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Rigid Bisphenanthrolines: Synthesis, Structure and Self-Assembly at a Solid–Liquid Interface

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Dedicated to Prof. Dr. Dr. h.c. mult. S. Hünig on the occasion of his 85th birthday

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Several rigid linear bisphenanthrolines with and without bulky groups at the bisimine sites were synthesized. For three representatives, the solid-state structures were elucidated. Their potential for self-assembled monolayers was explored by scanning tunneling microscopy (STM) at the solid–liquid interface, and the resulting architectures were found to be promising candidates for templating metal-ion nanopatterns.

Introduction

Various self-assembly strategies have paved the way for the exploration of structural and functional supramolecular architectures over the past decade.[1,2] Apart from hydrogen bonding as a directing supramolecular motif, the coordination driven approach has assumed a particular standing in the preparation of complex aggregates.[1,2] The latter approach most often relies on the coordination of transition-metal cations to multisite ligands, such as polypyridines, for example in oligomeric strands.

Amid the rigid, multisite ligands, oligo-2,2′-bipyridines, oligo-1,10-phenanthrolines, and oligo-terpyridines are the most commonly used systems because of their strong coordination by various metal ions and because of their rodlike shape that allows them to assemble in a predictable fashion.[3,4] While there are numerous grids[2c] amongst the known supramolecular (dynamic) motifs, racks[4e] and ladders[5] have received much less coverage because of the problems with their inherent heteroleptic construction, which cannot be solved by simply using self-recognition and positive cooperativity principles.[5] Recently, Schmittel et al. have proposed two general strategies to engineer heteroligand, metallo-supramolecular structures, using the HETPHEN[6] (*het*eroleptic *phen*anthroline complexes) and the HETTAP[7] (*het*eroleptic *t*erpyridine *a*nd *p*henanthroline complexes) concept. Ligands designed along those notions will exclusively lead to dynamic heteroleptic aggregation in solution when combined with the appropriate metal ions.

As both the HETPHEN and HETTAP concept[6,7] critically depend on the proper fine tuning of steric hindrance and π–π interactions, the linear bisphenanthrolines[8] must be equipped with bulky substituents[9] at the bisimine binding sites. Several oligo-phenanthrolines have already been prepared earlier[10] and used in the self-assembly of nanoscale structures such as heteroleptic grids,[4c] racks,[4e] ring-in-ring structures,[11] and nanobasket,[4d] nanobox,[5b] and nanoladder motifs.[7] In this paper, we present the synthesis of several new rigid bisphenanthrolines, some of which have anthracenyl and alkylaryl[6] groups as steric stoppers, their structures, and their self-assembly at the solid–liquid interface.

Results and Discussion

Synthesis of Bisphenanthrolines 5 and 6

The sterically bulky aryl groups were introduced in the 2- and 9-position of the starting phenanthroline **1a** by a stepwise protocol developed by Sauvage (Scheme 1).[12] The intermediate addition products were isolated and oxidized

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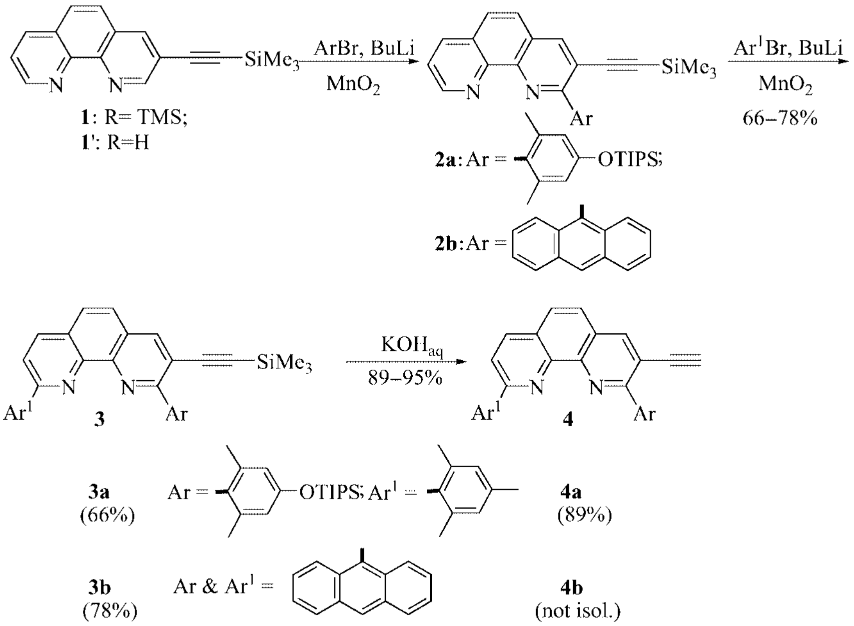
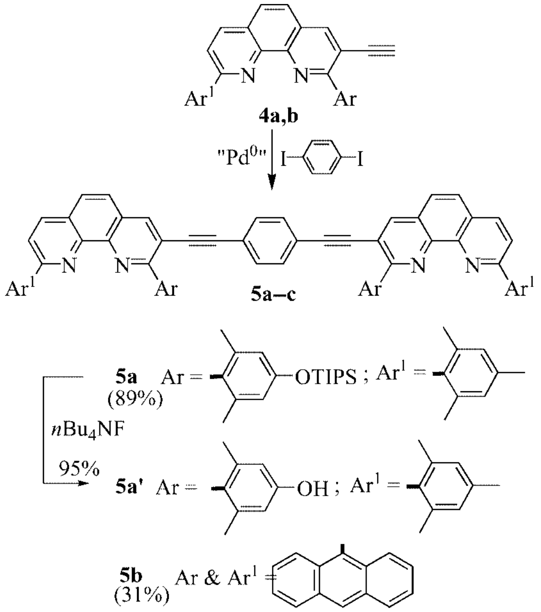


Scheme 1. Synthesis of 3-ethynylphenanthrolines **4a**,**b** as building blocks.

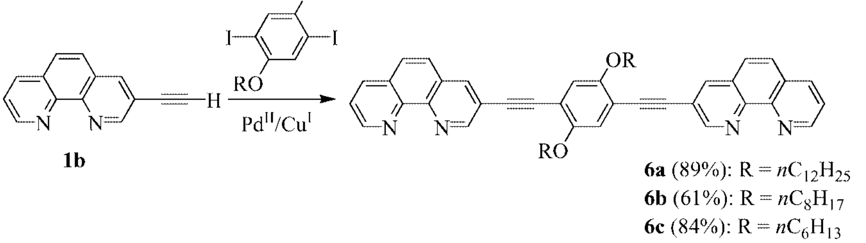
with activated manganese dioxide to afford the diarylated phenanthrolines **3a**,**b**.[13] Deprotection of **3a**,**b** with aqueous KOH afforded **4a**,**b** that served as versatile precursors for the preparation of bisphenanthrolines **5a**–**c**.

Similar to the procedure in a previous report,[10] Pd/Cu-catalyzed Sonogashira coupling[14] of **4a** and **4b** with 1,4-diiodobenzene afforded the corresponding bisphenanthrolines **5a** and **5b**, respectively, in good to moderate yields (89% and 31%, see Scheme 2). Homocoupled phenanthrolines were found in trace amounts even under stringently dry conditions. Hence, for best yields, the reaction was monitored by ESI-MS spectroscopy. Isolation of pure **5a** was readily achieved by column chromatography and subsequent recrystallization from cyclohexane. **5a′** was obtained in 95% yield by the deprotection of **5a** with Bu$_4$NF and was isolated after repeated recrystallization from DMF. The spectra of both **5a** and **5a′** show a broad fluorescence band extending up to 500 nm with discrete maxima at 391 and 411 nm. All bisphenanthrolines were characterized by ^{1}H- and ^{13}C NMR spectroscopy, ESI-MS, UV/Vis spectroscopy, and elemental analysis.

In order to realize heteroligand assemblies in combination with **5a**,**b**, as shown for multi-component grid and rack



Scheme 2. Synthesis of bisphenanthrolines **5a**,**b** by PdCl$_2$(PPh$_3$)$_2$-catalyzed Sonogashira coupling.



Scheme 3. Synthesis of 2,9-unsubstituted bisphenanthrolines **6a**–**c**.

motifs,[4c,4d] access to 2,9-unshielded phenanthroline building blocks is equally warranted.[4c] Grummt and Klemm et al.[15] have reported on the synthesis of several bisphenanthrolines, including **6a**, and their photophysical properties;[15] however, their self-assembly behavior at the solid–liquid interface and in solution had not been explored. Ligands **6a**–**c** were synthesized under similar conditions as mentioned above through a Sonogashira coupling reaction (Scheme 3).

Structures of Bisphenanthrolines 5 and 6

Bisphenanthroline **5a′** proved to be insoluble in many solvents [acetone, chlorinated solvents (sparingly soluble), nitromethane, DMSO, and acetonitrile], while it was soluble in DMF upon heating. When the DMF solution of **5a′** was cooled, suitable single crystals for X-ray crystal structure analysis were obtained (Figure 1).[16] To the best of our knowledge, **5a′** is the first single-crystal structure of this series of rigid bisphenanthrolines.

The stick and space-filling representation of **5a′** is depicted in Figure 1. Surprisingly, this molecule exhibits a *cisoid* conformation in the solid state that is most likely driven by weak intermolecular hydrogen bonding (2.8 Å) that leads to extended arrays of molecules at the intermolecular level (Figure 1c). An intramolecular hydrogen bond between the two phenolic OH groups is precluded (O···O distance: 4.84 Å). From the space-filling representation, the amount of steric bulk around the phenanthroline binding site becomes obvious. It is this shielding that prevents any homoleptic complex formation even at elevated temperatures.

Suitable single crystals of **6a**[17] (Figure 2) and **6b**[18] (Figure 3) were obtained by the slow evaporation of a dichloromethane solution. The single-crystal structure analysis of **6a** provides ample information about intermolecular packing as a result of π–π stacking ($\approx$3.5 Å) and parallel alignment of the alkyl chains (Figure 2b). In a manner similar to that of **5a′**, this molecule also crystallizes in a *cisoid* conformation. Ligands **6a** and **5a′** exhibit a length of almost 3 nm (**6a**: 26.4 Å, **5a′**: 26.4 Å) along the bisphenanthroline axis, which might be the reason why it was difficult to obtain suitable quality single crystals for this series of compounds. Intermolecular interactions between dichloromethane (solvent) and the phenanthroline bisimine site could also be noticed; however, because of the poor crystal quality, the role of the solvent was not explored in more detail.

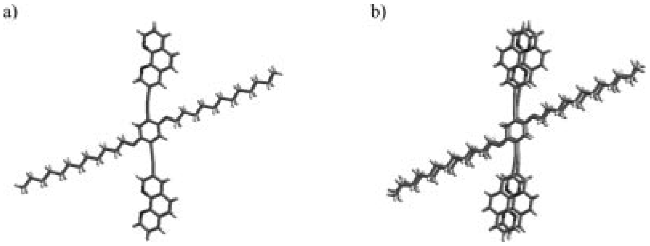


Figure 2. Single-crystal structure of **6a**: a) stick representation, b) solid-state dimer arising from intermolecular π–π stacking ($\approx$ 3.5 Å) between neighboring phenanthrolines.

The single-crystal structure of **6b** that shows a *transoid* arrangement of the two phenanthroline binding sites is represented in Figure 3. The molecule is centrosymmetric with a crystallographic inversion center at the midpoint of the central planar benzene ring. The phenanthroline group is almost planar, with a mean deviation of 0.021 Å from an

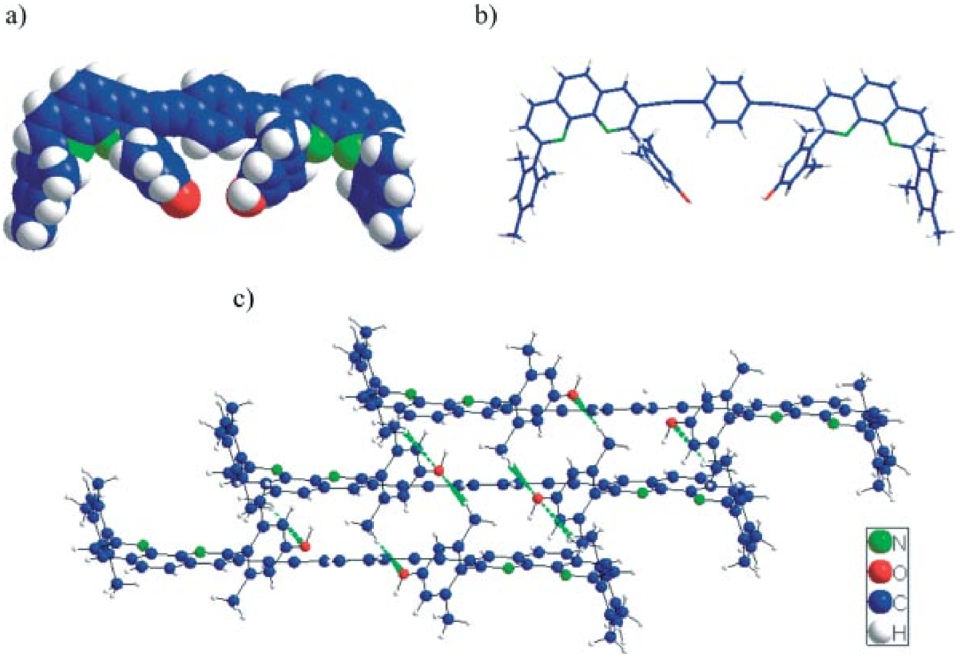


Figure 1. Single-crystal structure of **5a′**: a) space-filling representation, b) stick representation, c) intermolecular hydrogen bonding (2.8 Å).

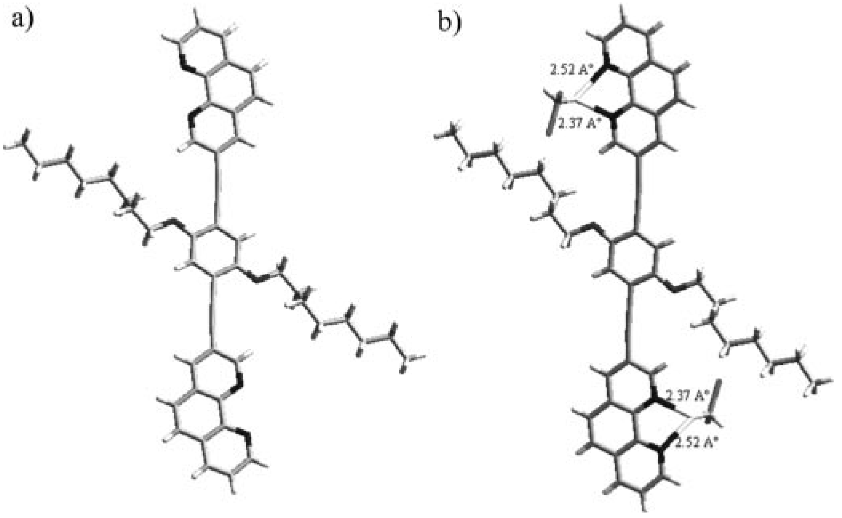


Figure 3. Single crystal structure of **6b**: a) stick representation, b) intermolecular interactions between the solvent (dichloromethane) and **6b** (N···H ≈ 2.37–2.52 Å).

ideal plane. The asymmetric unit contains dichloromethane as solvent. The dichloromethane molecule donates a weak bifurcated hydrogen bond to the nitrogen atoms N1 and N2 (Figure 3b). A similar bifurcated interaction involving a chloroform molecule was found in a 1,10-phenanthroline-3-ylethynyl compound reported by Lindner et al.[19] The solvent is also involved in six intermolecular C–H···Cl interactions with H···Cl distances between 2.93 and 3.14 Å. The crystal packing also shows a number of intermolecular π–π interactions with C···C distances between 3.39 and 3.52 Å and a number of weak intermolecular C–H···π(C) interactions.

Self-Assembly of 6 at the Solid–Liquid Interface

In recent years we have witnessed the significance of the self-assembly of organic compounds in the context of nanomaterials and nanotechnology. In particular, nanopatterning has become one of the major topics in these fields.[20] Scanning tunneling microscopy (STM) with its sub-molecular resolution has proven to be a useful technique for the analysis of self-assembled monolayers from organic molecules at solid–liquid interfaces in terms of their structural and electronic properties.[21] Several groups have investigated the patterning of organic molecules and supramolecular aggregates, such as hydrogen-bonded assemblies[22] at the solid–liquid interface. Organic molecules possessing coordinating functionalities such as pyridine,[23] bipyridine,[24] phenanthroline or terpyridine,[25] and bis(salicylidene)s[26] are of particular interest because of their potential use in preparing metallo-supramolecular aggregates.[4,23]

Recently, DeSchryver[24] and Schubert[25] have reported on the surface patterning of bipyridines and terpyridines. Ordered monolayers of these metal-coordinating ligands could potentially act as templates to generate highly ordered metal surfaces.[25,27] In the following part of the paper, we report the formation of highly ordered monolayers of two bisphenanthrolines (**6a** and **6c**) at the solid–liquid interface. Their self-assembly on surfaces is of special interest because of their photophysical properties[28] and their potential for the construction of nano-ordered metallo-supramolecular aggregates.[4]

Figure 4a and b display STM current images of highly ordered monolayers of **6a**,**c** at the solid–liquid interface between highly oriented pyrolytic graphite (HOPG) and 1,2,4-trichlorobenzene. The bright areas that correspond to a high-tunneling probability are attributed to the conjugated, rodlike parts of the molecules, since the energy differences between their frontier orbitals and the Fermi level of HOPG are rather small.[29] The two-dimensional arrangements can be described by unit cells with parameters $a = (1.39 \pm 0.07)$ nm, $b = (2.83 \pm 0.20)$ nm, and $\alpha = (75 \pm 4)^\circ$, and $a = (2.11 \pm 0.10)$ nm, $b = (2.37 \pm 0.2)$ nm, and $\alpha = (58 \pm 2)^\circ$ for **6a** and **6c**, respectively. Obviously, the length of the alkyl chains of the two derivatives drastically influences the molecular arrangement. For the longer O–C_{12} alkyl chains in **6a**, the molecules align with their long molecular axis parallel to the long unit cell vector, whose length corresponds well to the length of the rodlike part of the molecule, as illustrated in Figure 4c. The 2D-model of such an arrangement (Figure 5), however, requires that the O–C_{12} side chains are folded to fill the void between the parallel rows of bisphenanthrolines. For **6c**, rows of staggered molecules are observed, as depicted in Figure 4d. The distances between the molecules within a row and in adjacent rows are about 0.6 nm and 1.0 nm, respectively, which allows the shorter C_6 alkyl chain to extend in an all-*anti* conformation. In both cases, the distances between neighboring phenanthroline units appear large enough for the insertion and complexation of metal ions. Thus, these monolayers can be envisaged to serve as templates for the nanopatterning of surfaces with metal ions[30] in which the details of the nanopatterns can be controlled by appropriately chosen alkyl chains. The realization of such patterns will be the focus of future work.

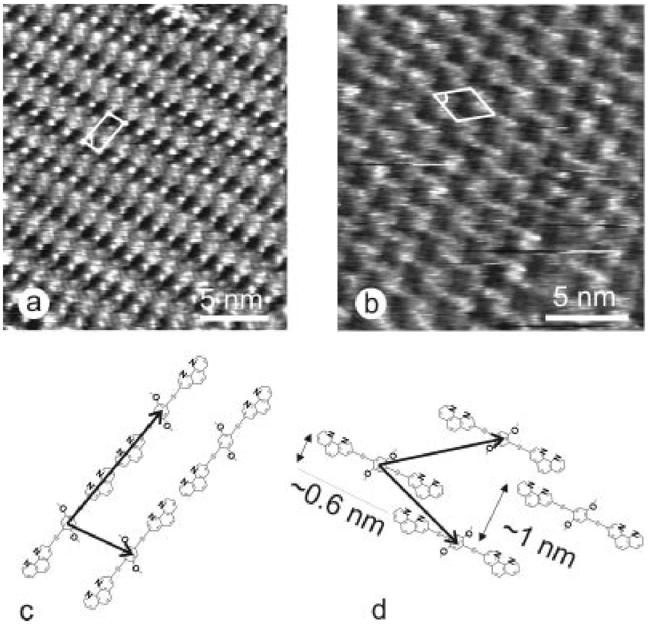


Figure 4. STM current images of highly ordered monolayers at the solid–liquid interface of (a) **6a**, and (b) **6c**. (c) and (d) are representations of the respective unit cells; the directions of the long molecular axes with respect to the unit cell are indicated. In (d), the distances between the long molecular axes of adjacent molecules are also indicated. Tunneling parameters: sample bias $U_s = -1.0$ V and average tunneling current $I_t = 330$ pA and $I_t = 80$ pA for (a) and (b), respectively.

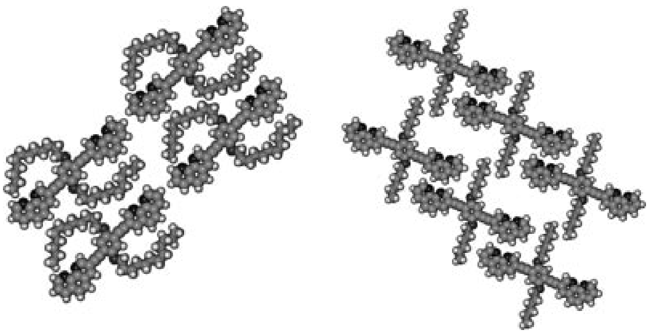


Figure 5. Visualization of the arrangement of **6a** (left) and **6c** (right) on the HOPG surface (by Hyperchem 6.02; www.hyper.com).

Conclusions

Several rigid, linear bisphenanthrolines with and without bulky aryl groups at the bisimine sites were synthesized through covalent coupling. For three representatives, the solid-state structures were elucidated. Their potential was explored for self-assembled monolayers by scanning tunneling microscopy (STM) at solid–liquid interfaces, and the resulting monolayers were found to be promising candidates for templating metal-ion nanopatterns. Future studies will focus on the surface chemistry of these ligands in the presence of metal cations and on their photophysical studies.

Experimental Section

All reagents were commercially available and used without further purification. The solvents were dried with appropriate desiccants and distilled prior to use (CH_2Cl_2 from P_2O_5, MeCN from P_2O_5, and NaH, diethyl ether from sodium). ^1H NMR spectra were recorded with Bruker AC 200 (200 MHz) and Bruker AC 400 (400 MHz) spectrometers (using the deuterated solvent as the lock and residual solvent as the internal reference). IR spectra were recorded with a Perkin–Elmer 1605 FT-IR instrument. Microanalyses were carried out with a Carlo Erba Elemental Analyzer 1106. Electrospray mass spectra (ESI-MS) were recorded using a ThermoQuest LCQ Deca. The degree of lithiation was readily monitored by GC, while progress of the substitution at phenanthroline was best controlled by ESI-MS. Compound **1** was prepared according to known procedures.[10] For a complete characterization of **6a**, see ref.[15]

STM at the solid–liquid-interface[31] was performed by using a home-built beetle-type scanning tunneling microscope, interfaced with a commercial controller (Omicron). STM tips were prepared by mechanically cutting a 0.25-mm thick Pt/Ir (80%/20%) wire. A drop of an almost saturated solution of the bisphenanthrolines in 1,2,4-trichlorobenzene was applied to the basal plane of freshly cleaved, highly oriented pyrolytic graphite (HOPG). The lattice of the underlying substrate could be visualized during measurements by simply changing the tunneling parameters to allow small tunneling impedance. This allows in-situ *x-y* calibration of the piezo-scanner and drift-correction of the images recorded.

Molecular modeling was performed with Hyperchem 6.02 (www.hyper.com).

General Procedure for the 2,9-Arylation of Phenanthrolines 1 and 2: In a typical procedure, a 2.5 M solution of *n*-butyllithium in hexane (8.30 mmol) was slowly added to a solution of the corresponding bromoarene (8.30 mmol) in diethyl ether (20 mL) at 0 °C. The solution was stirred for 4 h at room temperature, then a suspension of **1** or **2** (4.15 mmol) in diethyl ether (20 mL) was added at 0 °C over 10 min. The solution immediately turned dark violet. The mixture was stirred for 24 h at room temperature. Prolonged reaction times led to the formation of unwanted products. The additions were very sensitive to moisture. Best yields were obtained by monitoring the reaction using ESI-MS. After the reaction was complete, saturated NH_4Cl (25 mL) was added, and the layers were separated. The aqueous layer was extracted 3–4 times with dichloromethane (4×50 mL). The combined organic extracts were stirred with activated MnO_2 (83.1 mmol) for 12 h. The mixture was then filtered through Celite and dried with $MgSO_4$, and the solvents evaporated. The resulting solid was separated by column chromatography (SiO_2, initially hexane, then later dichloromethane). The products were obtained as white to pale yellow solids.

2-[2,6-Dimethyl-4-(triisopropylsilanyloxy)phenyl]-3-trimethylsilanylethynyl[1,10]phenanthroline (2a): Yield: 1.40 g (61%). ^1H NMR ($CDCl_3$, 200 MHz): δ = 9.21 (d, J = 4.5 Hz, 1 H), 8.39 (s, 1 H), 8.23 (d, J = 8.1 Hz, 1 H), 7.77 (s, 2 H), 7.59 (dd, J = 8.1, 4.5 Hz, 1 H), 6.60 (s, 2 H), 2.01 (s, 6 H), 1.16 (m, 21 H, TIPS), 0.06 (s, 9 H, TMS) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 163.8, 156.4, 151.6, 147.1, 145.8, 140.0, 139.9, 138.3, 136.8, 130.1, 127.8, 127.4, 126.8, 123.9, 121.3, 118.9 (arom.), 102.8 (2 C, ethynyl), 21.2, 19.1, 13.8, 0.49 ppm. IR (KBr): $\tilde{\nu}$ = 2945, 2868, 2152, 1601, 1466, 1397, 1319, 1249, 1160, 1047, 996, 858, 843, 812, 686, 608 cm^{-1}. ESI-MS $[C_{34}H_{44}N_2OSi_2+H]^+$: calcd. m/z = 553.3; found m/z = 553.6. $C_{34}H_{44}N_2OSi_2$ (552.90): calcd. C 73.86, H 8.02, N 5.07; found C 73.75, H 7.94, N 4.95.

2-Anthracen-9-yl-3-trimethylsilanylethynyl[1,10]phenanthroline (2b): Yield: 0.88 g (47%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 9.07 (d, *J* = 4.5 Hz, 1 H), 8.64 (s, 1 H, anthracene), 8.57 (s, 1 H), 8.31 (d, *J* = 8.4 Hz, 1 H), 8.11–8.16 (m, 2 H, anthracene), 7.95 (s, 2 H), 7.63 (dd, *J* = 8.4, 4.5 Hz, 1 H), 7.46–7.53 (m, 4 H, anthracene), 7.29–7.38 (m, 2 H, anthracene), 0.54 (s, 9 H, TMS) ppm. ^{13}C NMR (CD_2Cl_2, 50 MHz): δ = 160.4, 150.7, 139.0, 138.9, 136.0, 131.4, 130.2, 129.4, 128.5, 127.7, 127.6, 127.5 (2 C), 126.0, 125.9, 125.7, 125.6, 125.1, 123.3, 121.4 (arom.), 88.2, 77.2 (ethynyl), –1.4 ppm. ESI-MS $[C_{31}H_{24}N_2Si + H]^+$: calcd. *m*/*z* = 453.2; found *m*/*z* = 453.4. $C_{31}H_{24}N_2Si$ (452.62): calcd. C 82.26, H 5.34, N 6.19; found C 82.30, H 5.43, N 6.17.

2-[2,6-Dimethyl-4-(triisopropylsilanyloxy)phenyl]-9-(2,4,6-trimethylphenyl)-3-trimethylsilanylethynyl[1,10]phenanthroline (3a): Yield: 1.84 g (66%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.39 (s, 1 H), 8.25 (d, *J* = 8.3 Hz, 1 H), 7.81 (s, 2 H), 7.56 (d, *J* = 8.3 Hz, 1 H), 6.92 (s, 2 H), 6.57 (s, 2 H), 2.30 (s, 3 H), 2.12 (s, 6 H), 2.03 (s, 6 H), 1.21 (m, 21 H, TIPS), 0.09 (s, 9 H, TMS) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 145.3, 144.9, 142.9, 139.0, 138.1, 137.3, 136.1, 135.7, 132.8, 128.3, 128.2, 128.1, 127.6, 126.8, 126.6, 125.5, 124.7, 119.9, 118.1, 115.6 (arom.), 98.9, 94.2 (ethynyl), 20.1, 19.6, 17.9 (2 C), 12.8, –1.0 (aliph.) ppm. IR (KBr): $\tilde{\nu}$ = 3442, 2943, 2865, 2152 (*v* C≡C), 1602, 1459, 1393, 1321, 1249, 1162, 1048, 996, 858, 846, 810, 686, 641 cm^{-1}. ESI-MS $[C_{43}H_{54}N_2OSi_2 + H]^+$: calcd. *m*/*z* = 671.4; found *m*/*z* = 671.8. $C_{43}H_{54}N_2OSi_2$ (671.07): calcd. C 76.96, H 8.11, N 4.17; found C 76.65, H 8.30, N 4.01.

2,9-Dianthracen-9-yl-3-trimethylsilanylethynyl[1,10]phenanthroline (3b): Yield: 2.04 g (78%). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 8.62 (s, 1 H, phenanthroline), 8.44–8.49 (m, 2 H, anthracene), 8.35 (d, *J* = 8.3 Hz, 1 H, phenanthroline), 8.04 (s, 2 H, phenanthroline), 7.95–7.97 (m, 4 H, anthracene), 7.66–7.78 (m, 4 H, anthracene), 7.65 (d, *J* = 8.3 Hz, 1 H, phenanthroline), 7.22–7.61 (m, 8 H, anthracene), –0.41 (s, 9 H, TMS) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 161.1, 159.4, 146.7 (2 C), 145.4, 139.5 (2 C), 136.4 (2 C), 135.7 (2 C), 134.5, 133.8, 131.7 (2 C), 130.9, 128.7, 128.6 (2 C), 128.1, 127.9 (2 C), 126.8 (2 C), 126.0, 125.6, 125.3, 122.1 (arom.), 102.7 80.9 (ethynyl), –0.67 ppm. ESI-MS $[C_{45}H_{32}N_2Si + H]^+$: calcd. *m*/*z* = 629.2; found *m*/*z* (%) = 629.6 (100). $C_{45}H_{32}N_2Si$ (628.83): calcd. C 85.95, H 5.13, N 4.45; found C 85.63, H 5.07, N 4.83.

Procedures for TMS or TIPS Deprotection

TMS Deprotection: Typically, the 3-trimethylsilanylethynylphenanthroline building block (**4a**,**b**, 0.195 mmol) was first dissolved in THF/MeOH, then aqueous KOH (1 N, 10 mL) was added. After stirring for 12 h, the solution was diluted with aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were dried with $MgSO_4$, and the solvents were removed to yield a colorless solid. It was further purified by column chromatography (SiO_2, dichloromethane) to yield the product as a white crystalline material. Compound **4b** was used without further characterization in the synthesis of **5b**.

4a: Yield: 104 mg (89%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.45 (s, 1 H), 8.26 (d, *J* = 8.1 Hz, 1 H), 7.83 (br. s, 2 H), 7.57 (d, *J* = 8.1 Hz, 1 H), 6.92 (s, 2 H), 6.61 (s, 2 H), 3.06 (s, 1 H), 2.31 (s, 3 H), 2.13 (s, 6 H), 2.05 (s, 6 H), 1.24 (m, 21 H, TIPS) ppm. ^{13}C NMR ($CDCl_3$, 50 MHz): δ = 162.8, 161.4, 156.4, 146.9, 146.2, 141.3, 141.2, 138.8, 138.5, 137.2, 133.7, 129.5, 129.4, 128.5, 127.9, 127.5, 126.4, 126.3, 120.1, 119.6 (arom.), 83.1, 81.7 (ethynyl), 24.8, 21.5, 19.0 (2 C), 13.7 (aliph.) ppm. IR (KBr): $\tilde{\nu}$ = 3412, 2924, 2866, 2110 (C≡C), 1603, 1460, 1395, 1319, 1159, 1046, 884, 849, 810, 686, 639 cm^{-1}. ESI-MS $[C_{40}H_{46}N_2OSi + H]^+$: calcd. *m*/*z* = 599.3; found *m*/*z* = 599.7. $C_{40}H_{46}N_2OSi$ (598.89): calcd. C 80.22, H 7.74, N 4.68; found C 79.89, H 7.69, N 4.55.

TIPS Deprotection:[32] A solution of **5a** (200 mg, 157 µmol) and $(nBu)_4NF\cdot3H_2O$ (248 mg, 786 µmol) in a mixture of THF (12 mL) and H_2O (12 mL) was stirred for 12 h under argon at room temperature. An aqueous buffer solution (pH 7.0) was added until a solid began to precipitate. THF and water were then evaporated under vacuum. The resulting solid was washed with water several times to afford phenol **5a′** (146 mg) as a light yellow solid in 95% yield. Data for **5a′** is given below.

General Procedure for Sonagashira Coupling Reactions (5a–b, 6a–c): 3-Ethynyl-phenanthrolines **1′** or **4** (1.66 mmol), CuI (1.66 mmol), 1,4-diiodobenzenes (0.83 mmol), and $[PdCl_2(PPh_3)_2]$ (0.166 mmol) were stirred in dry benzene (15 mL) and NEt_3 (15 mL) under argon at 80 °C for 24 h. The reaction was monitored by ESI-MS or TLC. After removal of the solvents, the remaining solid was dissolved in CH_2Cl_2 and washed with aqueous KCN (50 mL, 2% w/v). The residue was purified by column chromatography (SiO_2, hexane at first and CH_2Cl_2 later) to furnish a white crystalline product.

5a: Yield: 987 mg (89%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 8.52 (s, 2 H), 8.34 (d, *J* = 8.1 Hz, 2 H), 7.89 (s, 4 H), 7.56 (d, *J* = 8.1 Hz, 2 H), 7.13 (s, 4 H, phenyl spacer), 6.93 (s, 4 H), 6.67 (s, 4 H), 2.30 (s, 6 H), 2.01 (br. s, 24 H), 1.10 (m, 42 H, TIPS) ppm. ^{13}C NMR (CD_2Cl_2, 50 MHz): δ = 161.5, 160.6, 155.5, 137.6, 137.5, 136.4, 136.2, 135.7, 131.4, 131.3, 131.1, 128.2, 128.0, 127.9, 127.7, 127.0, 126.9, 125.6, 125.0, 122.9, 119.9, 118.4 (arom.), 94.1, 88.7 (ethynyl), 20.2, 17.7 (3 C), 12.7 ppm. IR (KBr): $\tilde{\nu}$ = 3407, 3044, 2944, 2865, 1720 (C≡C), 1602, 1537, 1504, 1458, 1395, 1320, 1165, 1047, 992, 917, 885, 847, 809, 685, 637 cm^{-1}. ESI-MS $[C_{86}H_{94}N_4O_2Si_2 + H]^+$: calcd. *m*/*z* = 1271.7; found *m*/*z* (%) = 1272.0 (70). ESI-MS $[C_{86}H_{94}N_4O_2Si_2 + 2H]^{+2}$: calcd. *m*/*z* = 637.3; found *m*/*z* (%) = 637.4 (100). $C_{86}H_{94}N_4O_2Si_2\cdot\frac{3}{4}CH_2Cl_2$ (1335.56): calcd. C 78.01, H 7.21, N 4.20; found C 78.26, H 7.64, N 3.97.

5a′: ^{1}H NMR ([D$_7$]DMF, 200 MHz): δ = 9.52 (s, 2 H, –OH), 8.86 (s, 2 H), 8.64 (d, *J* = 8.1 Hz, 2 H), 8.16 (s, 4 H), 7.76 (d, *J* = 8.1 Hz, 2 H), 7.28 (s, 4 H, phenyl spacer), 6.97 (s, 4 H), 6.68 (s, 4 H), 2.31 (s, 6 H), 2.03 (s, 12 H), 2.01 (s, 12 H) ppm. ^{13}C NMR ([D$_7$]DMF, 50 MHz): δ = 163.1, 162.5 (2 C), 161.9, 161.8, 160.7, 157.9, 145.4, 138.8 (2 C), 137.7, 137.6, 137.1, 135.9, 132.6, 131.9, 128.4, 127.5 (2 C), 123.3, 119.9, 114.5 (arom.), 89.9 (2 C, ethynyl), 20.1, 18.1, 13.5 ppm. IR (KBr): $\tilde{\nu}$ = 3284, 2919, 2854, 2210 (C≡C), 1612, 1503, 1456, 1397, 1315, 1157, 1030, 909, 848, 775, 638 cm^{-1}. ESI-MS $[C_{68}H_{54}N_4O_2 + H]^+$: calcd. *m*/*z* = 960.2: found *m*/*z* (%) = 959.9 (100). ESI-MS $[C_{68}H_{54}N_4O_2 + 2H]^{+2}$: calcd. *m*/*z* = 480.2; found *m*/*z* (%) = 480.9 (70). $C_{68}H_{54}N_4O_2\cdot\frac{1}{4}CH_2Cl_2$ (980.42): calcd. C 83.61, H 5.60, N 5.71; found C 83.96, H 5.71, N 5.81 (see also single crystal structure).

5b: Yield: 306 mg (31%). ^{1}H NMR [CD_2Cl_2/trifluoroacetic acid (0.3:0.01 mL), 200 MHz]: δ = 8.89 (d, *J* = 8.3 Hz, 2 H), 8.35 (s, 2 H), 8.21 (d, *J* = 8.3 Hz, 2 H, phenanthroline), 8.05 (s, 4 H), 7.90–7.94 (m, 6 H, anthracene), 7.51–7.60 (m, 8 H, anthracene), 6.88–6.99 (m, 12 H, anthracene), 6.72–6.81 (m, 8 H, anthracene), 6.60–6.64 (m, 2 H, anthracene) ppm. $C_{90}H_{50}N_4$ (1187.39): calcd. C 91.04, H 4.24, N 4.72; found C 91.10, H 4.01, N 4.90.

6a:[15] Yield: 629 mg (89%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 9.26 (br. s, 2 H), 9.16 (d, *J* = 4.2 Hz, 2 H), 8.35 (s, 2 H), 8.23 (d, *J* = 8.5 Hz, 2 H), 7.78 (d, *J* = 8.6 Hz, 2 H), 7.76 (d, *J* = 8.6 Hz, 2 H), 7.67–7.58 (m, 2 H), 7.10 (s, 2 H, phenyl), 4.07 (t, *J* = 7.1 Hz, 4 H, –OCH$_2$–), 1.85 (q, *J* = 7.1 Hz, 4 H, aliph.), 1.15–1.09 (m, 36 H, aliph.), 0.79 (t, *J* = 6.4 Hz, 6 H, –CH$_3$) ppm. ESI-MS $[C_{58}H_{66}N_4O_2 + H]^+$: calcd. *m*/*z* = 851.5; found *m*/*z* (%) = 851.7 (100). ESI-MS $[C_{58}H_{66}N_4O_2 + 2H]^{2+}$: calcd. *m*/*z* = 426.6; found *m*/*z* (%) = 426.6 (25). $C_{58}H_{66}N_4O_2$ (851.17): calcd. C 81.84, H 7.82, N 6.58; found C 81.40, H 7.91, N 6.70 (see also single crystal structure).

6b: Yield: 374 mg (61%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 9.23 (br. s, 2 H), 9.13 (d, *J* = 4.5 Hz, 2 H), 8.36 (s, 2 H), 8.26 (d, *J* = 8.1 Hz, 2

H), 7.82 (d, J = 8.3 Hz, 2 H), 7.80 (d, J = 8.3 Hz, 4 H), 7.64 (dd, J = 8.1, 4.5 Hz, 2 H), 7.15 (s, 2 H, phenyl), 4.10 (t, J = 6.4 Hz, 4 H, $-OCH_2-$), 1.98–1.84 (m, 4 H, aliph.), 1.66–1.56 (m, 4 H, aliph.), 1.52–1.26 (m, 16 H, aliph.), 0.82 (t, J = 6.9 Hz, 6 H, $-CH_3$) ppm. ^{13}C NMR (CD_2Cl_2, 50 MHz): δ = 153.9, 151.7, 150.5, 146.0, 144.9, 137.8 (2C), 135.9, 129.1, 127.9, 126.1, 123.2, 119.5, 116.9, 113.7 (arom.), 92.0, 90.1 (ethynyl), 69.7 (H_2CO), 31.9, 29.4 (2 C), 26.1, 22.7 (2 C), 13.9 (aliph.) ppm. IR (KBr): $\tilde{\nu}$ = 3027, 2921, 2851, 2204 ($C\equiv C$), 1589, 1552, 1505, 1467, 1411, 1383, 1277, 1218, 1123, 1097, 1062, 970, 908, 833, 734, 694 cm^{-1}. ESI-MS $[C_{50}H_{50}N_4O_2 + H]^+$: calcd. m/z = 739.4; found m/z (%) = 739.6 (100). $C_{50}H_{50}N_4O_2$ (738.96): calcd. C 81.27, H 6.82, N 7.58; found C 81.29, H 6.90, N 7.32 (see also single crystal structure).

6c: Yield: 476 mg (84%). ^1H NMR (CD_2Cl_2, 200 MHz): δ = 9.20 (s, 2 H), 9.11 (d, J = 4.5 Hz, 2 H), 8.35 (s, 2 H), 8.23 (d, J = 8.4 Hz, 2 H), 7.77 (d, J = 8.4 Hz, 2 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.61 (dd, J = 8.4, 4.5 Hz, 2 H), 7.13 (s, 2 H, phenyl), 4.09 (t, J = 6.4 Hz, 4 H, $-OCH_2-$), 1.97–1.64 (m, 4 H, aliph), 1.60–1.32 (m, 12 H, aliph.), 0.82 (t, J = 6.9 Hz, 6 H, $-CH_3$) ppm. ^{13}C NMR (CD_2Cl_2, 100 MHz): δ = 151.9, 148.7, 144.1, 142.8, 136.1, 134.1, 130.2, 127.0, 125.8, 124.1, 121.3 (2 C), 117.8, 114.9, 111.9 (arom.), 90.2, 88.4 (ethynyl), 54.1 (H_2CO), 29.9, 27.8, 27.5, 24.2, 20.7 ppm. ESI-MS $[C_{46}H_{42}N_4O_2 + H]^+$: calcd. m/z = 683.3: found m/z (%) = 683.1 (100). $C_{46}H_{42}N_4O_2$ (682.85): calcd. C 80.91, H 6.20, N 8.20; found C 80.54, H 6.32, N 8.12.

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[16] Crystal data for **5a′**: $C_{68}H_{54}N_4O_2 \cdot 4DMF$ (DMF = dimethylformamide), M = 1251.54, monoclinic, space group $C2/c$, a = 32.113(6) Å, b = 15.049(3) Å and c = 14.506(3) Å, α = 90°, β = 93.72(3)°, γ = 90°, V = 6996(2) $Å^3$, T = 193(2) K, Z = 4, D_c = 1.188 g/cm^3, $\lambda(Mo\text{-}K_\alpha)$ = 0.71073 Å, 8207 reflections measured, 5570 unique (R_{int} = 0.0509) which were used in all calculations. R_1 = 0.0781 $[I > 2\sigma(I)]$ and wR_2 = 0.1679, GOF = 1.075. CCDC reference number CCDC-299815. The CCDC data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] Crystal data for **6a**: Suitable single crystals were obtained by the slow evaporation of a dichloromethane solution containing **6a**. Solvent could be located partially. $C_{58}H_{66}N_4O_2 \cdot nCH_2Cl_2$, M = 1016.97, triclinic, space group $P\bar{1}$, a = 11.973(2) Å, b = 13.924(3) Å and c = 18.606(4) Å, α = 75.53(11)°, β = 82.81(3)°, γ = 73.32(3)°, V = 2872.3(10) $Å^3$, T = 193(2) K, Z = 2, D_c = 1.176 g/cm^3, $\lambda(Mo\text{-}K_\alpha)$ = 0.71073 Å, 12600 reflections measured, 8519 unique (R_{int} = 0.0310) which were used in all calculations. R_1 = 0.1138 $[I > 2\sigma(I)]$ and wR_2 = 0.3082, GOF = 1.041. CCDC reference number CCDC-299301.

[18] Crystal data for **6b**: Suitable single crystals were obtained by the slow of evaporation of dichloromethane solution containing **6b**. $C_{50}H_{50}N_4O_2 \cdot 2CH_2Cl_2$, M = 908.79, triclinic, space group $P\bar{1}$, a = 10.8660(16) Å, b = 10.987(2) Å and c = 12.019(2) Å, α = 102.442(11)°, β = 105.003(12)°, γ = 114.479(9)°, V = 1173.4(4) $Å^3$, T = 155(2) K, Z = 1, D_c = 1.286 g/cm^3, $\lambda(Mo\text{-}K_\alpha)$ = 0.71073 Å, 20884 reflections measured, 7645 unique (R_{int} = 0.0428) which were used in all calculations. R_1 = 0.0458 $[I > 2\sigma(I)]$ and wR_2 = 0.1167, GOF = 1.028; max/min residual density 0.587/–0.337 e$Å^{-3}$. CCDC reference number CCDC-299302.

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