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Synthesis of Multi-1,10-phenanthroline Ligands with 1,3-Phenylene Linkers and Their Lithium Complexes

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Abstract: The synthesis of two multisite ligands containing four and five 1,10-phenanthroline (phen) chelates in line, respectively, is presented. The connectors are 1,3-phenylene linkers. The two ligands were prepared following multistep procedures, the two key reactions being the Suzuki coupling reaction between aromatic nuclei and the nucleophilic addition of aryllithium derivatives onto a phen fragment. The coordination chemistry of both ligands with Li^+ ions was very clean and selective, whereas their reaction with copper(I) led to intractable mixtures of insoluble complexes. The tetraphen and the pentaphen compounds afforded almost quantitatively the four- and five-lithium double-stranded helical complexes, respectively. The helical systems are probably highly wound, as indicated by NMR measurements. The pronounced strain of the 5-Li^+ complex is reflected by the easy loss of a lithium cation, as shown by electrospray mass spectrometry.

Keywords: chelates · coordination chemistry · copper · helical complexes · lithium · N ligands

Introduction

Transition metals have been used as three-dimensional templates with particular efficiency in the preparation of various interlocking or knotted topologies. The key feature of this approach is the ability of the metal centers to gather various coordinating organic fragments and predispose them to a geometry which is very favorable for the formation of catenanes, rotaxanes and knots.

Since the synthesis of the first [2]catenane built around a copper(I) center,[1,2] many other novel topologies have been synthesized in the course of the last two decades.[3] Recent examples include catenanes and rotaxanes constructed around an octahedral center[4] and the Borromean rings built under thermodynamic control around six zinc cations.[5]

Multinuclear double-stranded helical complexes have been synthesized by various groups[6,7] and triple-stranded helices have also been reported.[8] Double-stranded helices represent an interesting family of accessible precursors to multiply interlocking [2]catenanes and knots, as depicted in Figure 1.[9]

Doubly interlocking catenanes have indeed been made[10] following the strategy shown in Figure 1.[9] The Li^+ ion was

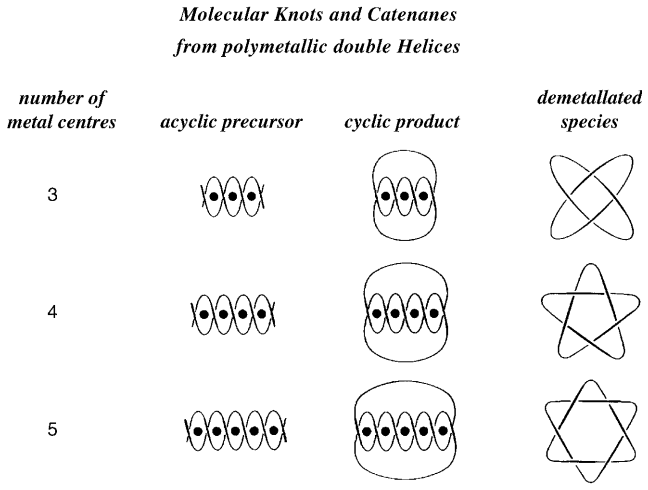

Figure 1. Double-stranded helical complexes ("helicates", as defined by Lehn and co-workers[7]), which are topologically planar systems, can lead to knots and "links" (i.e., catenanes) through appropriate connections between the ends of the strands. The number of metal centers used to gather and orient the two strands will determine the number of crossings and thus the topology of the final object.

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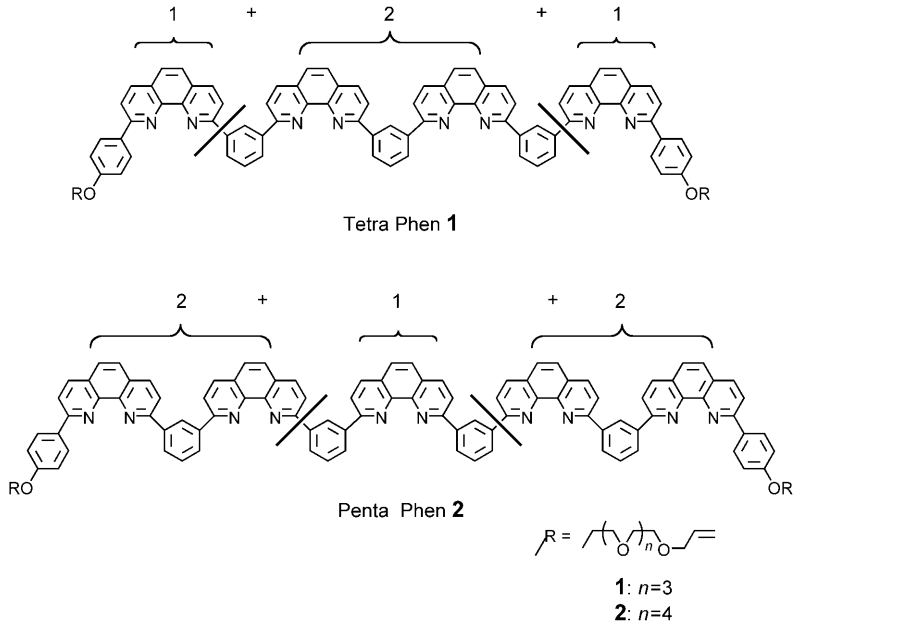
used as the gathering metal which forms relatively labile complexes with 1,10-phenanthroline (phen) derivatives, thus allowing the three-metal double-stranded helical precursor to be prepared under thermodynamic control.

Since the pentafoil knot 5_1 (see reference [11] for nomenclature) and the star of David 6_1^2 (or triply interlocking [2]catenane) are particularly attractive, we decided to apply the strategy shown in Figure 1 to the preparation of these species. To achieve this it was necessary to make multi-phen ligands in which each phen chelate is connected to its neighbor(s) through 1,3-phenylene linkers. From previous work,[12] we know that this is an appropriate connector and, used in conjunction with 2- and 9-substituted phen, it appeared very likely that the desired helical complexes would form once the ligands have been made and treated with Li^+ or Cu^I.

The two target ligands are represented in Scheme 1. In this report we describe the synthesis of these tetra- and pentaphen ligands as well as the formation of their helical complexes with Li^+ ions.



Scheme 1. Retrosynthetic analysis of the target compounds **1** and **2**; compound **1** can be constructed by assembling two mono-1,10-phenanthroline fragments to a central two-phen building block whereas the synthesis of compound **2** involves a central mono-phen and two peripheral two-phen fragments. The thick oblique lines indicate which bonds will be formed in the condensation reaction between the various building blocks.

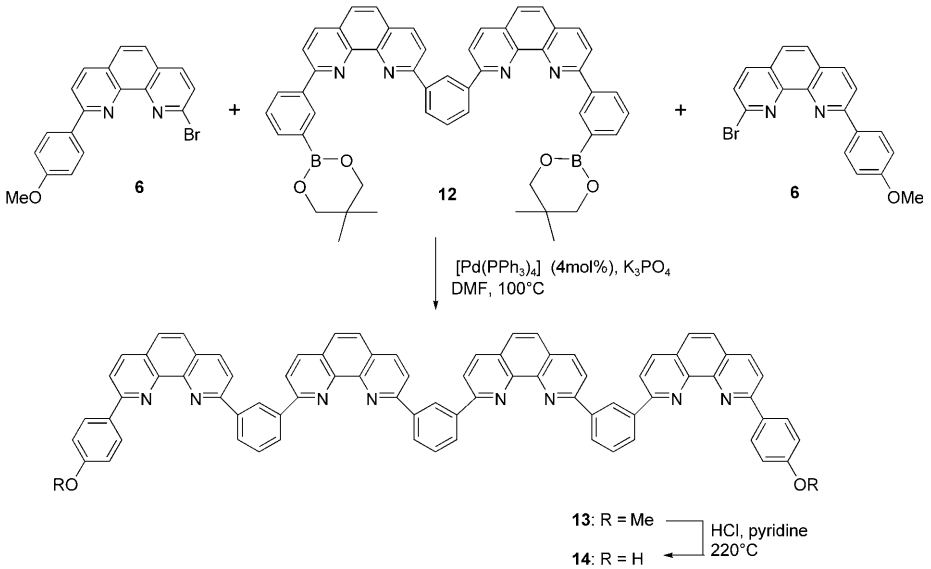
Results and Discussion

A retrosynthetic analysis of the preparation of **1** and **2** depicts how both multichelates can be synthesized from judicious combination of several small functionalized building blocks (Scheme 1).

According to Scheme 1, both the tetraphenanthroline and the pentaphenanthroline should be obtained by Suzuki cross-coupling reactions between monophenanthrolines or diphenanthrolines that have either a boronic or a reactive halide (bromide or iodide) functionality.

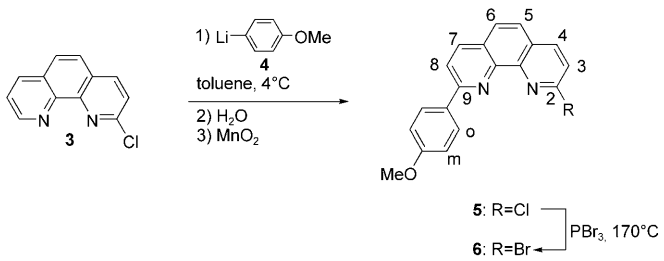
Synthesis of the tetraphenanthroline 1: After several attempts the most convenient strategy for the synthesis of the tetraphenanthroline appeared to be the one described in Scheme 2.

*Preparation of 2-bromo-9-(p-anisyl)phenanthroline (**6**)*: Bromophenanthroline **6** was prepared in two steps starting from 2-chlorophenanthroline (**3**) which could be obtained on a large scale (20 g) by following a previously reported procedure.[13] *p*-Lithioanisole (**4**), obtained from *p*-bromoanisole by an interconversion reaction with two equivalents of *tert*-butyllithium, was added to **3** at a low temperature (3–4 °C) without altering the position of the chloride. After hydroly-



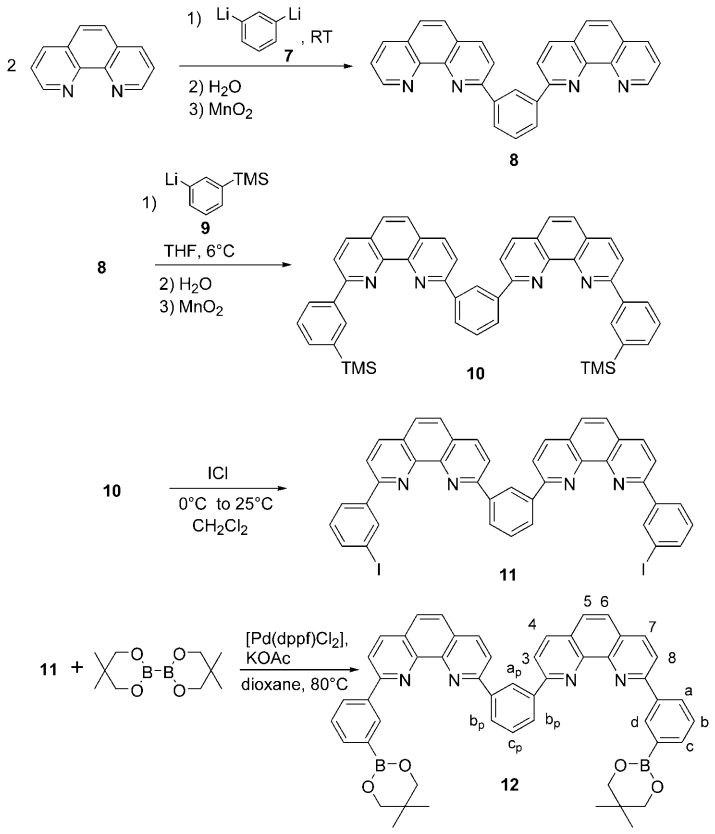
Scheme 2. Strategy for the synthesis of an end-functionalized tetraphenanthroline by a double Suzuki cross-coupling reaction.

sis, rearomatization with MnO_2, and column chromatography over silica gel, 2-chloro-9-(*p*-anisyl)phenanthroline (**5**) was obtained in 62% yield (Scheme 3).[14,15] Subsequent exchange of the chloride at the 2-position was performed by following a modification of the procedure described in the literature.[16] Chloride **5** and neat PBr_3 (170°C) were refluxed under argon for a short time (45 minutes). No major degradation of **5** or **6** was observed despite the very harsh reaction conditions as long as the reaction time was kept short (here, a maximum of 45 min) and the reaction carried out under an inert atmosphere (argon).



Scheme 3. Synthesis of 2-bromo-9-(*p*-anisyl)phenanthroline (**6**).

Bromide **6** was obtained in 81% yield after hydrolysis of the crude product on crushed ice, neutralization, and filtration of the precipitate.



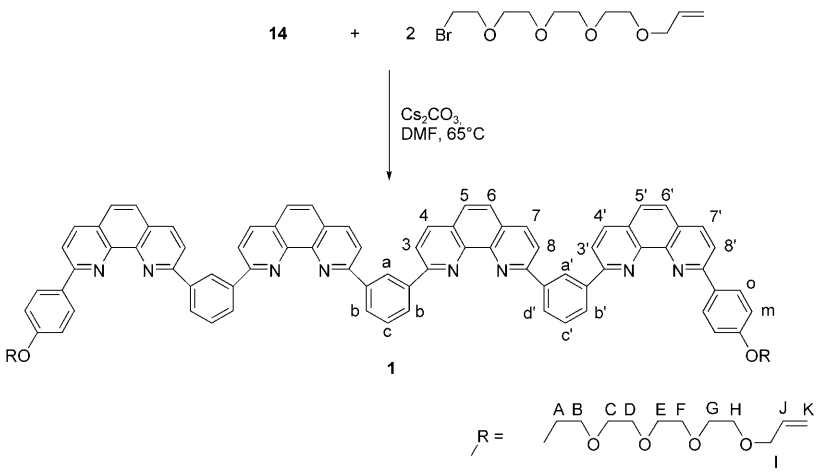
Scheme 4. Multistep preparation of diboronic ester **12**.

*Synthesis of the diboronic diphenanthroline **12***: The diboronic ester **12** was obtained in several steps as depicted in Scheme 4. In the first step the two phenanthrolines were connected to a 1,3-phenylene bridge by reacting 1,3-dilithiobenzene with two equivalents of 1,10-phenanthroline dissolved in THF at room temperature.[12] Diphenanthroline **8**, isolated in 40% yield after column chromatography over silica gel, was subsequently treated with 1-lithio-3-trimethylsilylbenzene (**9**) at 5–7°C for 3 h.[17] After hydrolysis and rearomatization with MnO_2, pure diphenanthroline **10** was obtained in 58% yield after column chromatography over silica gel. The third step, namely the exchange of the trimethylsilyl groups with iodine, involved the addition of a solution of ICl in CH_2Cl_2 to a degassed solution of **10** in CH_2Cl_2 at 0°C under argon. After the addition of ICl, the solution was allowed to warm to room temperature and then stirred for 3 h. After extractive workup and purification of the crude product by column chromatography over alumina, the diiodide **11** was obtained as a colorless solid in 98% yield. Whilst the formation of a boronic acid or ester of a substrate containing one or several chelates by quenching the corresponding lithio or magnesium intermediate with $B(OMe)_3$ appeared impossible, the use of commercially available bis-neopentyl diboron in the presence of $[Pd(dppf)Cl_2]\cdot CH_2Cl_2$ as catalyst allowed the diester **12** to be prepared in 58% yield.[18] In this work, this new methodology developed by Miyaura and co-workers appeared destined for success.

Formation of the tetraphenanthroline core (see Scheme 2): Owing to the poor solubility of diphenanthroline **12**, the double cross-coupling reaction between **12** and two equivalents of **6** could only be performed in DMF.[19] Synthesis of the tetraphenanthroline **13** was thus easily achieved by heating a mixture of **6** and **12** (in a ratio of 2:1) dissolved in DMF in the presence of the catalyst $[Pd(PPh_3)_4]$ and K_3PO_4 for two days at 100°C under an argon atmosphere (Scheme 2). After workup and column chromatography over silica gel, tetraphenanthroline **13** was obtained as a brown solid in 60% yield. Its ^1H NMR spectrum as well as its mass spectrum, with its large molecular ion peak found at *m*/*z* 1156.3 $[M+H]^+$ (calcd at 1156.3), were in full agreement with the structure proposed for tetraphenanthroline **13.**

Subsequent deprotection, achieved by refluxing **13** for three hours in pyridinium hydrochloride (210–220°C), led to the diphenol **14**. [20] Despite such harsh conditions, diphenol **14** was nevertheless obtained as a poorly soluble brown solid in 95% yield.

*Synthesis of the diolefinic tetraphenanthroline **1***: As shown in Scheme 5, the diphenol **14** was functionalized with two olefinic chains derived from tetra(ethylene glycol).[21] Tetraphenanthroline **1** appeared to be a good precursor with which to achieve cyclization to the pentafoil knot by ring-closing metathesis (RCM; see Figure 1). Incidentally, the solubility of tetraphenanthroline **13** could be increased markedly by the introduction of two such chains at its extremities.

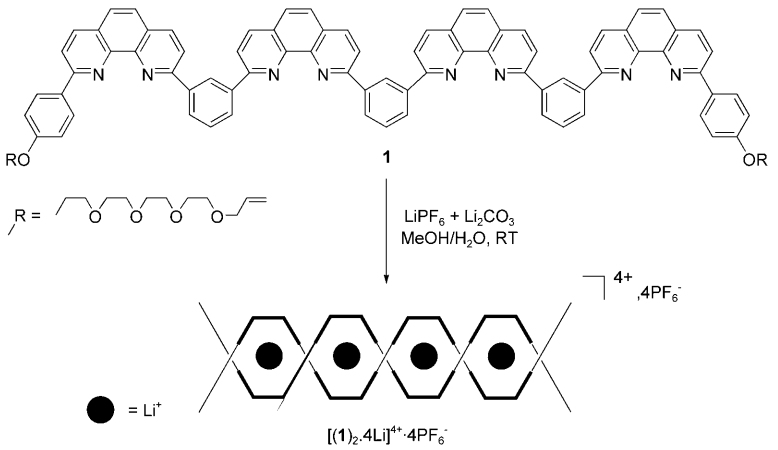


Scheme 5. Synthesis of diolefinic tetraphenanthroline **1**.

The nucleophilic substitution reaction between the diphenolate derived from **14** and the bromo-allyl-poly(ethylene glycol) chain took place under classic conditions, that is, by heating diphenol **14** dissolved in DMF in the presence of a large excess of the bromo-allyl chain and Cs_2CO_3 at 65 °C for one day. Column chromatography of the crude product over silica gel afforded pure **1** in 80 % yield.

Coordination properties of ligand 1: Owing to the well-known high affinity of copper(I) towards –N–N- chelate-containing ligands, we investigated the coordination chemistry of copper(I) with ligand **1** first.[22] Addition of Cu-$(CH_3CN)_4$·PF_6 dissolved in CH_3CN to a CH_2Cl_2 solution of ligand **1** under argon led only to an intractable mixture of oligomeric dark red copper(I) complexes. This surprising result can only be explained in terms of the high stability and the inertness of the kinetic polynuclear copper(I) complexes which precludes any self-repair process. Indeed, no equilibration was observed on refluxing the oligomeric copper(I) complexes in acetonitrile for several days. According to the literature and from our own experience, the use of lithium cations should lead to much less stable complexes that are able to equilibrate in favor of the thermodynamically most stable complex with a double helix structure.[10,12,22,23] Addition, under argon, of $LiPF_6$ dissolved in methanol to ligand **1** dissolved in CH_2Cl_2 (ratio of Li^+/ligand **1** = 4:2) led upon addition of a small amount of basic Li_2CO_3, necessary to neutralize the residual acidity of $LiPF_6$ (traces of HPF_6), to a single pale yellow complex (Scheme 6).

The ^{1}H NMR spectrum of this latter complex exhibits a strong chemical upfield shift for some of the protons in the aromatic region. Interestingly the most affected protons, for which $\Delta\delta < -2$ ppm, are the protons H-3′, H-3, H-8, H-a′, and H-a, which are located very close to the crossing points of the double-stranded helix (Table 1). Previous studies of helices and molecular knots have shown that the signature for such intertwined or knotted structures was precisely a strong chemical upfield shift for all the protons located in close proximity to the crossing points. Moreover, the high-resolution ES-MS spectrum has a major peak at *m*/2 1718.6457 for $[(\mathbf{1})_2{\cdot}4Li]^{4+}{\cdot}(2PF_6)^{2-}$ (calcd 1718.6466). It is therefore clear that the complex $[(\mathbf{1})_2{\cdot}4Li]^{4+}{\cdot}(4PF_6)^{4-}$ most probably has a double-helix structure.[12,24,25]

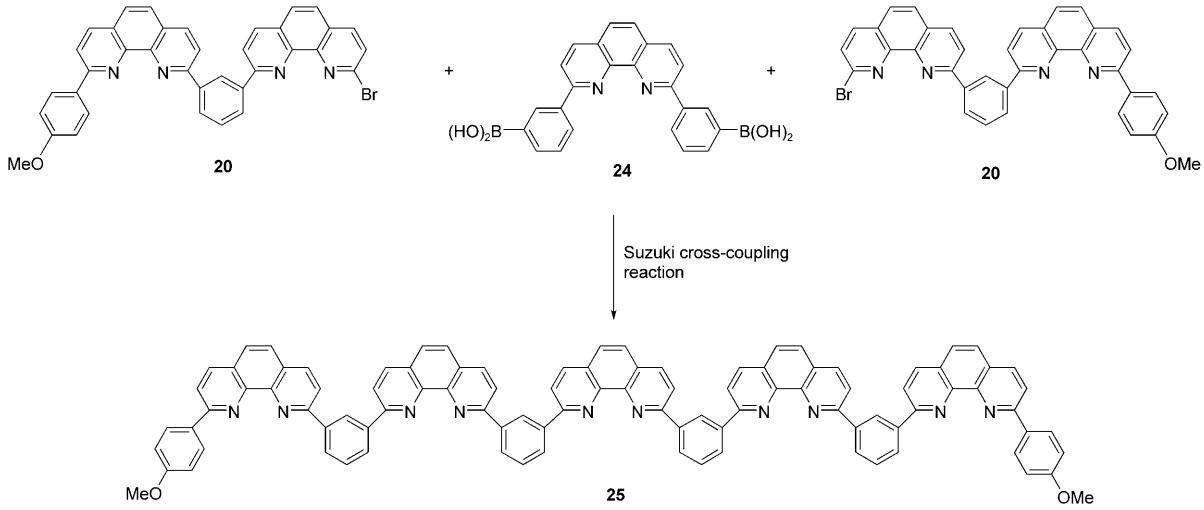


Scheme 6. Formation of a double helix around four lithium cations.

Table 1. Chemical shifts [ppm] for **1** and $[(\mathbf{1})_2{\cdot}4Li]^{4+}{\cdot}(4PF_6)^{4-}$.[a]

	H-*o*	H-*m*	H-3′	H-a′	H-b′	H-d′	H-c′	H-8	H-3	H-a	H-b	H-c	H-A	H-B
1	8.42	7.02	8.30	9.70	8.63	8.52	7.76	8.30	8.30	9.75	8.58	7.75	4.18	3.88
$(\mathbf{1})_2{\cdot}4Li$	6.70	5.59	6.20	7.45	6.70	6.70	6.94	6.00	6.00	7.45	6.70	6.89	3.25	3.47
$\Delta\delta$[b]	−1.72	−1.43	−2.10	−2.25	−1.93	−1.82	−0.82	−2.30	−2.30	−2.30	−1.88	−0.86	−0.93	−0.41

[a] Solvent: CD_2Cl_2 for **1**, CD_3CN for $[(\mathbf{1})_2{\cdot}4Li]^{4+}{\cdot}(4PF_6)^{4-}$. [b] $\Delta\delta = \delta[(\mathbf{1})_2{\cdot}4Li] - \delta(\mathbf{1})$.

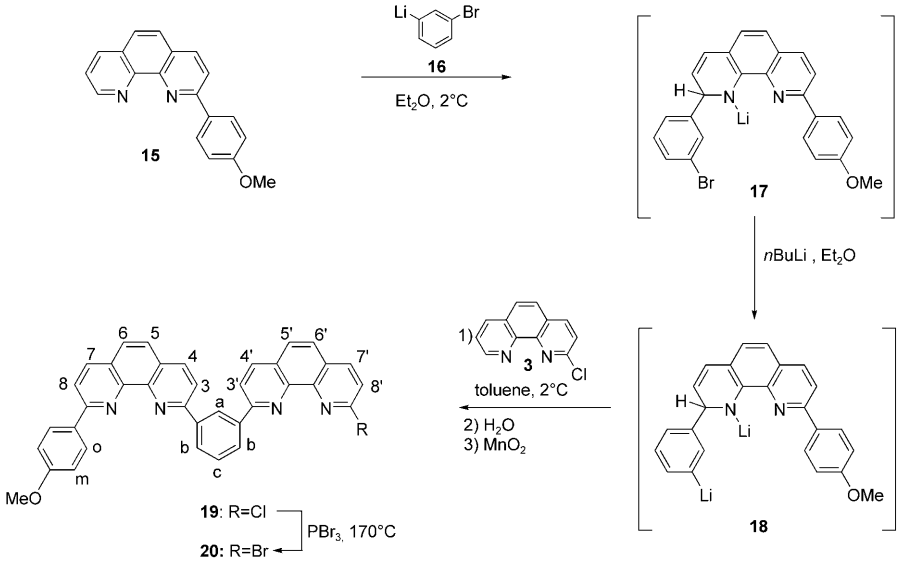


Scheme 7. Strategy and building blocks for the synthesis of a pentaphenanthroline.

Synthesis of the pentaphenanthroline 2: The strategy used for the synthesis of pentaphenanthroline is shown in Scheme 7.

*Synthesis of diphenanthroline **19***: Starting from mono-*p*-anisylphenanthroline **15**, which can be easily prepared on a 10 g scale, diphenanthroline **19** was obtained by following the multistep procedure depicted in Scheme 8.[15]

A diethyl ether solution of 1-lithio-3-bromobenzene (**16**), prepared from 1,3-dibromobenzene by interconversion with one equivalent of *n*BuLi at a low temperature (2–4 °C), was added to a degassed suspension of **15** in diethyl ether also maintained at 2 °C.[17] Monitoring by TLC allowed us to see that after 2 h of stirring at 2–4 °C, **15** had been entirely transformed into the disubstituted phenanthroline **17**. The bromine atom in intermediate compound **17** was then submitted to a second interconversion reaction with 1.3 equivalents of *n*BuLi at 3 °C to afford the aromatic lithio intermediate **18**. TLC performed on a small aliquot withdrawn from the reaction mixture showed that this interconversion was complete after stirring for 2 h at 5–10 °C. The last step, the addition of the solution containing **18** to a degassed solution of 2-chlorophenanthroline in toluene, was also performed at 2–4 °C. After stirring and warming to room temperature, the mixture was hydrolyzed with water and rearomatized with MnO_2. Column chromatography over silica gel afforded pure diphenanthroline **19** in 34 % yield. It should be emphasized here that the rearomatization of **17** followed by interconversion with *n*BuLi and addition of **3** did not yield any trace of **19**. We had previously observed that a free chelate (phenanthroline or terpyridine) inhibits the interconversion step. As a consequence, it is necessary to use the intermediate **17**, in which the coordinating site is occupied by a Li^+ ion, immediately. Repetition of this multistep process clearly showed that its success was strongly related to the temperature and reaction time used in each sequence in order to preserve the potentially reactive sites that are the bromine in compound **16** and **17** and the chlorine in **19.**

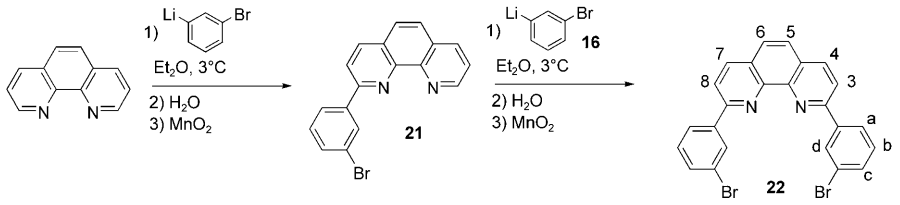


Scheme 8. Multistep synthesis of diphenanthroline **19**.

*Preparation of bromide **20***: Several attempts to perform the cross-coupling reaction between chloride **19** and the diboronic ester **23** or acid **24** (see later)

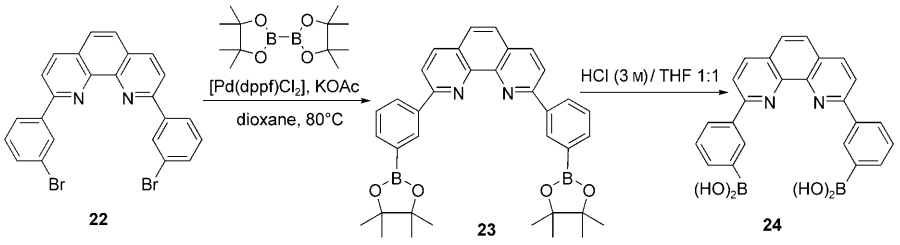
following the procedure developed by Fu and co-workers failed owing to the very low solubility of the diphenanthroline **19** in dioxane or THF.[26] Therefore it appeared necessary to exchange the chlorine for the more reactive bromine atom. Bromide **20** was obtained in 65% yield after stirring the chloride **19** for 40 min in refluxing neat PBr_3 (Scheme 8).[16]

*Synthesis of the 2,9-disubstituted phenanthroline **22***: The presence of the reactive bromine atom in 1-lithio-3-bromobenzene (**16**) precludes its use in excess at room temperature, which are the classic conditions used in the direct formation of a 2,9-disubstituted phenanthroline.[14,27] This difficulty was easily circumvented by performing two successive monosubstitution reactions at a low temperature (Scheme 9).[15,28]



Scheme 9. Preparation of the 2,9-disubstituted phenanthroline **22** by two distinct monosubstitution reactions.

Anhydrous 1,10-phenanthroline was treated with a slight excess of 1-lithio-3-bromobenzene (**16**) in diethyl ether at 2–4°C for 2 h. After hydrolysis, rearomatization with MnO_2, and purification by column chromatography over silica gel, pure 2-(*m*-bromophenyl)phenanthroline **21** was obtained in 32% yield as a colorless solid. Subsequently, **21** was submitted to a second monosubstitution reaction by **16** under the same conditions as described above to afford the 2,9-disubstituded phenanthroline **22** in 24% yield. The low yields can be explained by secondary cascade interconversions that occur on the bromine atoms present in **21** and **22** even at 2–4°C. An attempt to reduce the occurrence of these secondary interconversion reactions by lowering the temperature to −5°C was very disappointing since no reaction at all occurred at this temperature. Thus it appeared that **21** and **22** can only be prepared in a very narrow range of temperatures.



Scheme 10. Synthesis of diboronic ester **23** and diboronic acid **24**.

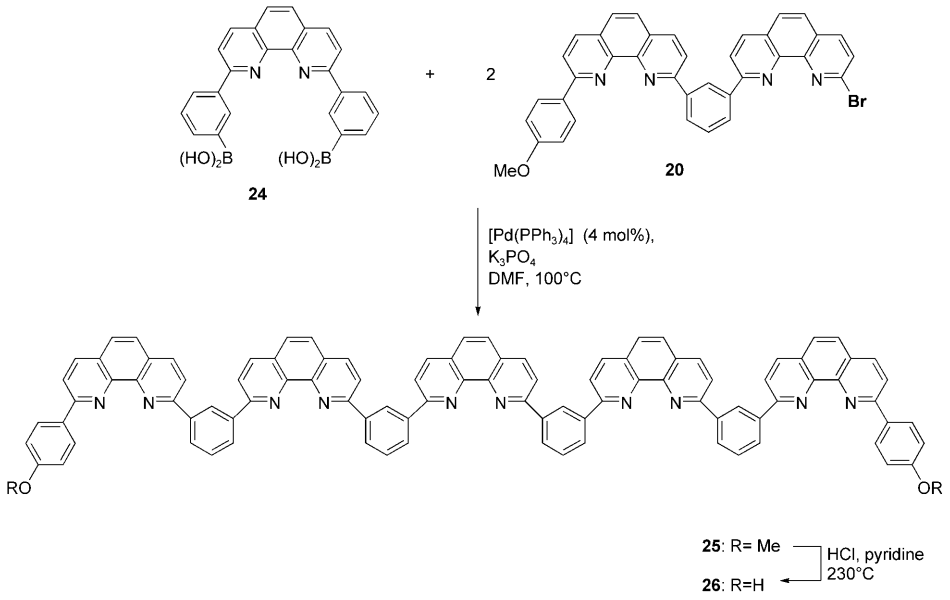
*Preparation of the diboronic ester **23***: Following the methodology developed by Miyaura and co-workers, the diboronic ester **23** was obtained in 90% yield by refluxing the dibromide **22** with bis-pinacolatodiboron in dioxane for 12 h in the presence of $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ as catalyst (Scheme 10).[18]

The diboronic acid **24** was obtained in 99% yield by stirring a solution of **23** in THF (30 mL) and 3 M HCl (30 mL) at room temperature for four days.[29]

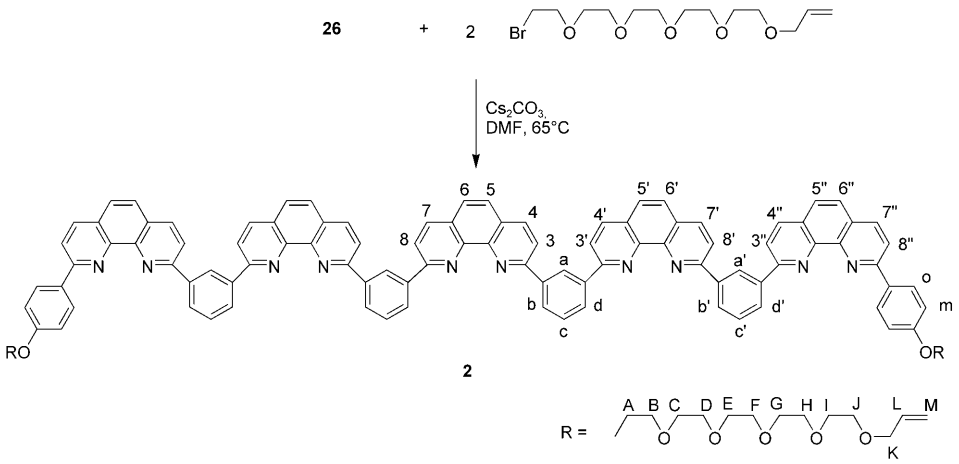
*Synthesis of pentaphenanthroline **25***: The double Suzuki cross-coupling reaction between two bromo-diphenanthrolines **20** and one central diboronic phenanthroline **24** was again performed in DMF at 100°C in the presence of K_3PO_4 and $[Pd(PPh_3)_4]$ as catalyst over a period of two days (Scheme 11).

Although the coupling procedure used was similar to the one which afforded the tetraphenanthroline **13**, workup and isolation had to be adapted to the special features exhibited by the pentachelate **25**. Indeed the poor solubility of **25**, related to its strong tendency to bind or coordinate trace amounts of cations (Li^+, Na^+, H^+, K^+, etc.) present in solvents, glassware, and solid supports like silica gel or alumina, prohibited the use of classic column chromatography in the purification process.

As a result of the special features of compound **25**, the solid crude product, obtained by addition of a large amount of water to a DMF solution and filtration of the precipitated crude solid, was suspended in CH_2Cl_2 and poured onto a dry silica gel column. All products other than **25** were eluted with CH_2Cl_2 containing increasing amounts of MeOH. Desorption of **25** from the solid support was achieved by taking advantage of its coordination properties, namely its strong affinity towards lithium cations. The silica gel from the column was poured into a beaker and recovered with a CH_2Cl_2/MeOH (93:7) solution before a large excess of $LiPF_6$ was added under a stream of argon. After stirring for four days, the heterogeneous mixture was filtered through a sintered glass. The ^1H NMR spectrum of the filtrate showed that it contained both lithium complexes and protonated ligand **25**. Subsequent addition of CF_3COOH to the filtrate afforded fully protonated, soluble **25** in 83% yield. Complex $(\mathbf{25}{\cdot}5H)^{5+}{\cdot}5PF_6^-$ was fully characterized by ^1H NMR spectroscopy and by its mass spectrum, with intense peaks at *m*/*z* 1410.5 $[M+H]^+$, 705.5 $[M+2H]^{2+}$, 470.7 $[M+3H]^{3+}$, and 353.3 $[M+4H]^{4+}$.



Scheme 11. Double cross-coupling reaction affording pentaphenanthroline **25**.



Scheme 12. Synthesis of diolefinic pentaphenanthroline **2** with the numbering scheme.

*Synthesis of the diphenol pentaphenanthroline **26***: Deprotection of the methoxy groups of **25** was performed in refluxing pyridinium hydrochloride following the procedure already used for the preparation of diphenol **14**.[20] Diphenol **26** was obtained in 93% yield as an ochre solid almost insoluble in all solvents but DMF (Scheme 11).

*Synthesis of the diolefinic pentaphenanthroline **2***:The diphenolate of **26** formed in DMF at 65 °C in the presence of Cs_2CO_3 was treated with an excess of the bromo-allyl-poly(ethylene glycol) chain derived from penta(ethylene glycol).[21] Owing to the coordination properties expected of a pentachelate like **2**, use of column chromatography in the purification process was avoided. The solid crude product was merely washed first with diethyl ether in order to remove excess of the bromo-allyl chain and thereafter with water to eliminate Cs_2CO_3. This very simple purification procedure afforded the very soluble diolefinic pentaphenanthroline **2** in 62% yield (Scheme 12).

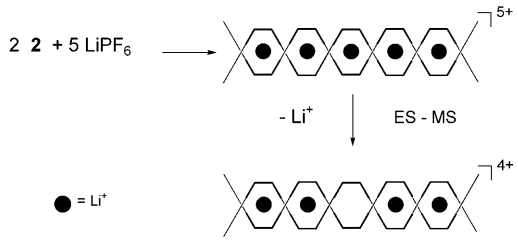
Coordination properties of 2: *Lithium complex $[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(5PF_6)^{5-}$*: Pentachelate **2** exhibits the same, although enhanced, coordination properties as tetrachelate **1**. Like **1**, ligand **2** forms only a mixture of oligomeric complexes in the presence of copper(I) whereas it forms, in the presence of $LiPF_6$, a single, well-defined complex $[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(5PF_6)^{5-}$ (Scheme 13).

Its ^1H NMR spectrum, characterized by large chemical upfield shifts for most of the protons of the aromatic region (see Table 2), is in good agreement with a double-helix structure. Its mass spectrum confirms the ratio of two molecules of ligand **2** to five Li^+ ions with the peaks for *m*/2 observed at 2136.8278 (calcd 2137.0241) for $[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(3PF_6)^{3-}$, *m*/3 at 1376.1988 (calcd 1376.3613) for $[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(2PF_6)^{2-}$, *m*/4 at 995.9139 (calcd 996.0299) for $[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(PF_6)^{-}$, *m*/5 at 767.7443 (calcd 767.8311) for

Table 2. Chemical shifts [ppm] for **2**, $[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(5PF_6)^{5-}$ and $[(\mathbf{2})_2{\cdot}3Li{\cdot}2Cu]^{5+}{\cdot}(5PF_6)^{5-}$.[a]

	H-*o*	H-*m*	H-3,8	H-3′	H-8′	H-3″	H-a	H-a′	H-4,7	H-4′	H-7′	H-4″	H-7″	H-A	H-B
2	8.41	7.03	8.29	8.27	8.36	8.30	9.78	9.69	8.05	8.10	8.36	8.04	8.21	4.17	3.87
$(\mathbf{2})_2{\cdot}5Li$	6.65	5.56	5.90	5.94	6.10	6.05	7.24	7.64	7.37	7.47	7.50	7.53	8.14	3.32	3.60
$\Delta_1\delta$[b]	−1.76	−1.47	−2.39	−2.33	−2.26	−2.25	−2.54	−2.05	−0.68	−0.63	−0.86	−0.51	−0.07	−0.85	−0.27
$(\mathbf{2})_2{\cdot}2Cu{\cdot}3Li$	6.75	5.52	5.90	6.11	5.95	6.04	7.23	8.33	7.38	7.46	7.48	7.52	8.16	3.34	3.55
$\Delta_2\delta$[b]	0.10	−0.04	0	0.17	−0.15	−0.01	−0.01	0.69	0.01	−0.01	−0.02	−0.01	0.02	0.02	−0.05

[a] Measured in CD_2Cl_2. [b] $\Delta_1\delta = \delta[(\mathbf{2})_2{\cdot}5Li] - \delta(\mathbf{2})$; $\Delta_2\delta = \delta[(\mathbf{2})_2{\cdot}2Cu{\cdot}3Li] - \delta[(\mathbf{2})_2{\cdot}5Li]$.

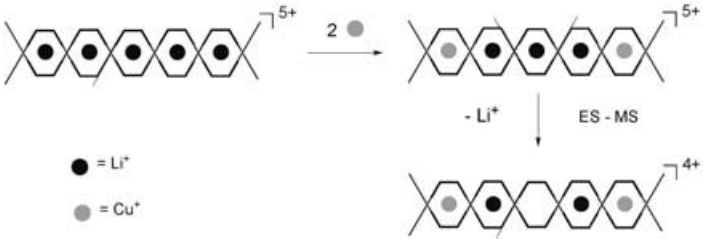


Scheme 13. Formation of complexes $[(\mathbf{2})_2{\cdot}5\mathrm{Li}]^{5+}{\cdot}(5\mathrm{PF}_6)^{5-}$ and $[(\mathbf{2})_2{\cdot}4\mathrm{Li}]^{4+}{\cdot}(4\mathrm{PF}_6)^{4-}$.

$[(\mathbf{2})_2{\cdot}5\mathrm{Li}]^{5+}$. The occurrence of a series of peaks corresponding to the m/z for the complex $[(\mathbf{2})_2{\cdot}4\mathrm{Li}]^{4+}{\cdot}(4\mathrm{PF}_6)^{4-}$ strongly suggests the presence of a highly wound structure in which the lithium cation in the central cavity could very easily be expelled under the conditions of mass spectrometry. No evidence for the presence of $[(\mathbf{2})_2{\cdot}4\mathrm{Li}]^{4+}{\cdot}(4\mathrm{PF}_6)^{4-}$ in solution could be found from careful analysis of the ^{1}H NMR spectrum. Nevertheless, if such a species exists, the symmetrical spectrum (in this case, the superposition of the spectra of $[(\mathbf{2})_2{\cdot}5\mathrm{Li}]^{5+}{\cdot}(5\mathrm{PF}_6)^{5-}$ and $[(\mathbf{2})_2{\cdot}4\mathrm{Li}]^{4+}{\cdot}(4\mathrm{PF}_6)^{4-}$) tends to indicate that the cavity must be in the central position of the double helix.

^{1}H NMR studies confirm the presence of a double-helix structure which is very strained in its central part. Indeed, the difference in the chemical shifts ($\Delta\delta$) increases on going from the centre of the double helix to its extremities: $\Delta\delta =$ −2.39 (H-3,8), −2.33 (H-3′), −2.26 (H-8′), −2.25 (H-3″), −2.54 (H-a), and −2.05 ppm (H-a′).

*Heteronuclear lithium-copper(*I*) complex $[(\mathbf{2})_2{\cdot}3\mathrm{Li}{\cdot}2\mathrm{Cu}]^{5+}{\cdot}(5\mathrm{PF}_6)^{5-}$*: Although obtained easily and in good yield (76%), the lithium complex $[(\mathbf{2})_2{\cdot}5\mathrm{Li}]^{5+}{\cdot}(5\mathrm{PF}_6)^{5-}$ is not very stable. In particular it completely decomposes in the presence of polar solvents containing oxygen, for example, in DMF. Addition of two equivalents of the copper(I) salt $\mathrm{Cu}(\mathrm{CH_3CN})_4{\cdot}\mathrm{PF}_6$ afforded in quantitative yield a dark red complex $[(\mathbf{2})_2{\cdot}3\mathrm{Li}{\cdot}2\mathrm{Cu}]^{5+}{\cdot}(5\mathrm{PF}_6)^{5-}$ whose helical structure is locked by a copper(I) cation located at each end of the complex (Scheme 14). Its ^{1}H NMR spectrum is characterized by



Scheme 14. Heteronuclear complexes $[(\mathbf{2})_2{\cdot}3\mathrm{Li}{\cdot}2\mathrm{Cu}]^{5+}{\cdot}(5\mathrm{PF}_6)^{5-}$ and $[(\mathbf{2})_2{\cdot}2\mathrm{Li}{\cdot}2\mathrm{Cu}]^{4+}{\cdot}(4\mathrm{PF}_6)^{4-}$.

chemical shifts similar to those of the lithium complex $[(\mathbf{2})_2{\cdot}5\mathrm{Li}]^{5+}{\cdot}(5\mathrm{PF}_6)^{5-}$ with $\Delta\delta$ close to zero for most of the protons (see Table 2). The only small variations in the observed chemical shifts δ occur at the extremities of the complex and reflect the differences in size of the Cu^+ and Li^+ cations. In the ES-MS spectrum, along with the m/z peaks expected for complex $[(\mathbf{2})_2{\cdot}3\mathrm{Li}{\cdot}2\mathrm{Cu}]^{5+}{\cdot}(5\mathrm{PF}_6)^{5-}$, peaks appear that correspond to the complex $[(\mathbf{2})_2{\cdot}2\mathrm{Li}{\cdot}2\mathrm{Cu}]^{4+}{\cdot}(4\mathrm{PF}_6)^{4-}$ in which the strain has been relieved by expulsion of the central lithium cation.

Conclusions

Two new multi-phenanthroline ligands **1** and **2** have been synthesized. After preliminary work aimed at selecting the best synthetic strategy, the following retrosynthetic approaches were defined: the tetraphen compound was constructed from a central phen-1,3-phenylene-phen motif and two peripheral 2,9-diaryl-phen building blocks. In contrast, the synthetic strategy for the pentaphen molecule involves the coupling of a central 2,9-disubsituted-phen to two diphen fragments.

Two double-helical structures based on **1** or **2** were obtained which display similar properties. Both helices are assembled around lithium cations and are very strained, as proved by ^{1}H NMR and mass spectrometry studies.

Cyclization reactions under ring-closing metathesis conditions were attempted with the tetraphen and pentaphen lithium complexes attached to olefinic fragments. Unfortunately, the desired topologies (pentafoil knot 5_1 and the star of David 6_1^2, respectively) could not be isolated as yet.

Metal-exchange reactions conducted on the lithium complex of the pentaphen ligand showed that selective replacement of the terminal lithium cations by copper(I) takes place, the kinetic inertness of the more central Li^+ ions preventing them from being substituted for Cu^I. A Cu–Li–Li–Li–Cu complex was thus obtained. These helical complexes are likely to be electronically or electrostatically highly coupled, in analogy with previous observations of the two-copper system. This is partly due to the conjugated character of the ligands. This feature, combined with the length of the helical complexes, makes them particularly promising compounds for long-range electron transfer. Interestingly, the five-Li^+ compound contains two sets of 16 six-membered aromatic groups attached to one another and the overall length of the helical complex has been estimated to be 28 Å.

Experimental Section

General: All chemicals were of the best commercially available grade and used without further purification. Dry solvents were distilled from suitable desiccants (Et_2O, THF, and dioxane from Na/benzophenone). Column chromatography was performed with silica gel 60 (Merck 9385, 230–400 mesh) or aluminium oxide 90 (neutral, act. II–III, Merck 1097). ^{1}H and ^{13}C NMR spectra were recorded with a Bruker WP 200 SY (200 MHz), AVANCE 300 (300 MHz), AVANCE 400 (400 MHz), or AVANCE 500 (500 MHz) spectrometer using deuteriated solvent as the lock. The spectra were collected at 25 °C and the chemical shifts were ref-

erenced to residual solvent protons as internal standards (^{1}H: $CDCl_3$ 7.27 ppm, [D_6]DMSO 2.50 ppm, CD_2Cl_2 5.32 ppm, CD_3CN 1.94 ppm; ^{13}C: CD_3Cl 77 ppm, CD_2Cl_2 53.7 ppm. Mass spectra were obtained with a VG ZAB-HF spectrometer (FAB) and a VG-BIOQ triple quadrupole in positive mode (ES-MS).

2-Chloro-9-(*p*-anisyl)phenanthroline (5): 2-Chlorophenanthroline **3** was prepared in three steps from commercial 1,10-phenanthroline according to the literature procedure,[13] whereas *p*-lithioanisole **4** was prepared by interconversion of *p*-bromoanisole with two equivalents of *t*BuLi; a THF solution (50 mL) of *p*-lithioanisole **4** (15 mmol) was obtained by slow addition of *t*BuLi (30 mmol) to a THF solution (40 mL) of *p*-bromoanisole (2.806 g, 15 mmol) at −78 °C under argon. The lithioanisole solution was thereafter added to a degassed suspension of **3** (2.147 g, 10 mmol) in toluene (100 mL) maintained at 3–4 °C. The initial pale yellow suspension of **3** turned dark red instantaneously. After addition of this lithioanisole solution, the dark solution was stirred under argon at +4 °C for an additional 2 h. Thereafter the reaction was quenched by addition of water (20 mL) and the resulting mixture was evaporated to dryness. The orange-brown residue thus obtained was taken up in a mixture of CH_2Cl_2 and water and decanted. The aqueous layer was washed and extracted with more CH_2Cl_2. The bright yellow organic phase was then rearomatized by successive addition of batches of MnO_2 (12 g). The rearomatization was monitored by TLC. After the quite slow rearomatization step the solution was dried by addition of $MgSO_4$. The black MnO_2/$MgSO_4$ slurry was filtered through sintered glass. After evaporation of the solvent a dark yellow glass (3.190 g) was obtained as the crude product which was purified by column chromatography over silica gel (eluent: CH_2Cl_2 and MeOH). Pure compound **5** was obtained as a pale yellow solid (1.980 g, 6.17 mmol) in 62 % yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.36 (d, J = 8.8 Hz, 2H, H-*o*), 8.26 (d, J = 8.6 Hz, 1H, H-7), 8.18 (d, J = 8.3 Hz, 1H, H-4), 8.08 (d, J = 8.6 Hz, 1H, H-8), 7.77 (AB, J = 8.6 Hz, 2H, H-5,6), 7.61 (d, J = 8.3 Hz, 1H, H-3), 7.08 ppm (d, J = 8.8 Hz, 2H, H-*m*); ^{13}C (100 MHz, CD_2Cl_2): δ = 161.18, 156.97, 150.75, 146.21, 144.93, 139.03, 136.80, 131.83, 129.03, 127.94, 127.72, 126.92, 125.02, 123.94, 120.19, 114.26, 55.42 ppm; HR FAB-MS: m/z: 321.0790 $[M+H]^+$, calcd 321.0795.

2-Bromo-9-(*p*-anisyl)phenanthroline (6): Exchange for the chlorine in **5** by a bromine atom was performed following a modification to a procedure described in the literature.[16] Under a stream of argon, neat PBr_3 (30 mL) was poured into a small two-necked round-bottom flask containing **5** (600 mg, 1.95 mmol). The resulting bright yellow mixture was then refluxed at 170 °C for 45 min under argon. The yellow color progressively turned greenish-black during the heating process. After reflux the dark suspension was stirred overnight at room temperature under argon. Subsequent careful hydrolysis on crushed ice afforded a yellow suspension of **6** in a strongly acidic medium (pH 1). NaOH pellets were then added until the solution became slightly basic (pH 8), and the bromide **6** was extracted with a mixture of CH_2Cl_2 and $CHCl_3$. After decanting the mixture, the organic phase was dried over $MgSO_4$, filtered, and evaporated to dryness to yield 620 mg of a colorless solid. This crude product was purified by column chromatography over silica gel (eluent: CH_2Cl_2/hexane 1:1 to pure CH_2Cl_2) to afford pure **6** in 81 % yield (577 mg, 1.58 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (d, J = 9.0 Hz, 2H, H-*o*), 8.27 (d, J = 8.5 Hz, 1H, H-7), 8.09 (d, J = 8.5 Hz, 1H, H-8), 8.08 (d, J = 8.8 Hz, 1H, H-4), 7.98 (AB, J = 8.7 Hz, 2H, H-5,6), 7.72 (d, J = 8.8 Hz, 1H, H-3), 7.09 (d, J = 9.0 Hz, 2H, H-*m*), 3.90 ppm (s, 3H, OCH_3); ^{13}C (75 MHz, $CDCl_3$): δ = 161.16, 157.29, 146.81, 144.84, 142.45, 138.27, 136.80, 131.77, 129.28, 127.95, 127.73, 127.49, 127.01, 125.06, 120.24, 114.26, 55.43 ppm; ES-MS: m/z: 366.2 $[M+H]^+$, calcd 366.2.

Diphenanthroline 8: 1,3-Dilithiobenzene (**7**) was prepared by adding four equivalents of *t*BuLi (45 mmol, 25 mL of a 1.8 mol L^{-1} solution) dropwise to a degassed THF solution (70 mL) of 1,3-dibromobenzene (2.832 g, 12 mmol) at −78 °C. After all the *t*BuLi had been added, the solution was allowed to warm to +5 °C twice. The clear pale yellow dilithiobenzene solution was then added through a cannula to a degassed solution of anhydrous phenanthroline (4.0 g, 22.2 mmol) in THF (140 mL) at room temperature under argon. The initial pale yellow solution of phenanthroline in THF immediately turned dark red. This mixture was stirred for 48 h at room temperature under argon before being quenched with water at 0 °C. The mixture was evaporated to dryness and the orange residue was taken up in CH_2Cl_2/H_2O, the organic layer decanted and rearomatized with MnO_2 (27 g). An equivalent amount of $MgSO_4$ was added to the stirred mixture. After stirring for 1 h, the $MgSO_4$/MnO_2 slurry was filtered through a sintered glass and the solvent evaporated to dryness to afford 6.05 g of a crude mixture which was submitted to column chromatography over alumina (eluent: CH_2Cl_2/hexane, 80:20). A second chromatography over silica gel (eluent: CH_2Cl_2/2 to 5 % MeOH) afforded pure **8** (1.939 g, 4.46 mmol) in 40 % yield as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.26 (dd, J_1 = 4.4, J_2 = 1.8 Hz, 2H, H-9), 9.19 (t, J = 1.7 Hz, 1H, H-a), 8.55 (dd, J_1 = 7.9, J_2 = 1.7 Hz, 2H, H-b), 8.36 (AB, J = 8.4 Hz, 2H, H-3,4), 8.28 (dd, J_1 = 8.2, J_2 = 1.8 Hz, 2H, H-7), 7.83 (AB, J = 8.9 Hz, 4H, H-5,6), 7.78 (d, J = 7.9 Hz, 1H, H-c), 7.66 ppm (dd, J_1 = 8.2, J_2 = 4.4 Hz, 2H, H-8); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.51, 150.24, 145.99, 140.09, 136.92, 136.33, 129.48, 129.25, 129.14, 127.76, 127.18, 126.55, 126.27, 122.97, 122.35, 121.19 ppm; HR FAB-MS: m/z: 435.1608 $[M+H]^+$, calcd 435.1610.

Diphenanthroline 10: A THF solution (70 mL) containing lithio derivative **9** [7 mmol, prepared from 1-bromo-3-trimethylsilylbenzene (1.603 g, 7 mmol) and *t*BuLi (14 mmol)] [17] was added through a cannula to a degassed suspension of diphenanthroline **8** (0.950 g, 2.18 mmol) in anhydrous toluene (120 mL) at 6 °C. Upon addition of **9** onto **8** the initial pale-yellow suspension turned dark red. The mixture was stirred under argon for 3 h at 7 °C. Subsequent hydrolysis with water at 0 °C afforded a bright yellow mixture from which THF was distilled under vacuum. After the mixture had been decanted, the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL) and the combined organic phases were rearomatized with MnO_2 (7 g). $MgSO_4$ (10 g) was added to dry the organic phase and the MnO_2/$MgSO_4$ slurry was filtered through sintered glass (porosity 4). Evaporation of the solvents yielded 1.510 g of a pale yellow glass. Pure compound **10** was obtained after column chromatography over silica gel (eluent: CH_2Cl_2/2 % MeOH) in 58 % yield (0.924 g, 1.26 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.35 (t, J = 1.8 Hz, 1H, H-a_p), 8.80 (dd, J_1 = 7.7, J_2 = 1.8 Hz, 2H, H-b_p), 8.74 (br s, 2H, H-d), 8.46 (m, 2H, H-a), 8.41 (br s, 4H, H-3,4), 8.35 (d, J = 8.4 Hz, 2H, H-7), 8.21 (d, J = 8.4 Hz, 2H, H-8), 7.85 (s, 4H, H-5,6), 7.84 (t, J = 7.7 Hz, 1H, H-c_p), 7.68 (dt, J_1 = 7.7, J_2 = 1.6 Hz, 2H, H-c), 7.56 (t, J = 7.7 Hz, 2H, H-b), 0.40 ppm (s, 18H, $SiMe_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.02, 156.49, 146.18, 146.16, 141.04, 139.72, 138.56, 136.94, 136.91, 134.53, 132.72, 129.62, 129.13, 128.09, 128.06, 127.92, 126.21, 126.09, 126.01, 120.04, 119.97, −0.95 ppm; HR FAB-MS: m/z: 731.3020 $[M+H]^+$, calcd 731.3026.

Diiodo-diphenanthroline 11: Diphenanthroline **10** (570 mg, 0.8 mmol) was placed in a two-necked round-bottom flask and dissolved in CH_2Cl_2 (100 mL). The solution was purged three times with Ar/vacuum and cooled to 0 °C in an ice-bath. ICl (160 mg, 1.02 mmol) in CH_2Cl_2 (10 mL) was added and the ice-bath was removed. After 4 h, the solution was quenched with a saturated solution of $Na_2S_2O_5$. The aqueous layer was extracted with CH_2Cl_2 and dried with $MgSO_4$. After purification by chromatography on alumina (CH_2Cl_2), **11** was isolated as a white solid (650 mg, CH_2Cl_2 adduct) in 98 % yield. ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.19 (t, J = 7.8 Hz, 2H, H-b), 7.78 (dt, J = 7.8, J = 1.6 Hz, 2H, H-c), 7.86 (t, J = 7.6 Hz, 1H, H-c_p), 7.87 (d, J = 8.8 Hz, 2H, H-6), 7.91 (d, J = 8.8 Hz, 2H, H-5), 8.12 (d, J = 8.4 Hz, 2H, H-8), 8.38 (d, J = 8.4 Hz, 2H, H-7), 8.45 (d, 4H, H-3,4), 8.47 (m, 2H, H-a), 8.65 (dd, J = 7.7, J = 1.8 Hz, 2H, H-b_p), 8.80 (t, J = 1.6 Hz, 2H, H-d), 9.59 ppm (t, J = 1.8 Hz, 1H, H-a_p); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.82, 159.30, 155.63, 155.40, 143.06, 141.39, 140.36, 138.02, 137.71, 136.46, 135.09, 131.34, 130.76, 129.19, 129.09, 128.12, 127.63, 127.03, 124.81, 124.29, 116.97, 113.15 ppm; FAB-MS: m/z: 839.1 $[M+H]^+$, calcd 839.4.

Diphenanthroline diboronic ester 12: Diiodo-diphenanthroline **11** (650 mg, 0.68 mmol), bis-neopentyl diboron (340 mg, 1.49 mmol), KOAc (400 mg, 4.10 mmol), and [Pd(dppf)Cl_2]·CH_2Cl_2 (33 mg, 0.04 mmol) were dissolved in freshly distilled dioxane (60 mL). The mixture was stirred under argon at 80 °C for five days. The solution was then cooled to room temperature and water (60 mL) was added. The product was extracted from the aqueous phase with CH_2Cl_2. The organic phase was dried with $MgSO_4$, filtered, and evaporated. The resulting black solid was then purified by chromatography over silica using CH_2Cl_2/MeOH as eluent. The

product underwent substantial decomposition on the column (hydrolysis of the diol protecting group). A black solid (320 mg) was recovered. ^{1}H NMR and mass spectrometric analyses were in good agreement with the expected structure of **12** (58% yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 1.04 (s, 12H, CH_3), 3.80 (s, 8H, CH_2), 7.63 (t, $J=7.7$ Hz, 2H), 7.84 (m, 4H), 7.98 (dt, $J_1=7.3$, $J_2=1.1$ Hz, 2H), 8.28 (d, $J=8.4$ Hz, 2H), 8.33 (d, $J=8.4$ Hz, 2H), 8.39 (d $J=8.4$ Hz, 2H), 8.50 (d, $J=8.4$ Hz, 2H), 8.78 (dd, $J_1=7.7$, $J_2=1.6$ Hz, 2H), 8.80 (brs, 2H), 8.87 (dt, $J_1=7.9$, $J_2=1.5$ Hz, 2H), 9.74 ppm (t, $J=1.8$ Hz, 1H); FAB-MS: m/z: 811.4 $[M+H]^+$, calcd 811.5.

Tetraphenanthroline 13: Diphenanthroline **12** (295 mg, 0.36 mmol), bromophenanthroline **6** (265 mg, 0.728 mmol), $Pd(PPh_3)_4$ (60 mg, 0.04 mmol), and K_3PO_4 (230 mg, 1.1 mmol) were added to DMF (20 mL). After the mixture was degassed, the solution was stirred at 100°C for two days. The reaction mixture was then allowed to cool to room temperature. Upon addition of water (30 mL), a precipitate was formed. The solid was filtered and purified over silica ($CH_2Cl_2/CHCl_3$/4 to 7% MeOH) to give the product **13** (252 mg) as a brown solid in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=3.83$ (s, 6H, OCH_3), 6.99 (d, $J=8.3$ Hz, 4H, H-*m*), 7.38 (d, $J=8.1$ Hz, 2H, H-5′), 7.49 (d, $J=8.7$ Hz, 2H, H-5), 7.53 (d, $J=8.1$ Hz, 2H, H-6′), 7.61 (d, $J=8.7$ Hz, 2H, H-6), 7.68 (t, $J=$ 7.9 Hz, 1H, H-c), 7.73 (t, $J=7.9$ Hz, 2H, H-c′), 8.00 (d, $J=8.4$ Hz, 2H, H-4′), 8.04 (d, $J=8.5$ Hz, 2H, H-8′), 8.06 (d $J=9.6$ Hz, 2H, H-4), 8.21 (d, $J=8.3$ Hz, 2H, H-7′), 8.30–8.39 (m, 12H, H-7,8,3,3′, H-*o*), 8.48 (brd, 2H, H-d′), 8.56 (dd, 2H, H-b), 8.64 (brd, 2H, H-b′), 9.68 (brs, 2H, H-a′), 9.72 ppm (brs, 1H, H-a); FAB-MS: m/z: 1156.3 $[M+H]^+$, calcd 1156.3.

Diphenol 14: Pyridine (17 mL) was poured into a three-necked flask. While stirring, HCl (36%, 19 mL) was slowly added. The reaction was highly exothermic and fuming. After addition of HCl the flask was fitted with a distillation head. To distil the water from the mixture the flask was heated with a mantle until the internal temperature reached 210–220°C (boiling point of anhydrous pyridine hydrochloride). The distillation head was then removed and the mixture was allowed to cool to 140°C. A powder funnel was placed in the large middle neck and, whilst bubbling argon gas through the right neck, tetraphenanthroline **13** (252 mg, 0.22 mmol) was poured in one batch into the flask through the left neck. The reaction flask was then fitted with a water condenser equipped with a two-way Claisen adaptor connected on one side to a source of Ar and on the other side to a mineral oil bubbler. After establishing an argon atmosphere in the flask, the contents were stirred under reflux for 3 h (internal temperature 210–220°C).The hot brown stirred mixture was cooled to 110°C and diluted by slow and careful injections of hot water. The resulting brown suspension was poured into a conical flask containing hot water (60 mL). The solution was allowed to cool to room temperature and then the suspension was neutralized by the addition of KOH pellets to the flask until a pH of 7.3 was obtained. Then the solid was filtered and air-dried on a porous dish overnight and finally dried in a vacuum desiccator in the presence of KOH to obtain diOH-tetraphenanthroline **14** as a brown solid (235 mg, 95% yield). ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=6.88$ (d, $J=8.4$ Hz, 4H), 7.62 (t, $J=8.0$ Hz, 3H), 7.70 (d, $J=8.8$ Hz, 2H), 7.82 (d, $J=8.8$ Hz, 2H), 7.91 (d, $J=8.8$ Hz, 2H), 7.98 (d, $J=8.8$ Hz, 2H), 8.24 (d, $J=8.6$ Hz, 2H), 8.29 (d, $J=8.6$ Hz, 2H), 8.40 (d, $J=8.4$ Hz, 4H), 8.44–8.74 (m, 18H), 9.68 (brs, 2H), 9.82 (brs, 1H), 9.88 ppm (brs, 2H); FAB-MS: m/z: 1128.4 $[M+H]^+$, calcd 1128.3.

Diolefinic tetraphenanthroline 1: DiOH-tetraphenanthroline **14** (230 mg, 0.20 mmol) was dissolved in dry DMF (50 mL) and the solution was degassed and heated at 65°C. Cs_2CO_3 (1.32 g, 4.10 mmol) was then added and the solution stirred for 45 min. Bromo-allyl-poly(ethylene glycol) (0.422 g, 1.42 mmol) was dissolved in dry and degassed DMF (15 mL) and placed in an addition funnel. The bromo compound was then added dropwise to the diOH-tetraphenanthroline **14**. After 6 h, further Cs_2CO_3 (800 mg) and the bromo compound (400 mg) were added, and the solution was stirred for 1 day. Then DMF was removed under vacuum. The solid was washed with diethyl ether and then dissolved in CH_2Cl_2/H_2O (50:50 mL). The aqueous phase was extracted with CH_2Cl_2 (50 mL) and the organic layers were combined. The solvent was removed under vacuum to afford a clear brown solid (400 mg) which was purified by chromatography over silica gel (CH_2Cl_2/MeOH) to yield diallyl-tetraphenanthroline **1** (260 mg, 80% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=3.60$ (m, 24H, H-C,D,E,F,G,H), 3.88 (t, 4H, H-B), 3.97 (dt, 4H, H-I), 4.18 (t, 4H, H-A), 5.20 (m, 4H, H-K), 5.89 (m, 2H, H-J), 7.02 (d, $J=8.7$ Hz, 4H, H-*m*), 7.46 (d, $J=8.8$ Hz, 2H, H-5′), 7.59 (d, $J=8.8$ Hz, 2H, H-5), 7.60 (d, $J=8.7$ Hz, 2H, H-6′), 7.70 (d, $J=8.8$ Hz, 2H, H-6), 7.75 (t, 1H, H-c), 7.76 (t, $J=7.6$ Hz, 2H, H-c′), 8.04 (d, $J=8.7$ Hz, 2H, H-4′), 8.07 (d, $J=$ 8.7 Hz, 2H, H-8′), 8.13 (d, $J=8.5$ Hz, 2H, H-4), 8.30 (m, 10H, H-7,8,3,3′,7′), 8.42 (d, $J=8.7$ Hz, 4H, H-*o*), 8.52 (d, $J=7.0$ Hz, 2H, H-d′), 8.58 (d, $J=7.8$ Hz, 2H, H-b), 8.63 (d, $J=7.8$ Hz, 2H, H-b′), 9.70 (brs, 2H, H-a′), 9.75 ppm (brs, 1H, H-a); FAB-MS: m/z: 1560.6 $[M+H]^+$, calcd 1560.8.

$[(1)_2\cdot 4Li]^{4+}\cdot(4PF_6)^{4-}$: DiOH-tetraphenanthroline **1** (145 mg, 0.092 mmol) was dissolved in CH_2Cl_2/MeOH (8:2, 10 mL) under argon and $LiPF_6$ (32 mg, 0.21 mmol) was added to the solution. Li_2CO_3 (3 mg) was also added to adjust the pH to 7. The solution was stirred for 3 h and then the solvent was removed to quantitatively afford 176 mg of the double helix. ^{1}H NMR (300 MHz, CD_3CN): $\delta=3.25$ (m, 8H, H-A), 3.47 (m, 8H, H-B), 3.50–3.70 (m, 48H, H-C,D,E,F,G,H), 4.00 (dt, 8H, H-I), 5.20 (m, 8H, H-K), 5.59 (d, $J=8.4$ Hz, 8H, H-*m*), 5.92 (m, 4H, H-J), 6.00 (dd, 8H, H-8,3), 6.20 (d, $J=8.4$ Hz, 4H, H-3′), 6.75–6.68 (m, 20H, H-*o*, H-b,b′,d′), 6.89 (t, $J=7.5$ Hz, 2H, H-c), 6.94 (t, $J=7.9$ Hz, 4H, H-c′), 7.54–7.40 (m, 22H, H-4,4′,7,8′,a,a′), 7.65 (m, 12H, H-5,5′,6), 7.81 (d, $J=8.8$ Hz, 4H, H-6′), 8.22 ppm (d, $J=8.5$ Hz, 4H, H-7′); HR ES-MS: m/z: 1718.6457 $[M-2PF_6]^{2+}$, 1097.4533 $[M-3PF_6]^{3+}$, 786.8472 $[M-4PF_6]^{4+}$; calcd for $C_{200}H_{172}N_{16}O_{20}Li_4P_2F_{12}$ $[M-2PF_6]^{2+}$: 1718.6466.

Diphenanthroline 19: A solution of 1-lithio-3-bromobenzenze (**16**) [prepared from 1,3-dibromobenzene (2.08 g, 8.8 mmol) and *n*-BuLi (8.8 mmol) at a temperature of between 2 and 4°C] in Et_2O (60 mL) was added through a cannula to a degassed suspension of **15** (2.29 g, 8 mmol) in Et_2O (100 mL) maintained at 2°C. The dark red mixture of **17** obtained after addition of the lithio-derivative **16** was maintained with stirring at 4°C under argon for a further 2 h. *n*BuLi (6.8 mL, 10.6 mmol) was then injected rapidly (5 min) into this mixture at 3°C to give a solution of phenanthroline **18**. This solution was stirred at 5–10°C for 2 h before being added through a cannula to a degassed solution of 2-chlorophenanthroline (**3**) (1.932 g, 9 mmol) in toluene (150 mL) at 2–4°C. The resulting dark red solution was stirred overnight while the temperature slowly returned to room temperature. After hydrolysis at 0°C, the organic phase was decanted and the aqueous phase extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were treated with MnO_2 (47 g), dried with $MgSO_4$, and evaporated to dryness after filtration of the $MnO_2/MgSO_4$ slurry to afford a dark-brown crude. This was subjected to column chromatography over silica gel twice (eluent: CH_2Cl_2/1% MeOH) to give pure **19** in 34% yield (1.565 g, 2.72 mmol). ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta=9.35$ (t, $J=1.6$ Hz, 1H, H-a), 8.59 (dd, $J_1=7.9$, $J_2=1.7$ Hz, 2H, H-b), 8.45 (d, $J=8.9$ Hz, 2H, H-*o*), 8.42 (AB, 2H, H-3′, H-4′), 8.39 (d, $J=$ 8.4 Hz, 1H, H-4), 8.33 (d, $J=8.4$ Hz, 1H, H-3), 8.31 (d, $J=8.4$ Hz, 1H, H-7), 8.25 (d, $J=8.4$ Hz, 1H, H-7′), 8.12 (d, $J=8.4$ Hz, 1H, H-8), 7.82 (d, $J=8.8$ Hz, 1H, H-5′), 7.75 (t, $J=7.9$ Hz, 1H, H-c), 7.73 (d, $J=8.9$ Hz, 1H, H-6′), 7.74 (s, 2H, H-5,6), 7.57 (d, $J=8.2$ Hz, 1H, H-8′), 7.05 (d, $J=$ 8.9 Hz, 2H, H-*m*), 3.87 ppm (s, 3H, OMe); FAB-MS: m/z: 576.0 $[M+H]^+$, calcd 576.0.

Diphenanthroline 20: Exchange of the chlorine atom by the bromine atom was performed following a modification to the procedure described in the literature.[3] Under a stream of argon, pure PBr_3 (25 mL) was poured onto the neat solid diphenanthroline **19** (1.030 g, 1.79 mmol) in a two-necked round-bottom flask fitted with a reflux condenser. The resulting bright yellow mixture was then refluxed for 40 min at 170°C. During the heating, the initial yellow color rapidly turned greenish-black. The resulting dark suspension was stirred overnight at room temperature under argon. Subsequent careful hydrolysis on crushed ice afforded a yellow-greenish precipitate of **20** in a strongly acidic medium (pH 1). KOH pellets were added until the medium was slightly basic (pH 7.30), and then the bromide **20** was extracted with a mixture of CH_2Cl_2 and $CHCl_3$. After decanting the mixture, the combined organic phases were dried over $MgSO_4$, filtered, and evaporated to dryness to afford 975 mg of crude bromide **20**. This crude was purified by column chromatography on

silica gel (eluent: CH_2Cl_2/0–10% MeOH) to afford pure **20** in 65% yield (715 mg, 1.15 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 9.35 (t, J = 1.5 Hz, 1H, H-a), 8.59 (dd, J_1 = 7.7, J_2 = 1.5 Hz, 2H, H-b), 8.46 (d, J = 9.0 Hz, 2H, H-*o*), 8.43 (brs, 2H, H -3′,4′), 8.40 (d, J = 8.4 Hz, 1H, H-4), 8.37 (d, J = 8.4 Hz, 1H, H-3), 8.31 (d, J = 8.4 Hz, 1H, H-7), 8.14 (d, J = 8.4 Hz, 1H, H-7′), 8.12 (d, J = 8.4 Hz, 1H, H-8), 7.93 (d, J = 8.8 Hz, 1H, H-5′), 7.85 (t, J = 7.7 Hz, 1H, H-c), 7.82 (d, J = 8.8 Hz, 1H, H-6′), 7.81 (s, 2H, H-5,6), 7.78 (d, J = 8.4 Hz, 1H, H-8′), 7.07 (d, J = 9.0 Hz, 2H, H-*m*), 3.89 ppm (s, 3H, OMe); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 160.88, 157.69, 156.38, 156.19, 142.45, 139.54, 139.48, 138.35, 137.21, 137.02, 136.89, 131.99, 129.49, 129.31, 129.07, 128.76, 128.08, 127.99, 127.92, 127.83, 127.49, 127.01, 126.89, 126.04, 125.64, 125.52, 121.25, 120.16, 119.59, 114.09, 55.33 ppm; HR ES-MS: m/z: 619.1150 $[M+H]^+$, calcd 619.1133.

Monosubstituted phenanthroline 21: A solution of 1-lithio-3-bromobenzene **16** [prepared from 1,3-dibromobenzene (9.44 g, 40 mmol) by interconversion with *n*BuLi (25 mL, 40 mmol) at 2–4 °C] in diethyl ether (120 mL) was added to a degassed solution (150 mL) of anhydrous 1,10-phenanthroline (6.84 g, 38 mmol) in THF also maintained at 2–4 °C. After stirring for 2 h at 3–4 °C, the mixture was hydrolyzed by injection of water (50 mL) at a low temperature (0–5 °C). The solvents were evaporated and the dark-yellow crude taken up in CH_2Cl_2/H_2O. After decanting the mixture, the aqueous layer was extracted with CH_2Cl_2 (3× 100 mL). The combined organic phases were subsequently rearomatized with MnO_2 (30 g) and dried with $MgSO_4$. Filtration of the $MnO_2/MgSO_4$ slurry through sintered glass (porosity 4) and evaporation of the solvent afforded crude **21**. Pure **21** was obtained by column chromatography over silica gel (eluent: CH_2Cl_2/0–5% MeOH) as a pale-yellow glass in 32% yield (4.085 g, 12.194 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.25 (dd, J_1 = 4.2, J_2 = 1.7 Hz, 1H, H-9), 8.47 (dd, J_1 = 2.0, J_2 = 1.7 Hz, 1H, H-d), 8.33 (d, J = 8.4 Hz, 1H, H-4), 8.29 (m, 2H, H-7, H-a), 8.06 (d, J = 8.4 Hz, 1H, H-3), 7.81 (s, 2H, H-5,6), 7.66 (dd, J_1 = 8.1, J_2 = 4.2 Hz, 1H, H-8), 7.62 (ddd, J = 7.9 Hz, 1H, H-c), 7.42 ppm (t, J = 7.9 Hz, 1H, H-b); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.86, 150.40, 146.21, 146.02, 141.65, 136.97, 136.08, 132.17, 130.78, 130.23, 129.72, 127.72, 126.60, 126.53, 126.52, 126.20, 123.02, 120.48 ppm. HR FAB-MS: m/z: 335.0160 $[M+H]^+$, calcd 335.0184.

2,9-Bis(*m*-bromophenyl)-1,10-phenanthroline (22): A solution of 1-lithio-3-bromobenzene **16** [prepared from 1,3-dibromobenzene (3.54 g, 15 mmol) by interconversion with *n*BuLi (12 mL, 16 mmol) at 2–4 °C] in diethyl ether (40 mL) was added to a degassed solution of phenanthroline **21** (3.35 g, 10 mmol) in THF/Et_2O (40:50 mL) maintained at 2–4 °C. After stirring for 2 h at 3–4 °C, the mixture was hydrolyzed by injection of water (50 mL) at 0 °C. The solvents (THF and Et_2O) were evaporated and the dark yellow-brown crude taken up in CH_2Cl_2/H_2O. After decanting the mixture, the aqueous layer was extracted with CH_2Cl_2 (3× 50 mL). The combined organic phases were subsequently rearomatized with MnO_2 (26 g) and dried with $MgSO_4$. Filtration of the $MnO_2/MgSO_4$ slurry through sintered glass (porosity 4) and evaporation of the solvent afforded crude **22**. Pure **22** was obtained by column chromatography over silica gel (eluent: CH_2Cl_2/hexane, 80:20) as a colorless solid in 24% yield (1.19 g, 2.43 mmol). ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 8.71 (dd, J_1 = 2.0, J_2 = 1.7 Hz, 2H, H-d), 8.36 (m, 4H, H-4,7, H-a), 8.13 (d, J = 8.4 Hz, 2H, H-3,8), 7.82 (s, 2H, H-5,6), 7.64 (ddd, J = 7.9 Hz, 2H, H-c), 7.47 ppm (t, J = 7.9 Hz, 2H, H-b).

Diboronic ester 23: Under a stream of argon, dibromide **22** (490 mg, 1 mmol), bis-neopentyl diboron (558 mg, 2.2 mmol), and KOAc (589 mg, 6 mmol) were poured into a three-necked round-bottom flask. The solid mixture of compounds was covered with freshly distilled dioxane (70 mL). The resulting suspension was degassed three times and warmed to reflux (80 °C) before the catalyst $[Pd(dppf)Cl_2]$ (49 mg, 0.06 mmol) was added as a solid in one batch. Monitoring by TLC showed that the reaction was completed after heating overnight. The dark brown solution was poured into cold water (100 mL). The gray precipitate which was formed was filtered through paper and washed three times with cold water. The air-dried crude gray solid was redissolved in CH_2Cl_2 and purified by rapid column chromatography over silica gel (eluent: CH_2Cl_2/0–5% MeOH) to afford pure **23**in 90% yield (524 mg, 0.90 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.88 (m, J_1 = 7.9, J_2 = 1.8, J_3 = 1.2 Hz, 2H, H-a), 8.73 (brs, 2H, H-d), 8.31 (d, J = 8.4 Hz, 2H, H-4,7), 8.27 (d, J = 8.4 Hz, 2H, H-3,8), 7.96 (dt, J_1 = 7.3, J_2 = 1.2 Hz, 2H, H-c), 7.79 (s, 2H, H-5,6), 7.65 (t, J = 7.9 Hz, 2H, H-b), 1.41 ppm (s, 24H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.69, 146.14, 138.67, 136.8, 135.94, 133.53, 131.39, 131.07, 128.46, 127.96, 126.00, 120.11, 83.92, 24.99; HR FAB-MS: m/z: 585.3107 $[M+H]^+$, calcd 585.3096.

Diboronic acid 24: 3 M HCl (30 mL) was added, at room temperature, to diester **23** (521 mg, 0.892 mmol) dissolved in THF (30 mL). The resulting ochre-beige suspension was stirred at room temperature for four days. Subsequent evaporation of THF afforded a yellow precipitate in the remaining acidic aqueous phase. The latter was neutralized (pH 7.1) by addition of a concentrated KOH solution. The resulting neutral beige precipitate was isolated by filtration through paper, washed with water, and air-dried to afford pure diboronic acid **24** (373 mg, 0.888 mmol) in 99% yield. ^{1}H NMR (300 MHz, CD_3OD and 3 drops of a DCl solution in D_2O): δ = 8.88 (d, J = 8.6 Hz, 2H, H-4,7), 8.50 (brs, 2H, H-d), 8.41 (d, J = 8.6 Hz, 2H, H-3,8), 8.24 (m, 2H, H-a), 8.18 (s, 2H, H-5,6), 7.92 (d, J = 7.3 Hz, 2H, H-c), 7.54 ppm (t, J = 7.5 Hz, 2H, H-b); HR FAB-MS: m/z: 449.1867 $[M+H]^+$ (the dimethyl ester was formed in the conditions used for this product), calcd 449.1844.

Pentaphenanthroline 25: Diphenanthroline **20** (715 mg, 1.154 mmol), diboronic acid **24** (267 mg, 0.635 mmol), $[Pd(PPh_3)_4]$ (60 mg, 0.05 mmol), and K_3PO_4 (735 mg, 3.46 mmol) were poured as solids into a three-necked round-bottom flask under a stream of argon at room temperature. The mixture of solids was stirred and degassed three times before it was covered with dry and degassed DMF (50 mL) and heated to 100 °C. Except for K_3PO_4, all the solids dissolved at this temperature. The mixture was then stirred and heated for 48 h and further $[Pd(PPh_3)_4]$ was added (60 mg after 3 and 27 h). The resulting dark-brown reaction mixture was cooled to room temperature and diluted with water (200 mL). The beige precipitate which appeared was filtered through paper, washed with water and air-dried on a porous dish to afford 1.268 g of an ochre solid. The latter was suspended in CH_2Cl_2 (50 mL) and filtered through a column of dry silica gel. By using CH_2Cl_2 containing increasing amounts of MeOH (0–7%) as eluent all the organic compounds were eluted other than **25** which remained on the solid silica support. The silica gel in the column was then poured into a round-bottom flask, covered with CH_2Cl_2/MeOH (93:7) (150 mL) before $LiPF_6$ (680 mg, 4.5 mmol) was added under a stream of argon. The heterogeneous mixture was thereafter gently stirred at room temperature for four days under argon. The mixture was then decanted, filtered through sintered glass, and the silica gel washed with CH_2Cl_2 (100 mL) and CH_3CN (100 mL). CF_3COOH (1 mL) was added to the combined filtrate and washings. The bright yellow solution obtained was evaporated to dryness to afford fully protonated **25** (1.024 g, 0.794 mmol) in 83% yield. ^{1}H NMR (300 MHz, CD_3CN): δ = 9.74 (brs, 2H), 9.08 (d, J = 8.8 Hz, 2H), 8.63 (brs, 2H), 8.86 (d, J = 8.6 Hz, 2H), 8.35 (d, J = 8.5 Hz, 2H), 8.22 (d, J = 8.9 Hz, 2H), 8.12 (d, J = 8.9 Hz, 2H), 8.05–7.89 (m, 10H), 7.72 (m, 4H), 7.65 (s, 2H), 7.47 (m, 6H), 7.35 (m, 6H), 7.19 (m, 6H), 6.94 (d, J = 8.8 Hz, 2H), 5.97 (d, J = 8.7 Hz, 4H), 3.27 ppm (s, 6H); ES-MS: m/z: 1410.5 $[M+H]^+$, calcd 1410.6; 705.5 $[M+2H]^{2+}$, calcd 705.7; 470.7 $[M+3H]^{3+}$, calcd 470.8; 353.3 $[M+4H]^{4+}$, calcd 353.3.

Diphenol pentaphenanthroline 26: Starting from $(\mathbf{25}\cdot 5H)^{5+}\cdot 5PF_6^-$ (1.024 g, 0.479 mmol) and excess pyridinium chloride [prepared from pyridine (16 mL) and HCl (36%, 17.6 mL)], diphenol **26** (617 mg,0.446 mmol) was obtained in 93% yield by following the procedure used for the preparation of diphenol **14**. Owing to the very low solubility of **26**, no satisfactory NMR analysis could be obtained. ES-MS: m/z: 1382.5 $[M+H]^+$, calcd 1382.5; 1404.5 $[M+Na]^+$, calcd 1404.5; 691.5 $[M+2H]^{2+}$, calcd 691.7; 461.4 $[M+3H]^{3+}$, calcd 461.5; 346.3 $[M+4H]^{4+}$, calcd 346.4.

Diolefinic pentaphenanthroline 2: Diphenol pentaphenanthroline **26** (O.612 g, 0.443 mmol) was suspended in dry DMF (200 mL). The mixture was degassed and warmed to 65 °C and then Cs_2CO_3 (2.02 g, 8.86 mmol) was added. The mixture was stirred at 65 °C for 1 h before a degassed solution of bromo-allyl-poly(ethylene glycol) (1.05 g, 3.10 mmol) in DMF (15 mL) was slowly added through an addition funnel (over a period of half an hour). The mixture was stirred at 65 °C for 6 h after which addi-

tional Cs_2CO_3 (1.8 g) and olefinic chain (0.700 g, 2.05 mmol) were added. After stirring at 65 °C under argon overnight, the mixture was evaporated to dryness. The solid residue was washed four times with Et_2O (to remove excess olefinic chain) and thereafter suspended in water. The ochre-beige precipitate was filtered through paper and washed with water before being dried in air on a porous dish. Compound **2** thus obtained in 62 % yield (0.520 g, 0.273 mmol) was used without further purification. ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta = 9.78$ (brs, 2H, H-a), 9.69 (brs, 2H, H-a′), 8.63 (d, $J = 7.9$ Hz, 2H, H-d′), 8.60 (d, $J = 7.3$ Hz, 2H, H-d), 8.54 (m, 4H, H-b,b′), 8.41 (d, $J = 8.6$ Hz, 4H, H-*o*), 8.36 (brs, 4H, H-7′,8′), 8.30 (d, $J = 7.9$ Hz, 2H, H-3″), 8.29 (d, $J = 7.7$ Hz, 2H, H-3,8), 8.27 (d, $J = 8.2$ Hz, 2H, H-3′), 8.21 (d, $J = 8.6$ Hz, 2H, H-7″), 8.10 (d, $J = 8.2$ Hz, 2H, H-4′), 8.08 (d, $J = 8.6$ Hz, 2H, H-8″), 8.05 (d, $J = 7.7$ Hz, 2H, H-4,7), 8.04 (d, $J = 7.9$ Hz, 2H, H-4″), 7.72 (t, $J = 7.9$ Hz, 2H, H-c′), 7.66 (t, $J = 7.3$ Hz, 2H, H-c), 7.64 (d, $J = 8.6$ Hz, 2H, H-6′), 7.57 (d, $J = 8.6$ Hz, 2H, H-6″), 7.55 (d, $J = 8.6$ Hz, 2H, H-5′), 7.45 (d, $J = 8.6$ Hz, 2H, H-5″), 7.37 (s, 2H, H-5,6), 7.03 (d, $J = 8.6$ Hz, 4H, H-*m*), 5.88–5.85 (m, 2H, H-L), 5.26–5.11 (m, 4H, H-M), 4.17 (t, $J = 4.1$ Hz, 4H, H-A), 3.97–3.93 (m, 4H, H-K), 3.87 (t, $J = 4.1$ Hz, 4H, H-B), 3.76–3.50 (m, 32H, H-C,D,E,F,G,H,I,J); ES-MS: *m*/*z*: 1902.8 $[M+H]^+$, calcd 1903.2; 952.0 $[M+2H]^{2+}$, calcd 952.1; 634.9 $[M+3H]^{3+}$, calcd 635.0.

Lithium complex $[(\mathbf{2})_2{\cdot}5Li]^{5+}(5PF_6)^{5-}$: $LiPF_6$ (145 mg, 0.95 mmol) dissolved in MeOH (30 mL) was added to the brown solution of **2** (565 mg, 0.297 mmol) in CH_2Cl_2 (100 mL) at room temperature under a stream of argon. Upon addition of $LiPF_6$ the acidic solution (pH 3) was neutralized by the addition of small amounts of solid Li_2CO_3 and three drops of water. The resulting mixture was stirred under argon overnight. Monitoring by ^{1}H NMR spectroscopy allowed us to determine the necessary amount of Li_2CO_3 needed for the formation of the lithium complex. At the end of the reaction the solvents were evaporated to dryness to afford crude complex $[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(5PF_6)^{5-}$ (515 mg, 0.113 mmol) as an ochre glass in 76 % yield. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.14$ (d, $J = 8.4$ Hz, 4H, H-7″), 7.76 (d, $J = 9.0$ Hz, 4H, H-6″), 7.64 (m, 16H, H-a′, H-5″,5′,6′), 7.54 (s, 4H, H-5,6), 7.53 (d, $J = 8.4$ Hz, 4H, H-4″), 7.50 (d, $J = 8.4$ Hz, 4H, H-7′), 7.47 (d, $J = 8.4$ Hz, 4H, H-4′), 7.37 (d, $J = 8.8$ Hz, 4H, H-4,7), 7.34 (d, $J = 8.4$ Hz, 4H, H-8″), 7.24 (brs, 4H, H-a), 6.96 (t, $J = 7.7$ Hz, 4H, H-c′), 6.88 (t, $J = 7.5$ Hz, 4H, H-c), 6.66 (d, $J = 7.7$ Hz, 4H, H-d′), 6.65 (d, $J = 8.6$ Hz, 8H, H-*o*), 6.59 (d, $J = 6.4$ Hz, 4H, H-b′), 6.57 (d, $J = 8.2$ Hz, 4H, H-d), 6.49 (d, $J = 7.5$ Hz, 4H, H-b), 6.10 (d, $J = 8.4$ Hz, 4H, H-8′), 6.05 (d, $J = 8.4$ Hz, 4H, H-3″), 5.94 (d, $J = 8.4$ Hz, 4H, H-3′), 5.90 (d, $J = 8.8$ Hz, 4H, H-3,8), 5.90–5.77 (m, 4H, H-L), 5.56 (d, $J = 8.6$ Hz, 8H, H-*m*), 5.26–5.14 (m, 8H, H-M), 3.98 (td, $J = 5.9$ Hz, 8H, H-K), 3.75–3.63 (m, 64H, H-C,D,E,F,G,H,I,J), 3.60 (m, 8H, H-B), 3.32 ppm (m, 8H, H-A); HR ES-MS: *m*/*z*: *m*/2 at 2136.8278 ($[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(3PF_6)^{3-}$), calcd 2137.0241; *m*/3 at 1376.1988 ($[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(2PF_6)^{2-}$), calcd 1376.3613; *m*/4 at 995.9139 ($[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(PF_6)^{-}$), calcd996.0299; *m*/5 at 767.7443 ($[(\mathbf{2})_2{\cdot}5Li]^{5+}$), calcd 767.8311; *m*/2 at 2060.8009 ($[(\mathbf{2})_2{\cdot}4Li]^{4+}{\cdot}(2PF_6)^{2-}$), calcd 2061.0720; *m*/3 at 1325.5394 ($[(\mathbf{2})_2{\cdot}4Li]^{4+}{\cdot}(PF_6)^{-}$) calcd 1325.7266; *m*/4 at 958.1637 ($[(\mathbf{2})_2{\cdot}4Li]^{4+}$), calcd 958.0539.

Heteronuclear Li–Cu complexes $[(\mathbf{2})_2{\cdot}3Li{\cdot}2Cu]^{5+}{\cdot}(5PF_6)^{5-}$ and $[(\mathbf{2})_2{\cdot}2Li{\cdot}2Cu]^{4+}{\cdot}(4PF_6)^{4-}$: A degassed solution of $[Cu(CH_3CN)_4]^+{\cdot}PF_6^-$ (44 mg, 0.118 mmol) in CH_3CN (30 mL) was slowly added through a cannula to the degassed, ochre solution of $[(\mathbf{2})_2{\cdot}5Li]^{5+}{\cdot}(5PF_6)^{5-}$ (262 mg, 0.0574 mmol) in CH_2Cl_2 (70 mL) at room temperature. After half an hour all the copper had been added and the resulting solution was stirred at room temperature and under argon for 48 h during which time the initial ochre solution gradually turned dark red. The solvents were then evaporated to dryness to afford $[(\mathbf{2})_2{\cdot}3Li{\cdot}2Cu]^{5+}{\cdot}(5PF_6)^{5-}$ (267 mg, 0.057 mmol) in quantitative yield as a dark-red solid. ^{1}H NMR (500 MHz, CD_2Cl_2 + MeOD + ascorbic acid): $\delta = 8.33$ (brs, 4H, H-a′), 8.16 (d, $J = 8.5$ Hz, 4H, H-7″), 7.78 (d, $J = 9.0$ Hz, 4H, H-6″), 7.65 (d, $J = 9.0$ Hz, 4H, H-5″), 7.63 (AB, $J = 8.8$ Hz, 8H, H-5′,6′), 7.56 (s, 8H, H-5,6), 7.52 (d, $J = 8.4$ Hz, 4H, H-4″), 7.48 (d, $J = 8.2$ Hz, 4H, H-7′), 7.46 (d, $J = 8.1$ Hz, 4H, H-4′), 7.41 (d, $J = 8.5$ Hz, 4H, H-8″), 7.38 (d, $J = 8.2$ Hz, 4H, H-4,7), 7.23 (brs, 4H, H-a), 6.91 (t, $J = 7.5$ Hz, 4H, H-c′), 6.88 (t, $J = 7.5$ Hz, 4H, H-c), 6.75 (d, $J = 8.5$ Hz, 8H, H-*o*), 6.61 (d, $J = 7.5$ Hz, 4H, H-d′), 6.59–6.55 (m, 8H, H-d,b′), 6.50 (d, $J = 7.5$ Hz, 4H, H-b), 6.11 (d, $J = 8.1$ Hz, 4H, H-3′), 6.04 (d, $J = 8.4$ Hz, 4H, H-3″), 5.95 (d, $J = 8.2$ Hz, 4H, H-8′), 5.90 (d, $J = 8.2$ Hz, 4H, H-3,8), 5.93–5.85 (m, 4H, H-L), 5.52 (d, $J = 8.5$ Hz, 8H, H-*m*), 5.27–5.14 (m, 8H, H-M), 3.97 (td, $J = 5.6$ Hz, 8H, H-K), 3.75–3.59 (m, 64H, H-C,D,E,F,G,H,I,J), 3.55 (m, 8H, H-B), 3.34 ppm (m, 8H, H-A); HR ES-MS: *m*/*z*: *m*/3 at 1414.1270 ($[(\mathbf{2})_2{\cdot}3Li{\cdot}2Cu]^{5+}{\cdot}(2PF_6)^{2-}$), calcd 1414.O986; *m*/4 at 1024.3433 ($[(\mathbf{2})_2{\cdot}3Li{\cdot}2Cu]^{5+}{\cdot}(PF_6)^{-}$), calcd 1024.3329; *m*/5 at 790.4849 ($[(\mathbf{2})_2{\cdot}3Li{\cdot}2Cu]^{5+}$), calcd 790.4735; *m*/3 at 1363.4724 ($[(\mathbf{2})_2{\cdot}2Li{\cdot}2Cu]^{4+}{\cdot}(PF_6)^{-}$), calcd 1363.4639; *m*/4 at 986.3486 ($[(\mathbf{2})_2{\cdot}2Li{\cdot}2Cu]^{4+}$), calcd 986.3569.

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