Synthesis of Soluble, Linear Trisphenanthrolines

Michael Schmittel,* Christoph Michel, Andreas Wiegrefe

Center of Micro and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Strasse, 57068 Siegen, Germany
Fax +49(271)7403270; E-mail: schmittel@chemie.uni-siegen.de

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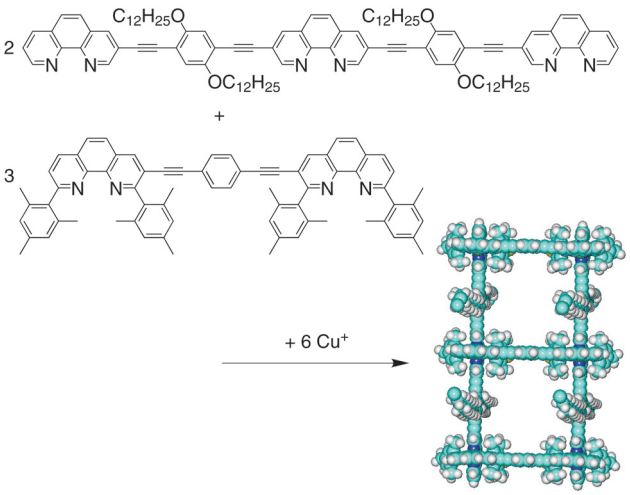
Abstract: The preparation of several soluble, linear trisphenanthrolines is described. The ligands are designed along the HETPHEN concept as precursors for heteroleptic bisphenanthroline metal ion complexes. Hence, they are important building blocks for various supramolecular structures, such as nanogrids, nanoladders and nanotubes.

Key words: coupling, grid nanostructures, palladium catalysis, phenanthroline ligands, supramolecular chemistry

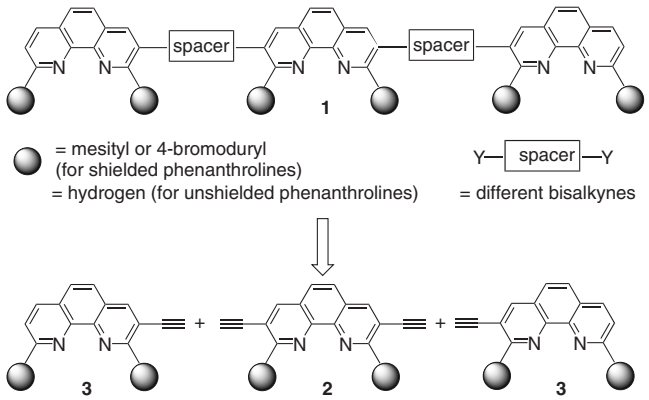
The last decade has witnessed an unparalleled chase for discrete, nanoscale supramolecular aggregates, such as nanogrids,[1] nanoclusters,[2] nanorods and several other nanoscaffolds/nanostructures,[3,4] built by modern methods of self-assembly strategies. Amongst all approaches, metal coordination and hydrogen bonding motifs are the most celebrated and effective tools to furnish such state-of-the-art supramolecular architectures.[5] Structurally rich aggregates based on metal coordination, however, are only practicable when sufficient control over heteroleptic metal-ligand binding is provided. In this context, we have recently engineered approaches to various heteroleptic bisphenanthroline metal units (metals: Cu^{I}, Ag^{I} and Zn^{II}) as core modules[6] to steer quantitative self-assembly processes to multiligand nanoaggregates with 2–6 nm dimensions.[7–9]

The conceptual heart of our strategy to heteroleptic metal modules is the HETPHEN concept[6] (heteroleptic bisphenanthroline metal complex) defining exactly the structural algorithms that have to be imbedded into phenanthroline ligands, i.e. the 2,9-disubstitution with various bulky aryl groups. While so far linear, flexible and cyclic bisphenanthrolines[10] have been exploited in our group, we have recently turned our interest to linear trisphenanthrolines. Such ligands have a large potential for the construction of heteroleptic nanostructures, such as [2 × 3] and [3 × 3] grids, triple decker structures and nanoladders. The first examples of [2 × 3] nanogrids have been communicated recently by our group (Scheme 1).[9]

As shown in Scheme 1, one set of the phenanthroline binding sites has to be sterically shielded by bulky 2,9-aryl substituents if the HETPHEN concept is applied.[6] As a benefit of the 2,9-disubstition the solubility of the notoriously less soluble phenanthroline derivatives is notably increased.[10] As counterpart for such a HEPTPHEN ligand, also the unshielded bis- or oligophenanthroline has to be available. Hence, we describe herein the preparation of six soluble, linear trisphenanthrolines with shielded or unshielded binding sites. While related unshielded linear trisbipyridines have been described in a communication,[11] details of the experimental procedure are still lacking.



Scheme 1 Formation of [2 × 3] nanogrids from linear trisphenanthrolines and bisphenanthrolines in the presence of copper(I) ions.[9]



Scheme 2 Retrosynthetic analysis.

The retrosynthetic analysis indicates that for the construction of trisphenanthrolines **1** the alkynyl substituted phenanthrolines **2** and **3** are required (Scheme 2).

While the terminal component **3** had been described earlier[10] to be available from the reaction sequence 3-bro-

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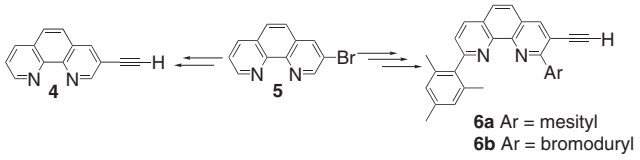
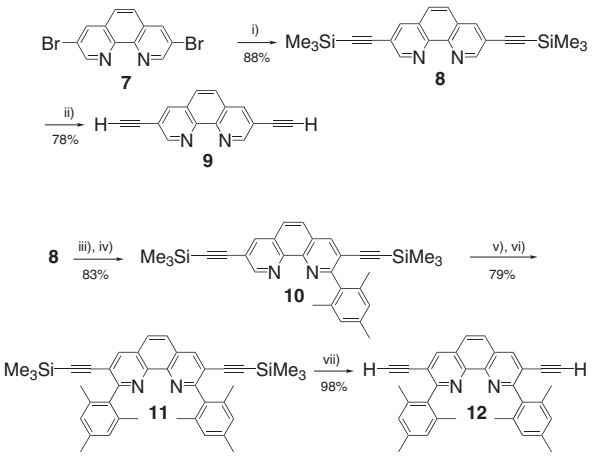


Scheme 3 Important building blocks as prepared according to recent references.[10,12]

mophenanthroline (**5**) to **6a**,**b** (Scheme 3), the bisalkynyl unit **12** had to be accessed for the first time. For the synthesis of **12** we reacted 3,8-dibromophenanthroline (**7**) along the established Sonogashira–Hagihara protocol[13] to furnish **8** in 88% yield. Mesityl groups were subsequently attached in 2- and 9-position by a stepwise nucleophilic substitution according to Sauvage.[14] The primary addition product was isolated and oxidized with activated MnO_2 to afford the monosubstituted phenanthroline **10**. In the next substitution step, a second mesityl group was introduced in 9-position following the same protocol as mentioned above.

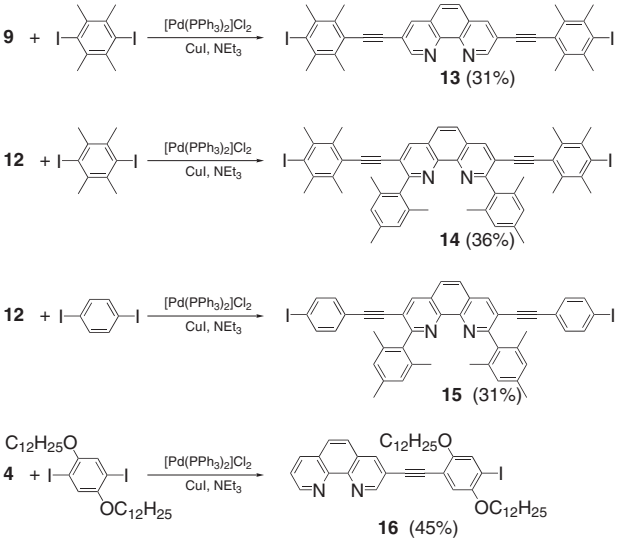
After deprotection of **8** and **11** with aqueous KOH we obtained the free alkynes **9** and **12** (Scheme 4) that both can be used as central building blocks for the construction of various trisphenanthrolines.



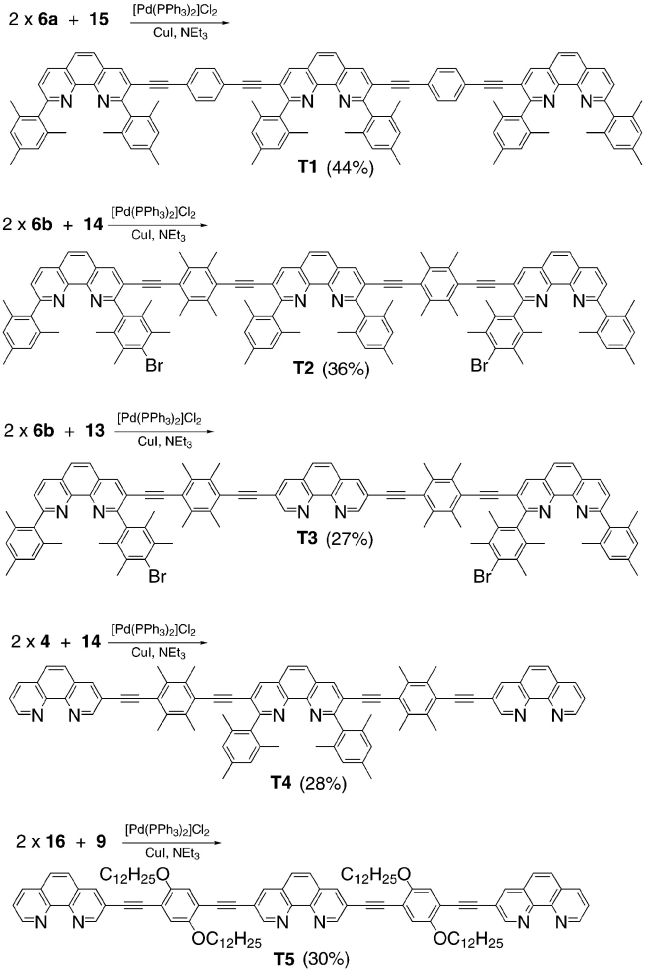
Scheme 4 i) HC≡C(TMS), $[PdCl_2(PPh_3)_2]$, CuI, benzene, NEt_3, 80–90 °C, 2 d; ii) KOH (aq); iii) MesBr, *n*-BuLi, Et_2O, r.t.; iv) H_2O, MnO_2, CH_2Cl_2, 20 h; v) MesBr, *n*-BuLi, Et_2O, r.t.; vi) MnO_2; vii) KOH (aq).

Pd-catalyzed Sonogashira–Hagihara couplings[15] of **4**, **9** and **12** with various 1,4-diiodobenzenes afforded the corresponding phenanthrolines **13**–**16** in yields from 31–45% (Scheme 5). To monitor the reaction progress it was most helpful to use ESI–MS spectroscopy. Isolation of the pure phenanthrolines was readily achieved by column chromatography and subsequent recrystallization from cyclohexane.

For the construction of the different trisphenanthrolines we followed each time the same strategy. Using Sonogashira–Hagihara coupling conditions {$[PdCl_2(PPh_3)_2]$, CuI, benzene, Et_3N, 80–90 °C, 24 h} we combined the



Scheme 5

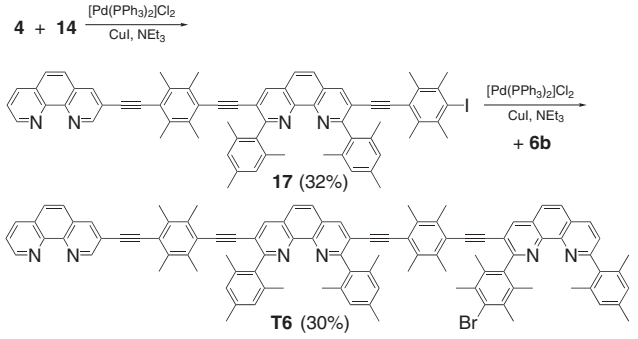


Scheme 6

various central phenanthroline units **13**–**15** with the different terminal units **4**, **6**, and **16**. As a result, we were able to receive the trisphenanthrolines **T1**–**T5** in yields from 27–44% (Scheme 6). For best yields, the reaction progress should be monitored by ESI–MS spectroscopy. Isolation

of the pure phenanthrolines was achieved after column chromatography.

As a reference we also synthesized the unsymmetrical trisphenanthroline **T6** that combines a sterically encumbered phenanthroline with an unhindered one. It can be prepared by Sonogashira–Hagihara coupling from the reaction of **14** with phenanthroline **4** affording **17** that was further reacted with **6b** (Scheme 7).



Scheme 7

It is widely accepted that bipyridine and phenanthroline binding sites are very useful in ligands due to their good coordinating behavior towards different metal ions.[16] This suggests to use **T1**–**T6** in various applications leading potentially to tunable fluorophores[17] and photoactive wires.[18,19] Moreover, they should be useful building blocks in metallosupramolecular chemistry.[20] Indeed, the ability of the new ligands **T1**–**T6** to form supramolecular coordination compounds is under intense investigation in our laboratories and has already led to the preparation of novel nanogrids,[9] nanotubes and nanoladders. The resulting complexes undergo useful light- and/or redox-induced processes. It is hence to be expected that **T1**–**T6** will find ample use in interesting applications.

In summary, a method for the convergent preparation of differently substituted trisphenanthrolines has been developed. As a key step the coupling of various diiodo compounds with substituted ethynylphenanthrolines was used.

All reagents were commercially available and used without further purification. The solvents were dried using the appropriate desiccants and distilled prior to use (CH_2Cl_2 from P_2O_5, MeCN from P_2O_5 and NaH, DMSO from calcium hydride under reduced pressure). ^{1}H NMR spectra were recorded on either Bruker AC 200 (200 MHz) or Bruker AVANCE 400 (400 MHz) spectrometers (using the deuterated solvent as the lock and residual solvent as the internal reference). IR spectra were recorded on a Perkin-Elmer (1605 and 1750 FT-IR). Microanalyses were carried out with a EuroEA 3000 CHNS of EuroVector. Electrospray mass spectra (ESI–MS) were recorded using a ThermoQuest LCQ Deca from Finnigan. Samples were dissolved in CH_2Cl_2 and were continuously infused through a syringe pump into the ion source at a flow rate of 10–15 μL min^{-1}. The extraction cone voltage (Vc) was at 10–20 V to avoid fragmentations. Preparative column chromatography and TLC were done on SiO_2 (silica gel 60 F_{254}, Merck). The degree of lithiation could readily be monitored by GC, while progress of substitution at phenanthroline is best controlled by ESI-MS. 3-Ethynyl[1,10]phenanthroline (**4**)[12] and **6a,b**[10] were prepared as described earlier. 3,8-Diethynyl[1,10]phenanthroline (**9**) has been described earlier, but without providing a complete set of spectral data.[21]

3,8-Bis(trimethylsilanylethynyl)-[1,10]phenanthroline (8)

A mixture of $[PdCl_2(PPh_3)_2]$ (315 mg, 450 μmol) and CuI (523 mg, 1.79 mmol) was added to a solution of **7** (2.42 g, 7.16 mmol), trimethylsilanylethyne (25.0 g, 43.4 mmol) and anhyd Et_3N (15 mL) in benzene (50 mL). After refluxing the mixture for 2 d under N_2 the solvent was evaporated. The black residue was dissolved in CH_2Cl_2 (150 mL), washed with 2% KCN solution (100 mL), water (100 mL) and dried over $MgSO_4$. The residue was purified by column chromatography (SiO_2, CH_2Cl_2, Et_2O, R_f 0.97) and recrystallized from $CHCl_3$. Yield: 2.53 g (6.30 mmol, 88%); a colorless solid; mp 183 °C.

IR (KBr): 3045 (s), 2956 (s), 2897 (w), 2154 (s), 1610 (w), 1482 (m), 1420 (s), 1316 (w), 1250 (s), 1171 (m), 1112 (m), 985 (m), 910 (m), 846 (m), 795 (m), 731 (m), 644 (s), 543 (w) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.31 (s, 18 H, 3′-H), 7.73 (s, 2 H, 5-H, 6-H), 8.31 (d, *J* = 2.0 Hz, 2 H, 4-H, 7-H), 9.18 (d, *J* = 2.0 Hz, 2 H, 2-H, 9-H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.2 (C-3′), 99.9 (C-1′), 101.6 (C-2′), 119.6 (C-3, C-8), 126.8 (C-4a, C-6a), 127.9 (C-5, C-6), 138.7 (C-4, C-7), 144.5 (C-1a, C-10a), 152.6 (C-2, C-9).

MS (ESI): *m*/*z* (%) = 373.6 (100) $[M + H]^+$.

Anal. Calcd for $C_{22}H_{24}N_2Si_2$: C, 70.91; H, 6.49; N, 7.52. Found: C, 70.57; H, 6.82; N, 7.72.

3,8-Diethynyl[1,10]phenanthroline (9)

3,8-Bis(trimethylsilanylethynyl)-[1,10]phenanthroline (**8**) (2.00 g, 5.36 mmol) was dissolved in THF (40 mL) and MeOH (40 mL) before aq KOH (1 N, 10 mL) was added. After stirring for 22 h the solution was diluted with aq NH_4Cl (40 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over $MgSO_4$. The solvents were removed yielding a colorless solid. Yield: 954 mg (4.18 mmol, 78%); a colorless solid; mp > 250 °C.

IR (KBr): 3140 (s), 2086 (w), 1588 (m), 1551 (m), 1499 (s), 1418 (s), 1264 (m), 1222 (s), 1096 (m), 904 (m), 838 (s), 729 (s) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.34 (s, 2 H, 2′-H), 7.62 (s, 2 H, 5-H, 6-H), 8.19 (d, *J* = 1.5 Hz, 2 H, 4-H, 7-H), 9.18 (d, *J* = 1.5 Hz, 2 H, 2-H, 9-H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 79.5 (C-1′), 81.1 (C-2′), 116.3 (C-3, C-8), 125.3 (C-4a, C-6a), 127.4 (C-5, C-6), 137.5 (C-4, C-7), 144.7 (C-1a, C-10a), 150.4 (C-2, C-9).

MS (ESI): *m*/*z* (%) = 229.3 (100) $[M + H]^+$.

Anal. Calcd for $C_{16}H_8N_2$: C, 84.19; H, 3.53; N, 12.27. Found: C, 84.17; H, 3.62; N, 12.12.

2-(2,4,6-Trimethylphenyl)-3,8-bis(trimethylsilanylethynyl)-[1,10]phenanthroline (10)

A 1.5 M solution of *n*-BuLi in pentane (4.00 mL, 6.00 mmol) was slowly added to a solution of 1-bromo-2,4,6-trimethylbenzene (1.19 g, 6.00 mmol) in anhyd Et_2O (50 mL) at 0 °C. The solution was allowed to stir for 1 h at 0 °C (GC control). After addition of 3,8-bis(trimethylsilanylethynyl)-[1,10]phenanthroline (**8**, 823 mg, 2.20 mmol) the solution assumed first a yellow and then a dark violet color. The mixture was stirred for 19 h at r.t. After addition of aq NH_4Cl (50 mL) the layers were separated and the aq layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were stirred with activated MnO_2 (5.0 g) for 3 h. The mixture was dried using $MgSO_4$ and filtered. After evaporation of the filtrate, the

resulting yellow solid was purified by column chromatography ($CHCl_3$, R_f 0.45). Yield: 896 mg (1.83 mmol, 83%); colorless solid; mp 255 °C.

IR (KBr): 2955 (s), 2919 (m), 2149 (s), 1613 (m), 1582 (w), 1542 (m), 1442 (m), 1402 (s), 1370 (w), 1248 (s), 1230 (s), 1185 (w), 978 (m), 920 (m), 859 (s), 758 (m), 695 (m), 643 (m) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.02 (s, 9 H, 3′-H), 0.30 (s, 9 H, 3″-H), 2.00 (s, 6 H, 7‴-H, 9‴-H), 2.31 (s, 3 H, 8‴-H), 6.88 (s, 2 H, 3‴-H, 5‴-H), 7.72 (d, *J* = 8.6 Hz, 1 H, 5-H), 7.78 (d, *J* = 8.6 Hz, 1 H, 6-H), 8.30 (d, *J* = 1.6 Hz, 1 H, 7-H), 8.35 (s, 1 H, 4-H), 9.17 (d, *J* = 1.6 Hz, 1 H, 9-H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.65 (C-3′), –0.16 (C-3″), 19.9 (C-7‴, C-9‴), 21.1 (C-8‴), 99.5 (C≡), 101.7 (C≡), 101.8 (C≡), 107.8 (C≡), 119.3, 126.3, 126.7, 126.9, 127.7 (2 ×), 128.1, 132.5, 134.1, 135.7, 137.2 (C-7), 138.6 (C-4), 144.6 (C-10a), 144.8 (C-1a), 152.6 (C-9), 163.6 (C-2).

MS (ESI): *m*/*z* (%) = 491.9 (100) $[M + H]^+$.

Anal. Calcd for $C_{31}H_{34}N_2Si_2$: C, 75.86; H, 6.98; N, 5.71. Found: C, 75.75; H, 7.17; N, 5.48.

2,9-Bis(2,4,6-trimethylphenyl)-3,8-bis(trimethylsilanylethynyl)-[1,10]phenanthroline (11)

Under an inert atmosphere a solution of 1-bromo-2,4,6-trimethylbenzene (2.77 g, 13.9 mmol) in anhyd Et_2O (100 mL) was treated dropwise with 2.5 M *n*-BuLi (7.0 mL, 17.5 mmol, solution in hexane) and stirred for 3 h at 0 °C. After addition of 2-(2,4,6-trimethylphenyl)-3,8-bis(trimethylsilanylethynyl)-[1,10]phenanthroline (**10**, 2.33 g, 4.76 mmol) the resulting purple solution was stirred for 48 h at r. t.. After hydrolysis with aq NH_4Cl (50 mL) and separation of the phases, the aq layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were stirred with activated MnO_2 (8.0 g) for 2 h. The black reaction mixture was filtered through celite, dried over $MgSO_4$ and the solvents were removed to furnish a bright yellow residue. Purification of the product was achieved by column chromatography ($CHCl_3$, R_f 0.68). The compound was recrystallized from cyclohexane. Yield: 2.29 g (3.76 mmol, 79%); colorless crystals; mp 307 °C.

IR (KBr): 2958 (s), 2906 (s), 2839 (m), 2147 (s), 1616, 1508 (m), 1438 (m), 1395 (m), 1248 (s), 1218 (m), 1180 (w), 1120 (w), 995 (w), 918 (m), 858 (s), 758 (m), 643 (m) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 0.03 (s, 18 H, 3′-H), 2.01 (s, 12 H, 7″-H, 9″-H), 2.27 (s, 6 H, 8″-H), 6.85 (s, 4 H, 3″-H, 5″-H), 7.79 (s, 2 H, 5-H, 6-H), 8.37 (s, 2 H, 4-H, 7-H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = –0.63 (C-3′), 19.9 (C-7″, C-9″), 21.1 (C-8″), 101.2 (C-1′), 101.9 (C-2′), 120.2 (C-3, C-8), 126.3 (C-4a, C-6a), 127.1 (C-3″), 127.9 (C-5, C-6), 135.7 (C-4″), 136.5 (C-2″), 137.3 (C-1″), 138.8 (C-4, C-7), 144.4 (C-1a, C-10a), 162.9 (C-2, C-9).

MS (ESI): *m*/*z* (%) = 610.0 (100) $[M + H]^+$.

Anal. Calcd for $C_{40}H_{44}N_2Si_2$: C, 78.89; H, 7.28; N, 4.60. Found: C, 78.60; H, 7.47; N, 4.44.

3,8-Diethynyl-2,9-bis(2,4,6-trimethylphenyl)-[1,10]phenanthroline (12)

2,9-Bis(2,4,6-trimethylphenyl)-3,8-bis(trimethylsilanylethynyl)-[1,10]phenanthroline (**11**, 690 mg, 1.13 mmol) was dissolved in THF (20 mL) and MeOH (20 mL) before aq KOH (1 N, 5 mL) was added. After stirring for 16 h the solution was diluted with aq NH_4Cl (20 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over $MgSO_4$. The solvents were removed. Yield: 515 mg (1.10 mmol, 98%); a colorless solid; mp > 300 °C.

IR (KBr): 3180 (s), 2965 (m), 2917 (s), 2855 (s), 2103 (s,), 1614, 1532 (m), 1451 (s), 1400 (s), 1289 (m), 1219 (m), 1147 (m), 1033 (w), 989 (s), 849 (s), 784 (m), 651 (s), 602 (s) cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.03 (s, 12 H, 7″-H, 9″-H), 2.28 (s, 6 H, 8″-H), 3.14 (s, 2 H, 2′-H), 6.88 (s, 4 H, 3″-H, 5″-H), 7.83 (s, 2 H, 5-H, 6-H), 8.46 (s, 2 H, 4-H, 7-H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.0 (C-7″, C-9″), 21.2 (C-8″), 80.5 (C-1′), 82.6 (C-2′), 119.1 (C-3, C-8), 126.3 (C-4a, C-6a), 127.1 (C-3″), 128.1 (C-5, C-6), 135.9 (C-4″), 136.4 (C-2″), 137.5 (C-1″), 140.3 (C-4, C-7), 144.8 (C-1a, C-10a), 162.2 (C-2, C-9).

MS (ESI): *m*/*z* (%) = 465.6 (100) $[M + H]^+$.

Anal. Calcd for $C_{34}H_{28}N_2 \cdot 0.5H_2O$: C, 86.22; H, 6.17; N, 5.91. Found: C, 86.57; H, 6.16; N, 5.90.

3,8-Bis(4-iodo-2,3,5,6-tetramethylphenylethynyl)-[1,10]phenanthroline (13)

Under a N_2 atmosphere a mixture of 3,8-diethynyl-[1,10]phenanthroline (**9**, 500 mg, 2.19 mmol) and 1,4-diiodo-2,3,5,6-tetramethylbenzene (8.68 g, 22.5 mmol) was dissolved in anhyd benzene (30 mL) and Et_3N (15 mL). After adding $[PdCl_2(PPh_3)_2]$ (250 mg, 352 μmol) and copper(I) iodide (250 mg, 1.32 mmol) the solution was heated for 24 h at 80 °C. The solvent was removed and the residue was dissolved in CH_2Cl_2 (150 mL). After washing with an aq solution of KCN (2 × 30 mL, 2%) and water (3 × 30 mL) the organic layer was dried ($MgSO_4$), filtered, and concentrated. Purification of the residue was effected by column chromatography first using hexane to get rid of unreacted 1,4-diiodo-2,3,5,6-tetramethylbenzene and than using CH_2Cl_2–EtOAc (95:5) [R_f 0.85]. Yield: 505 mg (678 μmol, 31%); a colorless solid; mp 281 °C (decomp).

IR (KBr): 2919, 2862, 2212 1615, 1575, 1474, 1446, 1381, 1279, 1130, 1060, 1033, 1000, 981, 910, 849, 827, 777, 648, 611, 533 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 12 H, 4′-H), 2.31 (s, 12 H, 5′-H), 7.76 (s, 2 H, 5-H, 6-H), 8.28 (d, *J* = 2.0 Hz, 2 H, 4-H, 7-H), 9.18 (d, *J* = 2.0 Hz, 2 H, 2-H, 9-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 (C-4′), 15.8 (C-5′), 88.3 (≡C), 94.3 (C–I), 94.6 (≡C), 119.9 (C-3, C-8), 122.2 (C-3′), 126.4 (C-4a, C-6a), 127.2 (C-5, C-6), 133.0 (C-8′), 136.1 (C-7′), 137. 4 (C-4, C-7), 144.6 (C-1a, C-10a), 162.4 (C-2, C-9).

MS (ESI): *m*/*z* (%) = 745.6 (100) $[M + H]^+$.

Anal. Calcd for $C_{36}H_{30}N_2I_2$: C, 58.08; H, 4.06; N, 3.76. Found: C, 57.88; H, 4.17; N, 3.94.

3,8-Bis(4-iodo-2,3,5,6-tetramethyl-phenylethynyl)-2,9-bis(2,4,6-trimethylphenyl)-[1,10]phenanthroline (14)

Under inert atmosphere 3,8-diethynyl-2,9-bis(2,4,6-trimethylphenyl)-[1,10]phenanthroline (**12**, 120 mg, 258 μmol) and 1,4-diiodo-2,3,5,6-tetramethylbenzene (1.00 g, 2.58 mmol) were dissolved in anhyd benzene (20 mL) and Et_3N (10 mL). After adding $[PdCl_2(PPh_3)_2]$ (50 mg, 70 μmol) and copper(I) iodide (50 mg, 263 μmol) the solution was heated for 28 h at 80 °C. The solvent was removed and the residue dissolved in CH_2Cl_2 (75 mL), where it was washed with an aq solution of KCN (2 × 25 mL, 2%) and water (2 × 30 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. Purification of the residue was accomplished by column chromatography first using hexane to get rid of unreacted 1,4-diiodo-2,3,5,6-tetramethylbenzene and than using CH_2Cl_2–MeOH (95:5). Yield: 91.2 mg (93 μmol, 36%); a colorless solid; mp 282 °C (decomp).

IR (KBr): 2925, 2856, 2211, 1615, 1578, 1484, 1442, 1382, 1275, 1125, 1058, 1033, 1011, 998, 917, 855, 822, 777, 655, 618, 520 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (s, 12 H, 7″-H, 9″-H), 2.22 (s, 6 H, 8″-H), 2.35 (s, 12 H, 4′-H), 2.41 (s, 12 H, 5′-H), 6.91 (s, 4 H, 3″-H, 5″-H), 7.80 (s, 2 H, 5-H, 6-H), 8.48 (s, 2 H, 4-H, 7-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 (C-4′), 15.8 (C-5′), 20.0 (C-7″, C-9″), 21.2 (C-8″), 88.3 (≡C), 94.3 (C–I), 94.6 (≡C), 119.9 (C-3, C-8), 122.2 (C-3′), 126.4 (C-4a, C-6a), 127.2 (C-5, C-6), 128.0 (C-3″), 133.0 (C-5′), 136.1 (C-4′), 136.4 (C-2″), 137. 4 (C-4, C-7), 137.5 (C-4″), 138.4 (C-1″), 144.6 (C-1a, C-10a), 162.4 (C-2, C-9).

MS (ESI): *m/z* (%) = 981.8 (100) $[M + H]^+$.

Anal. Calcd for $C_{54}H_{50}N_2I_2$: C, 66.13; H, 5.14; N, 2.86. Found: C, 66.08; H, 5.17; N, 2.78.

3,8-Bis(4-iodophenylethynyl)-2,9-bis(2,4,6-trimethylphenyl)-[1,10]phenanthroline (15)

A solution of 3,8-diethynyl-2,9-bis(2,4,6-trimethylphenyl)-[1,10]phenanthroline (**12**, 303 mg, 653 μmol) and 1,4-diiodobenzene (2.15 g, 6.53 mmol) in Et_3N (20 mL) and benzene (40 mL) was treated with $[PdCl_2(PPh_3)_2]$ (100 mg, 141 μmol) and copper(I) iodide (100 mg, 500 μmol). After the reaction mixture had been stirred for 18 h at 80 °C it was concentrated. The residue was dissolved in CH_2Cl_2 and then it was washed with an aq solution of KCN (2 × 25 mL, 2%) and water (20 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. Separation by column chromatography by increasing the polarity of the solvent (first hexane–CH_2Cl_2, then CH_2Cl_2–EtOAc, 95:5) furnished **15** [R_f 0.85 (CH_2Cl_2–EtOAc, 95/5)] besides other products. Yield: 166 mg (197 μmol, 31%); white solid; mp 262 °C (decomp).

IR (KBr): 2915, 2851, 2209, 1612, 1572, 1484, 1446, 1389, 1276, 1130, 1056, 1033, 1003, 991, 910, 847, 817, 777, 648, 608, 523 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 12 H, 7″-H, 9″-H), 2.32 (s, 6 H, 8″-H), 6.85 (d, *J* = 8.3 Hz, 4 H, 8′-H), 6.91 (s, 4 H, 3″-H, 5″-H), 7.61 (d, *J* = 8.3 Hz, 4 H, 5′-H), 7.84 (s, 2 H, 5-H, 6-H), 8.44 (s, 2 H, 4-H, 7-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (C-7″, C-9″), 21.2 (C-8″), 88.3 (≡C), 94.3 (C–I), 94.6 (≡C), 119.9 (C-3, C-8), 122.2 (C-3′), 126.4 (C-4a, C-6a), 127.2 (C-5, C-6), 128.0 (C-3″), 133.0 (C-4′), 136.1 (C-5′), 136.4 (C-2″), 137. 4 (C-4, C-7), 137.5 (C-1″), 138.4 (C-4″), 144.6 (C-1a, C-10a), 162.4 (C-2, C-9).

MS (ESI): *m/z* (%) = 869.4 (100) $[M + H]^+$.

Anal. Calcd for $C_{46}H_{34}N_2I_2 \cdot 1.5H_2O$: C, 61.69; H, 4.16; N, 3.13. Found: C, 61.68; H, 4.17; N, 2.94.

3-(2,5-Bis-dodecyloxy-4-iodo-phenylethynyl)-[1,10]phenanthroline (16)

3-Ethynyl[1,10]phenanthroline (**4**, 511 mg, 2.50 mmol), 1,4-didodecyloxy-2,5-diiodobenzene[22] (8.55 g, 12.2 mmol), copper(I) iodide (542 mg, 2.85 mmol) and $[PdCl_2(PPh_3)_2]$ (116.0 mg, 0.17 mmol) were dissolved in anhyd benzene (30 mL) and Et_3N (15 mL). After heating for 24 h at 80 °C, the solvent was removed and the residue dissolved in CH_2Cl_2 (40 mL). Thereafter, it was washed with an aq solution of KCN (2 × 25 mL, 2%) and water (20 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. Separation of **16** was achieved by column chromatography (CH_2Cl_2). Yield: 867 mg (1.12 mmol, 45%); a light yellow solid; mp > 300 °C.

IR (KBr): 3205 (s), 2202 (w), 1590 (m), 1477 (s), 1415 (s), 1261 (m), 1095 (m), 1053 (m), 1002 (s), 940 (m), 818 (s), 729 (s) cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.79 (t, *J* = 7.1 Hz, 6 H, CH_3), 1.23–1.78 (m, 40 H, CH_2), 3.96 (t, *J* = 6.1 Hz, 4 H, CH_2), 6.88 (s, 1 H, 5′-H), 7.34 (s 1 H, 2′-H), 7.60 (dd, J_1 = 8.3 Hz, J_2 = 4.1 Hz, 1 H, 8-H), 7.76 (d, *J* = 8.8 Hz, 1 H, 5-H), 7.83 (d, *J* = 8.8 Hz, 1 H, 6-H), 8.22 (dd, J_1 = 8.3 Hz, J_2 = 1.6 Hz, 1 H, 7-H), 8.34 (d, *J* = 2.2 Hz, 1 H, 4-H), 9.18 (dd, J_1 = 4.1 Hz, J_2 = 1.6 Hz, 1 H, 9-H), 9.26 (d, *J* = 2.2 Hz, 1 H, 2-H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 13.9 (CH_3), 22.2, 23.6, 25.3, 26.8, 28.0, 29.5, 29.6, 29.8, 31.2, 33.0 (CH2), 69.4 (CH_2O), 91.3 (≡C), 92.5 (C–I), 95.5 (≡C), 113.9 (C-3′), 116.5 (C-4′), 119.3 (C-3), 123.2 (C-8), 126.1 (C-4a, C-7′), 127.4 (C-1a, C-6a), 128.6 (C-5), 135.8 (C-6), 137.5 (C-7), 144.6 (C-4), 147.1 (C-10a), 149.8 (C-9), 151.4 (C-2), 152.5 (C-8′), 153.7 (C-5′).

MS (ESI): *m/z* (%) = 775.8 (100) $[M + H]^+$.

Anal. Calcd for $C_{44}H_{59}N_2IO_2$: C, 68.20; H, 7.67; N, 3.62. Found: C, 68.10; H, 7.75; N, 3.65.

3,8-Bis{4-[2,9-bis(2,4,6-trimethylphenyl)-[1,10]phenanthrolin-3-ylethynyl]phenylethynyl}-2,9-bis(2,4,6-trimethylphenyl)-[1,10]phenanthroline (T1)

Compound **15** (74.0 mg, 85.3 μmol), 2,9-bis(2,4,6-trimethylphenyl)-3-ethynyl-[1,10]phenanthroline (**6a**, 83.0 mg, 189 μmol), copper(I) iodide (26 mg, 136 μmol) and $[PdCl_2(PPh_3)_2]$ (26.0 mg, 37.0 μmol) were stirred in anhyd benzene (20 mL) and Et_3N (10 mL) under Ar at 80 °C for 20 h. The solvents were removed and the residue was dissolved in CH_2Cl_2 (50 mL). The resulting solution was washed with an aq solution of KCN (2%, 30 mL). The organic phase was dried over $MgSO_4$ and after removal of the solvent the residue was purified by column chromatography ($CHCl_3$, R_f 0.07). After recrystallization from CH_2Cl_2–hexane a yellow solid was furnished. Yield: 56.0 mg (37.5 μmol, 44%); mp > 300 °C.

IR (KBr): 2951 (s), 2917 (s), 2855 (s), 2207 (w), 1612 (m), 1579 (w), 1534 (w), 1505 (s), 1455 (s), 1401 (s), 1249 (m), 1144 (w), 1105 (w), 1064 (w), 1031 (w), 991 (w), 913 (m), 885 (w), 845 (s), 778 (w), 638 (w), 609 (w) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 12 H, 7″-H, 9″-H), 2.06 (s, 12 H, 7‴-H, 9‴-H), 2.17 (s, 12 H, 7⁗-H, 9⁗-H), 2.30 (s, 6 H, 8⁗-H), 2.34 (s, 12 H, 8″-H, 8‴-H), 6.92 (s, 12 H, 3″-H, 3‴-H, 3⁗-H, 5″-H, 5‴-H, 5⁗-H), 7.02 (s, 8 H, 4′-H, 5′-H), 7.58 (d, *J* = 8.1 Hz, 2 H, 8‴-H), 7.83 (d, *J* = 8.9 Hz, 2 H, 5‴-H), 7.85 (s, 2 H, 5-H, 6-H), 7.88 (d, *J* = 8.9 Hz, 2 H, 6‴-H), 8.29 (d, *J* = 8.1 Hz, 2 H, 7‴-H), 8.44 (s, 2 H, 4-H), 8.45 (s, 2 H, 4‴-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (C-7″, C-9″), 20.1 (C-7‴, C-9‴), 20.5 (C-7⁗, C-9⁗), 21.1 (C-8⁗), 21.2 (2 ×) (C-8″, C-8‴), 89.1 (2 ×) (C-2′, C-7′), 94.6 (C-8′), 94.9 (C-1′), 120.0 (C-8‴), 122.8, 122.9, 125.3 (2 ×), 125.8 (2 ×), 126.4, 126.9, 127.0, 127.2, 127.6, 127.9, 128.0, 128.5, 131.4 (2 ×) (C-4′, C-5′), 136.1, 136.2 (2 ×), 136.3 (2 ×), 136.8 (2 ×), 137.3, 137.4, 138.4, 138.5, 144.6, 144.7 (2 ×), 162.1 (C-9‴), 162.4 (2 ×) (C-2, C-2‴).

MS (ESI): *m/z* (%) = 1495.9 (100) $[M + H]^+$.

Anal. Calcd for $C_{110}H_{88}N_6 \cdot 0.5H_2O$: C, 87.91; H, 5.97; N, 5.59. Found: C, 87.79; H, 6.13; N, 5.53.

3,8-Bis{4-[2-(4-bromo-2,3,5,6-tetramethylphenyl)-9-(2,4,6-trimethylphenyl)-[1,10]phenanthrolin-3-ylethynyl]-(2,3,5,6-tetramethylphenylethynyl)}-2,9-bis(2,4,6-trimethylphenyl)-[1,10]phenanthroline (T2)

Compound **14** (40.0 mg, 40.8 μmol) and **6b** (43.8 mg, 82 μmol) were dissolved in benzene (10 mL) and Et_3N (5 mL). After adding $[PdCl_2(PPh_3)_2]$ (15.0 mg, 21.3 μmol) and copper(I)iodide (20.2 mg, 106 μmol) the mixture was heated at 80 °C for 24 h. The color changed from yellow to dark red. The solvents were removed. After dissolving the residue in CH_2Cl_2 (150 mL) it was washed with an aq solution of KCN (2 × 30 mL, 2%) and with water (3 × 30 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated. Purification of the product was accomplished by column chromatography (CH_2Cl_2; R_f 0.10). Recrystallization from $CHCl_3$–hexane yielded a yellow solid. Yield: 26.3 mg (14.6 μmol, 36%); mp > 300 °C.

IR (KBr): 2955 (s), 2917 (s), 2851 (s), 2209 (w), 1615 (m), 1571 (w), 1544 (w), 1505 (s), 1451 (s), 1411 (s), 1252 (m), 1144 (w),

1105 (w), 1051 (w), 1028 (w), 993 (w), 916 (m), 888 (w), 845 (s), 770 (w), 638 (w), 607 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 12 H, 7′-H, 10′-H), 1.98 (s, 12 H, 7″-H, 10″-H), 2.04 (s, 12 H, 7‴-H, 9‴-H), 2.08 (s, 12 H, 7⁗-H, 9⁗-H), 2.23 (s, 6 H, 8‴-H), 2.28 (s, 6 H, 8⁗-H), 2.38 (s, 12 H, 8″-H, 9″-H), 2.52 (s, 12 H, 8′-H, 9′-H), 6.91 (s, 4 H, 5‴-H, 3‴-H), 7.01 (s, 4 H, 3⁗-H, 5⁗-H), 7.47 (d, *J* = 8.0 Hz, 2 H, 8-H), 7.72 (s, 2 H, 5⁗-H, 6⁗-H) 7.84 (dd, J_1 = 9.8 Hz, J_2 = 1.8 Hz, 4 H, 5-, 6-H), 8.28 (d, *J* = 8.0 Hz, 2 H, 7-H), 8.38 (d, *J* = 2.3 Hz, 2 H, 4-H), 8.47 (s, 2 H, 4⁗-H, 7⁗-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8 (C-7′), 19.1 (C-8′), 20.0 (C-7″, C-10′), 20.3 (C-7‴, C-9‴), 20.5 (C-7⁗, C-9⁗), 20.7 (C-8″, C-9′), 21.2 (C-8⁗), 21.2 (C-8‴), 87.2 (C-9′), 88.3 (C-2′), 94.4 (C-10′), 95.0 (C-1′), 119.6 (C-8⁗) 119.7, 122.4, 122.8, 123.2, 123.9, 124.5, 125.6, 126.0, 126.8, 127.0, 127.4, 127.6, 127.9, 128.2, 128.5, 128.9, 131.2, 131.9, 134.6, 134.9, 135.2, 135.4, 136.0, 136.5, 136.8, 137.0, 137.2, 137.4, 137.6, 137.7, 138.2, 144.2, 144.9, 145.8, 146.5, 150.2, 151.9, 160.4 (C-9), 161.9 (C-2).

MS (ESI): *m*/*z* (%) = 1793.1 (100) $[M + H]^+$.

Anal. Calcd for $C_{120}H_{106}N_6Br_2 \cdot 2H_2O$: C, 78.84; H, 6.07; N, 4.60. Found: C, 78.79; H, 6.13; N, 4.49.

3,8-Bis{4-[2-(4-bromo-2,3,5,6-tetramethylphenyl)-9-(2,4,6-trimethylphenyl)-[1,10]phenanthrolin-3-ylethynyl]-(2,3,5,6-tetramethylphenylethynyl)}-[1,10]phenanthroline (T3)

Under N_2 atmosphere, **13** (75.0 mg, 100 μmol) and **6b** (107 mg, 200 μmol) were dissolved in benzene (25 mL) and Et_3N (10 mL). After adding $[PdCl_2(PPh_3)_2]$ (30.0 mg, 42.6 μmol) and copper(I) iodide (47.6 mg, 106 μmol) the mixture was heated at 80 °C for 24 h. The color changed from yellow to dark red. The solvents were removed and the residue was dissolved in CH_2Cl_2 (100 mL). Thereafter, it was washed with an aq solution of KCN (2 × 50 mL, 2%) and water (3 × 50 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated. Separation of the residue was achieved by column chromatography (CH_2Cl_2, R_f 0.22). An orange solid was furnished after recrystallization from $CHCl_3$–hexane. Yield: 41.1 mg (26.5 μmol, 27%); mp > 300 °C.

IR (KBr): 2951 (s), 2917 (s), 2855 (s), 2207 (w), 1612 (m), 1579 (w), 1534 (w), 1505 (s), 1455 (s), 1401 (s), 1249 (m), 1144 (w), 1105 (w), 1064 (w), 1031 (w), 991 (w), 913 (m), 885 (w), 845 (s), 778 (w), 638 (w), 609 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 12 H, 7′-H, 10′-H), 1.98 (s, 12 H, 7″-H, 10″-H), 2.06 (s, 12 H, 7‴-H, 9‴-H), 2.23 (s, 6 H, 8‴-H), 2.38 (s, 12 H, 8″-H, 9″-H), 2.52 (s, 12 H, 8′-H, 9′-H), 6.91 (s, 4 H, 3‴-H, 5‴-H), 7.47 (d, *J* = 8.0 Hz, 2 H, 8-H), 7.72 (s, 2 H, 5⁗-H, 6⁗-H), 7.84 (dd, J_1 = 9.8 Hz, J_2 = 1.8 Hz, 4 H, 5-H, 6-H), 8.28 (d, *J* = 8.0 Hz, 2 H, 7-H), 8.38 (d, *J* = 2.3 Hz, 2 H, 4⁗-H, 7⁗-H), 8.47 (s, 2 H, 4-H), 9.18 (d, *J* = 2.3 Hz, 2 H, 2⁗-H, 9⁗-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8 (C-7′, C-10′), 19.7 (C-8′, C-9′), 20.0 (C-7″, C-10″), 20.4 (C-7‴, C-9‴), 20.9 (C-8″, C-9″), 21.2 (C-8‴), 87.2 (C-9′), 88.3 (C-2′), 94.4 (C-10′), 95.0 (C-1′), 119.6, 119.7, 122.4, 122.8, 123.2, 124.5, 125.6, 126.0, 126.8, 127.0, 127.4, 127.6, 127.9, 128.2, 128.5, 128.9, 131.2, 131.9, 134.9, 135.2, 135.4, 136.0, 137.0, 137.2, 137.4, 137.6, 137.7, 138.2, 144.2, 144.9, 145.8, 146.5, 150.2, 152.4, 162.1 (C-9), 165.2 (C-2).

MS (ESI): *m*/*z* (%) = 1556.6 (100) $[M + H^+]$.

Anal. Calcd for $C_{102}H_{86}N_6Br_2 \cdot 2H_2O$: C, 76.97; H, 5.70; N, 5.28. Found: C, 76.79; H, 5.63; N, 5.19.

3,8-Bis{2,3,5,6-tetramethyl-4-([1,10]phenanthrolin-3-ylethynyl)-phenylethynyl}-2,9-bis-(2,4,6-trimethylphenyl)-[1,10]phenanthroline (T4)

Under N_2 atmosphere, **14** (60.0 mg, 61.2 μmol) and **4** (25.5 mg, 125 μmol) were dissolved in benzene (10 mL) and Et_3N (5 mL). After addition of $[PdCl_2(PPh_3)_2]$ (15.1 mg, 21.3 μmol) and copper(I) iodide (20.0 mg, 106 μmol) the mixture was heated at 80 °C for 24 h. The color changed from yellow to dark red. The solvent was removed and the residue was dissolved in CH_2Cl_2 (50 mL). After washings with an aq solution of KCN (2 × 20 mL, 2%) and water (3 × 20 mL), the organic layer was dried (Na_2SO_4), filtered, and concentrated. Purification of the product by column chromatography (CH_2Cl_2, R_f 0.25) and recrystallization from $CHCl_3$–hexane furnished an orange solid. Yield: 19.4 mg (17.1 μmol, 28%); mp > 300 °C.

IR (KBr): 2950 (s), 2914 (s), 2858 (s), 2212 (w), 1610 (m), 1583 (w), 1535 (w), 1507 (s), 1452 (s), 1410 (s), 1249 (m), 1144 (w), 1108 (w), 1060 (w), 1035 (w), 993 (w), 923 (m), 875 (w), 840 (s), 779 (w), 635 (w), 615 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.92 (s, 12 H, 10′-H, 11′-H), 2.01 (s, 12 H, 7″-H, 9″-H), 2.13 (s, 6 H, 8″-H), 2.30 (s, 12 H, 9′-H, 12′-H), 6.90 (s, 4 H, 3″-H, 5″-H), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 2 H, 8‴-H), 7.80 (d, *J* = 8.4 Hz, 2 H, 6‴-H), 7.85 (s, 2 H, 5-H, 6-H), 7.89 (d, *J* = 8.4 Hz, 2 H, 5‴-H), 8.26 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 2 H, 7‴-H), 8.38 (d, *J* = 1.9 Hz, 2 H, 4‴-H), 8.42 (s, 2 H, 4-H, 7-H), 9.19 (dd, J_1 = 4.4 Hz, J_2 = 1.8 Hz, 2 H, 9‴-H), 9.27 (d, *J* = 1.9 Hz, 2 H, 2‴-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.5 (C-9′, C-12′), 19.3 (C-10′, C-11′), 20.0 (C-7″, C-9″), 21.2 (C-8″), 87.7 (C-7′), 88.3 (C-2′), 94.6 (C-1′), 95 (C-8′), 119.2, 119.6, 121.8, 122.3, 122.7, 123.3, 124.6, 125.2, 126.8, 127.3, 127.4, 127.6, 127.9, 128.3, 128.5, 128.9, 131.1, 131.9, 135.8, 135.9, 137.2, 137.4, 137.6, 137.8, 138.0, 138.5, 144.8, 144.9, 145.8, 145.9, 150.5, 151.9, 160.4, 161.9 (C-2).

MS (ESI): *m*/*z* (%) = 1134.6 (100) $[M + H^+]$.

Anal. Calcd for $C_{82}H_{64}N_6 \cdot 1\,H_2O$: C, 85.53; H, 5.78; N, 7.30. Found: C, 85.41; H, 5.69; N, 7.19.

3,8-Bis{2,5-bisdodecyloxy-4-([1,10]phenanthrolin-3-ylethynyl)-phenylethynyl}-[1,10]phenanthroline (T5)

Under N_2 atmosphere, **9** (51.0 mg, 223 μmol) and **16** (348 mg, 449 μmol) were dissolved in benzene (20 mL) and Et_3N (15 mL). After addition of $[PdCl_2(PPh_3)_2]$ (15 mg, 21.5 μmol) and copper(I) iodide (20.0 mg, 106 μmol) the mixture was heated at 80 °C for 24 h. The color changed from yellow to dark red. The solvents were removed and the residue was dissolved in CH_2Cl_2. After washings with an aq solution of KCN (2 × 20 mL, 2%) and water (3 × 20 mL), the organic layer was dried (Na_2SO_4), filtered, and concentrated. Separation of the residue was accomplished by column chromatography (CH_2Cl_2–EtOAc, 90:10; R_f 0.12). Yield: 102 mg (67 μmol, 30%); a light orange solid; mp > 300 °C.

IR (KBr): 2208 (w), 1592 (m), 1477 (s), 1415 (s), 1268 (m), 1209 (s), 1095 (m), 1050 (m), 944 (m), 818 (s), 731 (s) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.1 Hz, 12 H, CH_3), 1.23–1.78 (m, 80 H, CH_2), 4.09 (t, *J* = 6.1 Hz, 8 H, OCH_2), 7.03 (s, 2 H, 4′-H), 7.05 (s, 2 H, 9′-H), 7.60 (dd, J_1 = 8.0 Hz, J_2 = 4.3 Hz, 2 H, 8-H), 7.68 (d, *J* = 8.8 Hz, 2 H, 5-H), 7.70 (s, 2 H, 5″-H, 6″-H), 7.74 (d, *J* = 8.8 Hz, 2 H, 6-H), 8.15 (dd, J_1 = 8.0 Hz, J_2 = 1.3 Hz, 2 H, 7-H), 8.20 (d, *J* = 1.8 Hz, 2 H, 4-H), 8.35 (d, *J* = 1.8 Hz, 2 H, 4″-H, 7″-H), 9.16 (dd, J_1 = 4.3 Hz, J_2 = 1.3 Hz, 2 H, 9-H), 9.20 (d, *J* = 1.8 Hz, 2 H, 2-H), 9.22 (d, *J* = 1.8 Hz, 2 H, 2″-H, 9″-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.9 (CH_2-*C*H_3), 14.5, 23.6, 26.8, 29.5 and 29.6 (overlapping signals), 30.2, 32.2, 46.5 (CH_2), 69.8 (CH_2O), 87.2 (C-7′), 88.3 (C-2′), 94.4 (C-8′), 95.0 (C-1′), 119.6, 119.7, 122.4, 122.8, 123.2, 126.8, 127.0, 127.4, 127.6, 127.9, 128.2, 128.6, 128.9, 131.2, 131.6, 131.9, 139.4, 139.5, 138.1, 138.2, 145.2, 145.5, 145.8, 146.2, 150.2, 152.4, 152.6, 155.2.

MS (ESI): *m*/*z* (%) = 1523.3 (100) $[M + H^+]$.

Anal. Calcd for $C_{104}H_{124}N_6O_4$: C, 82.06; H, 8.21; N, 5.52. Found: C, 82.09; H, 8.23; N, 5.59.

3-(4-Iodo-2,3,5,6-tetramethylphenylethynyl)-8-{2,3,5,6-tetramethyl-4-([1,10]phenanthrolin-3-ylethynyl)-phenylethynyl}-2,9-bis-(2,4,6-trimethylphenyl)-[1,10]phenanthroline (17)

Under N_2 atmosphere, **14** (60.0 mg, 61.2 μmol) and **3** (12.8 mg, 65.5 μmol) were dissolved in benzene (10 mL) and Et_3N (5 mL). After adding $[PdCl_2(PPh_3)_2]$ (7.6 mg, 10.6 μmol) and copper(I) iodide (10.0 mg, 53 μmol) the reaction mixture turned spontaneously from orange to dark red. It was heated at 80 °C for 24 h. The solvents were removed and the residue was dissolved in CH_2Cl_2 (150 mL). Thereafter it was washed with an aq solution of KCN (2 × 30 mL, 2%) and water (3 × 30 mL). The organic layer was dried (Na_2SO_4), filtered, and concentrated. Separation of the residue by column chromatography (CH_2Cl_2; R_f 0.21) and recrystallization from $CHCl_3$–hexane afforded a light yellow solid. Yield: 6.0 mg (19.5 μmol, 32%); mp 292 °C (decomp).

IR (KBr): 2931, 2846, 2222, 1617, 1575, 1484, 1441, 1388, 1264, 1125, 1048, 1033, 1010, 991, 917, 855, 822, 771, 650, 618, 525 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 6 H, CH_3), 2.04 (s, 12 H, 7″-H, 9″-H), 2.22 (s, 6 H, 8″-H), 2.30 (s, 6 H, CH_3), 2.35 (s, 6 H, CH_3), 2.41 (s, 6 H, CH_3), 6.90 (s, 4 H, 3″-H, 5″-H), 7.65 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 1 H, 8‴-H), 7.77 (d, J = 8.4 Hz, 2 H, 6-H, 6‴-H), 7.84 (d, J = 8.4 Hz, 2 H, 5-H, 5‴-H), 8.26 (dd, J_1 = 8.0 Hz, J_2 = 1.8 Hz, 1 H, 7‴-H), 8.29 (d, J = 8.3 Hz, 1 H, 7-H), 8.38 (d, J = 1.9 Hz, 1 H, 4‴-H), 8.48 (s, 1 H, 4-H), 9.21 (dd, J_1 = 4.4 Hz, J_2 = 1.8 Hz, 1 H, 9‴-H), 9.26 (d, J = 1.9 Hz, 1 H, 2‴-H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5 (CH_3), 15.8 (CH_3), 17.5 (CH_3), 19.3 (CH_3), 20.0 (C-7″, C-9″), 21.2 (C-8″), 87.7 (≡C), 88.3 (≡C), 94.3 (≡C), 94.6 (≡C), 95 (C_q-I) 119.2 (C-3‴), 119.6, 121.8, 122.4, 122.7, 123.3, 124.6, 125.2, 126.8, 127.3, 127.4, 127.6, 127.9, 128.3, 128.5, 128.9, 131.1, 131.3, 131.9, 132.5, 135.8, 135.9, 137.2, 137.4, 137.6, 137.8, 138.0, 138.5, 144.8, 144.9, 145.8, 145.9, 150.5 (C-9‴), 151.9 (C-2‴), 160.4 (C-9), 161.9 (C-2).

MS (ESI): *m/z* (%) = 1058.2 (100) $[M + H]^+$.

Anal. Calcd for $C_{68}H_{57}N_4I$: C, 77.26; H, 5.43; N, 5.30. Found: C, 77.20; H, 5.35; N, 5.17.

3-{4-[2-(4-Bromo-2,3,5,6-tetramethylphenyl)-9-(2,4,6-trimethylphenyl)-[1,10]phenanthrolin-3-ylethynyl]-2,3,5,6-tetramethylphenylethynyl}-2,9-bis(2,4,6-trimethylphenyl)-8-{2,3,5,6-tetramethyl-4-([1,10]phenanthrolin-3-ylethynyl)-phenylethynyl}-[1,10]phenanthroline (T6)

Under N_2 atmosphere, **17** (20.0 mg, 18.9 μmol) and **6b** (10.7 mg, 20.0 μmol) were dissolved in benzene (10 mL) and Et_3N (5 mL). After adding $[PdCl_2(PPh_3)_2]$ (7.6 mg, 10.7 μmol) and copper(I) iodide (10.0 mg, 53 μmol) the mixture was heated at 80 °C for 24 h. The color changed from yellow to dark red. The solvent was removed and the residue dissolved in CH_2Cl_2 (50 mL). Thereafter it was washed with an aq solution of KCN (2 × 20 mL, 2%) and with water (3 × 20 mL). The organic layer was dried (Na_2SO_4), filtered and concentrated. Separation of the residue by column chromatography (CH_2Cl_2; R_f 0.17) and recrystallization from $CHCl_3$–hexane yielded an orange solid. Yield: 8.30 mg (5.70 μmol, 30%); mp > 300 °C.

IR (KBr): 2962 (s), 2923 (s), 2858 (s), 2209 (w), 1615 (m), 1582 (w), 1533 (w), 1508 (s), 1452 (s), 1408 (s), 1244 (m), 1149 (w), 1111 (w), 1062 (w), 1039 (w), 998 (w), 921 (m), 880 (w), 839 (s), 771 (w), 619 (w) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.89 (s, 12 H, CH_3), 1.96 (s, 6 H, CH_3), 2.02 (s, 6 H, CH_3), 2.08 (s, 12 H, CH_3), 2.20 (s, 3 H, CH_3), 2.26 (s, 6 H, CH_3), 2.32 (s, 6 H, CH_3), 2.43 (s, 12 H, CH_3), 6.95 (s, 2 H, Mes-H), 7.08 (s, 4 H, Mes-H), 7.44 (d, J = 8.0 Hz, 1 H), 7.62 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 1 H), 7.70 (s, 2 H), 7.75 (d, J = 8.4 Hz, 1 H), 7.80 (dd, J_1 = 9.8 Hz, J_2 = 2.0 Hz, 2 H), 7.89 (d, J = 8.4 Hz, 1 H), 8.23 (d, J = 8.0 Hz, 1 H), 8.31 (d, J = 8.3 Hz, 1 H), 8.38 (d, J = 2.3 Hz, 2 H), 8.43 (d, J = 1.9 Hz, 1 H), 8.48 (s, 1 H, 4-H), 9.22 (dd, J_1 = 4.4 Hz, J_2 = 1.8 Hz, 1 H), 9.27 (d, J = 1.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8 (CH_3), 19.1 (CH_3), 20.0 (CH_3), 20.3 (CH_3), 20.5 (CH_3), 20.7 (CH_3), 21.2 (CH_3), 21.2 (CH_3), 87.2 (≡C), 88.3 (C≡C), 94.4 (≡C), 95.0 (≡C), 119.2, 119.4, 119.6, 122.4, 122.8, 123.2, 123.4, 123.9, 124.5, 125.6, 126.0, 126.8, 127.0, 127.2, 127.4, 127.6, 127.8, 128.0, 128.2, 128.4, 128.7, 128.9, 129.2, 131.2, 131.9, 134.6, 134.9, 135.2, 135.4, 136.0, 136.5, 136.8, 137.0, 137.2, 137.4, 137.6, 137.7, 138.2, 138.6, 138.9, 144.2, 144.9, 145.3, 145.7, 146.0, 146.5, 150.2, 151.0, 151.5, 151.9, 160.4 (C-9), 161.9 (C-2).

MS (ESI): *m/z* (%) = 1463.6 (100) $[M + H^+]$.

Anal. Calcd for $C_{101}H_{85}N_6Br$: C, 82.93; H, 5.86; N, 5.75. Found: C, 82.79; H, 5.83; N, 5.59.

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