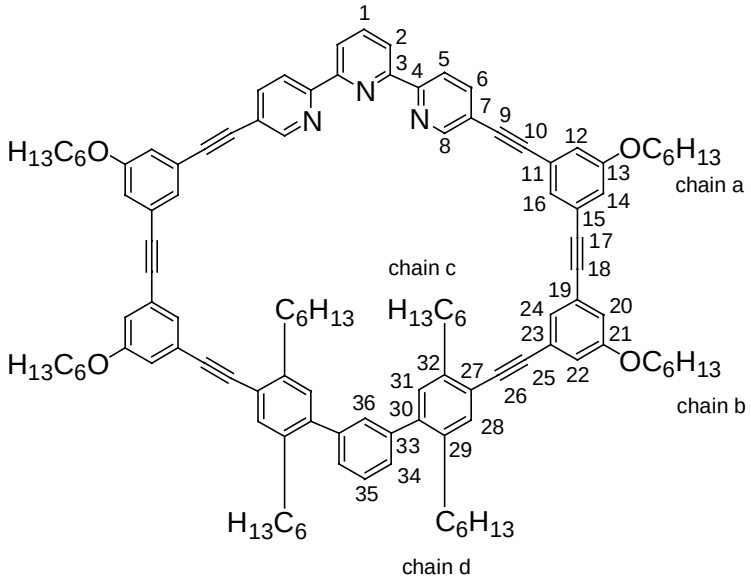
$C_{202}H_{194}N_6O_{14}$, M = 2929.78

^{1}H-NMR (500 MHz, $CDCl_3$,): δ = 8.78 (d, 2 H, ^{4}J = 1.5 Hz), 8.60 (d, 2 H, ^{3}J = 7.5 Hz), 8.46 (d, 2 H, ^{3}J = 7.5 Hz), 7.93-7.98 (m, 3 H), 7.66 (t, 2 H, ^{4}J = 1.5 Hz), 7.57-7.65 (m, 10 H), 7.51 (s br, 2 H), 7.44-7.49 (m, 6 H), 7.37 (t, 1 H, ^{4}J = 1.0 Hz), 7.09 (d, 2 H, ^{4}J = 1.5 Hz), 4.77 (d,

2 H, ^2J = 12.0 Hz), 4.73 (t, 2 H, ^3J = 3.5 Hz), 4.49 (s, 4 H), 4.48 (d, 2 H, ^2J = 13.0 Hz), 4.04 (t, 2 H, ^3J = 6.5 Hz), 3.91 (dt, 2 H, ^2J = 10.0 Hz, ^3J = 2.5 Hz), 3.55-3.59 (m, 2 H), 3.48 (t, 4 H, ^3J = 7.0 Hz), 1.85-1.91 (m, 2 H), 1.54-1.83 (m, 18 H), 1.44-1.52 (m, 2 H), 1.27-1.40 (m, 14 H), 0.87-0.92 (m, 9 H).

MS (**MALDI**, THA): m/z (%) = 2990.44 $[M+Cu]^+$, 2950.45 $[M+Na]^+$, 2928.55 $[M+H]^+$.

28,37,63,66-Tetrahexyl-15,22,44,51-tetrakis(hexoxy)-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 ***95d***



$C_{117}H_{133}N_3O_4$, M = 1645.35

The procedure was analogous to that described for **88** (**91b**: 160 mg, 0.15 mmol; **74b**: 121 mg, 0.15 mmol; CuI: 2.3 mg, 0.01 mmol; $Pd[P(Ph_3)]_4$: 14 mg, 0.01 mmol; toluene: 150 ml; triethylamine: 150 ml; 4 days at 60°C, 2 days at 75°C). Cycle **95d** was isolated as a yellow, amorphous material (42 mg, 0.026 mmol, 17 %) by preparative GPC.

^{1}H-NMR (500 MHz, $CDCl_3$, 310 K): δ = 8.82 (dd, 2 H, ^4J = 1.0 Hz, ^5J = 0.5 Hz, 8-H), 8.64 (d, 2 H, ^3J = 8.5 Hz, ^4J = 1.0 Hz, 5-H), 8.48 (d, 2 H, ^3J = 8.0 Hz, 2-H), 7.96 (dd, 2 H, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 6-H), 7.95 (t, 1 H, ^3J = 8.0 Hz, 1-H), 7.45 (s, 2 H, 28-H; t, 1 H, ^3J = 7.5 Hz, 35-H), 7.39 (t, 2 H, ^4J = 1.5 Hz, 16-H), 7.34 (t, 2 H, ^4J = 1.3 Hz, 24-H), 7.33 (dd, 2 H, ^3J = 7.3 Hz, ^4J = 1.8 Hz, 34-H), 7.26 (t, 1 H, ^4J = 2.0 Hz, 36-H), 7.12 (s, 2 H, 31-H), 7.08 (dd, 2 H, ^4J = 1.5 Hz, ^4J = 2.5 Hz, 14-H), 7.06 (dd, 2 H, ^4J = 1.5 Hz, ^4J = 2.5 Hz, 12-H), 7.05 (dd, 2 H, ^4J = 1.0 Hz, ^4J = 2.5 Hz, 22-H), 7.03 (dd, 2 H, ^4J = 1.5 Hz, ^4J = 2.5 Hz, 14-H), 4.01 (2 t, 8 H, ^3J = 6.5 Hz, α-CH_2 (a,b-chain)), 2.85 (t, 4 H, ^3J = 7.5 Hz, α-CH_2 (c-chain)), 2.62 (t, 4 H,

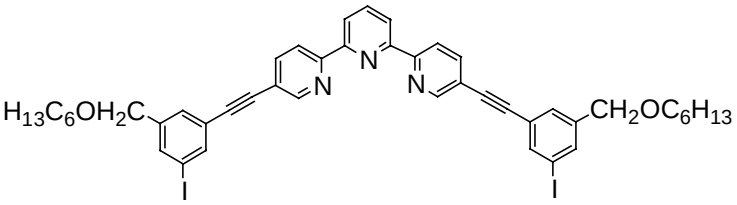
^3J = 7.5 Hz, α-CH_2 (d-chain)), 1.83 (2 quintets, 8 H, ^3J = 6.5 Hz, β-CH_2 (a,b-chain)), 1.79 (quintet, 4 H, ^3J = 7.5 Hz, β-CH_2 (c-chain)), 1.42-1.52 (m, 16 H, γ-CH_2 (a,b,c-chain), β-CH_2 (d-chain)), 1.32-1.40 and 1.18-1.28 (m, 20 H, and m, 16 H, all other -CH_2), 0.93 (t, 12 H, ^3J = 7.5 Hz, 4 -CH_3), 0.90 (t, 6 H, ^3J = 7.0 Hz, 2 -CH_3), 0.84 (t, 6 H, ^3J = 7.0 Hz, 2 -CH_3).

^{13}C-NMR (125.8 MHz, $CDCl_3$, 293 K): δ = 158.90 and 158.87 (13-C and 21-C), 154.67 (4-C), 154.44 (3-C), 151.25 (8-C), 142.38 (32-C), 141.92 (30-C), 141.34 (33-C), 139.62 (6-C), 137.97 (1-C), 137.70 (29-C), 132.96 (28-C), 130.51 (31-C), 130.14 (36-C), 128.04 (16-C), 127.82 (24-C), 127.65 (35-C), 127.51 (34-C), 124.87 and 124.00 (19-C and 23-C), 124.27 and 123.72 (11-C and 15-C), 121.44 (2-C), 121.14 (27-C), 120.49 (5-C), 120.13 (7-C), 117.86 (14-C), 117.48 (12-C), 117.39 (20-C), 117.04 (22-C), 92.90 (10-C), 91.60 (25-C), 89.18 (18-C), 88.74 (17-C and 26-C), 86.67 (9-C), 68.29 and 68.22 (α-C (a,b-chain)), 34.38 (α-C (c-chain)), 32.54 (α-C (d-chain)), 31.78, 31.53, 31.21, 30.88, 29.40, 29.14, 29.10, 25.66, 22.71, 22.60, 22.49 (all other CH_2-C), 14.18, 14.06, 14.05 (methyl-C (a,b,c,d-chain)).

MS (**FAB(+)**, MNBA/DMSO/CH_2Cl_2-Matrix): m/z (%) = 1646 $[M+H]^+$.

5,5‘‘-Bis[3-hexoxymethyl-5-iodophenyl)ethynyl]-2,2‘:6‘,2‘‘-terpyridine ***97***

$C_{45}H_{45}I_2N_3O_2$, M = 913.68



The procedure was analogous to that described for **43b** (**63**: 191 mg, 0.68 mmol; **96**:[28] 3.0 g, 6.82 mmol; CuI: 13 mg, 0.068 mmol; $Pd[P(Ph_3)]_4$: 79 mg, 0.068 mmol; triethylamine: 30 ml; toluene: 30 ml; reaction time: 3 days; reaction temperature: 60°C). The crude product was purified by column chromatography (aluminium oxide, hexane/ethyl acetate) to afford **97** (370 mg, 0.40 mmol, 60 %) as a yellow amorphous material. Most of **96** (2.33 g, 5.29 mmol, 78 %) was regained.

$\mathbf{R_f}$ = 0.44 (hexane/ethyl acetate 10:1, aluminium oxide).

^{1}H-NMR (270 MHz, $CDCl_3$): δ = 8.79 (d, 2 H, ^4J = 1.7 Hz, tpy-6,6‘‘-H), 8.60 (d, 2 H, ^3J = 8.3 Hz, tpy-3,3‘‘-H), 8.46 (d, 2 H, ^3J = 7.8 Hz, tpy-3‘,5‘-H), 7.96 (t, 1 H, ^3J = 7.8 Hz, tpy-4‘-H), 7.93 (dd, 2 H, ^3J = 8.3 Hz, ^4J = 2.1 Hz, tpy-4,4‘‘-H), 7.83 (t, 2 H, ^4J = 1.3 Hz, phenyl-H), 7.68 (s, 2 H, phenyl-H), 7.49 (s, 2 H, phenyl-H), 4.44 (s, 4 H, benzyl-H), 3.47 (t, 4 H, ^3J = 6.6 Hz, α-CH_2), 1.62 (quintet, 4 H, $^3J \approx 7$ Hz, β-CH_2), 1.23-1.42 (m, 12 H, γ-,δ-,ε-CH_2), 0.88 (t, 6 H, ^3J = 6.8 Hz, -CH_3).

^{13}C-NMR (67.9 MHz, $CDCl_3$): δ = 154.56, 154.22, 151.36, 140.98, 138.84, 137.56, 136.33, 129.46, 124.25, 121.32, 120.03, 119.58, 93.70, 91.63, 87.48, 71.15, 70.76, 31.49, 29.47, 25.67, 22.48, 13.97.

MS (**EI**, 80 eV, 140°C): m/z (%) = 915 (13.3), 914 (49.6), 913 (100.0) $[M]^+$, 828 (7.7) $[M-C_6H_{13}]^+$, 814 (9.7), 813 (21.4) $[M-OC_6H_{12}]^+$, 787 (7.0) $[M-I]^+$.

EA:	Calc.:	C:59.16	H:4.96	N:4.60
	Found:	C:59.12	H:4.77	N:4.62.