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Multiring Interlocked Systems via Transition Metal-Templated Strategy : the Single-Cyclization Synthesis of [3]-Catenates.

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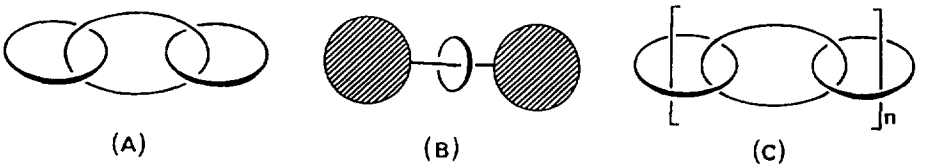
Abstract

The synthesis of a potential precursor of a multi-interlocking ring system is described. This precursor consists of two lipophilic 4,7-di-(n-hexyl)-2,9-di-phenyl-1,10-phenanthroline moieties linked by a diacetylenic bridge and ended by two alkyne groups. The Cu(I)-templated double threading of this bis-chelate string into two coordinating macrocycles was demonstrated. An intramolecular cyclization (Glaser oxidation) of this preorganized system leads to the corresponding dicopper(I) [3]-catenate in 48% yield.

Introduction

Non-covalent assemblies seem to be promising candidates for the elaboration of functional molecular materials, in relation with their electrical, photochemical or chemical properties. Simultaneously, molecular and polymer approaches were largely undertaken[1,2]. In the course of the last decade, our group has been interested in various catenanes and rotaxanes (figure 1) which represent the prototypical families of non-covalent assemblies[3,4,5]. The capabilities of these multi-component systems remain a very active area of research. Whereas since the first preparation of artificial fibers an extremely large variety of polymers have been synthesized and used as new materials for their rheological, mechanical, electronic properties and so on, no polymeric chain of catenated monomers (just like rings in a chain, figure 1, scheme c) has been synthesized[6,7] so far : polymers usually consist of covalent linking of small units, the monomers. It is expected that such polycatenanes would show unusual rheological properties, due to the non-covalent bonding (mechanical-like) of the monomers. We now report our progress towards catenane polymers. The principle of the synthesis of these non-covalent assemblies consists in the elaboration of a highly preassembled system, based on a generalized 3-dimensionnal template effect around a transition metal. The polymerization reaction itself is a cyclization reaction, based on Glaser coupling.



(A) is a [3]-catenane (among others), (B) is a rotaxane and (C) is a polycatenane consisting of 2n+1 interlocked rings.

Figure 1

Results and Discussion

The synthetic route to catenates and molecules of higher topological complexity has largely examplified the usefulness of transition metals, and in particular copper(I), in the assembling step of coordinating fragments before the cyclization reaction[5]. The first efficient strategy for [3]-catenate synthesis was based on a cyclodimerization (via a Glaser reaction) of a coordinating string which is threaded through a macrocycle by using copper(I) as the templating metal (figure 2, scheme a)[8]. In spite of the four connecting points, the [3]-catenate was obtained in a very good yield. Nevertheless, the formation of [3]-catenate was also accompanied by the formation of higher order oligomers, in particular of necklace-type compounds, consisting of several rings (up to six) separately interlocked to a large central cycle (up to 132-membered ring)[9]. Such an approach (figure 2, scheme b) being too risky when used for the elaboration of polycatenates, we decided to develop an alternative approach. The hypothetical procedure of Figure 2, scheme c, seems to be especially appealing since each cyclization step is a single reaction involving two reaction centers only. We now report the results obtained by testing this more sequential approach on the synthesis of the smallest oligomeric unit (figure 2, scheme d).

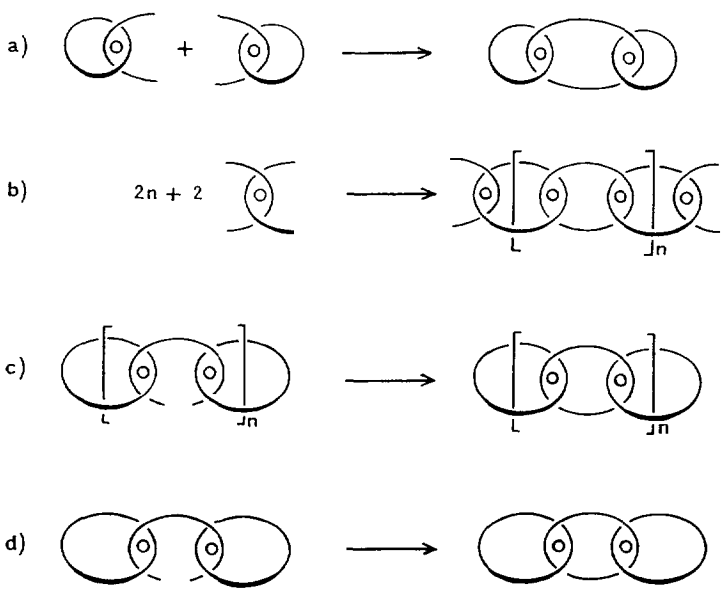


Figure 2

1. The single-cyclization approach and the design-criteria for the polycatenate precursors.

The polycatenate precursor would be a non-macrocyclic bis-chelate, each end bearing an alkyne group. The complexing moieties would be 2,9-di-aryl-1,10-phenanthroline units. The success of such an approach to obtain real oligomeric chains depends on the following conditions : (i) the ability of the bis-chelate to form open polycatenated structures (like those shown in figure 2, scheme c) in the presence of Cu(I), vs monomeric copper complexes resulting, for example, from the folding of the bis chelate around Cu(I), (ii) the single cyclisation reaction has to operate in high yields, (iii) the oligomeric material has to be soluble in common organic solvents in order to allow its characterization by usual physicochemical methods.

The fulfilment of these requirements was tested by using the model system represented in Figure 2, scheme d. The solubility criterium was overcome by grafting two lipophilic alkyl-chains (n-hexyl) on the 4 and 7 positions of the phenanthroline-cores (CPK models showed that grafting alkyl groups onto positions 5 and 6 of the phenanthroline would sterically hinder the threading of the bis-chelate). Threading of a bis-chelate string through two coordinating macrocycles has already been demonstrated in our laboratory[10]. Anchoring of n-hexyl chains on the phenanthroline moieties of the acyclic string requests larger macrocycles to be threaded. A 33-membered macrocycle was built instead of the 30-membered ring commonly used in our group until now[10]. Concerning the acyclic thread itself, we chose, based on a previous study[8], to synthesize a non-macrocyclic bis-chelate of 46 atoms, whose cyclization would lead to a 44 membered macrocycle.

2. Synthesis of the Precursors.

The organic precursors to [3]-and multi-copper(I) catenates are monochelate **7** or **8**, bis-chelate open chain **10** and macrocyclic bis-chelate **11** (figure 3)[11]. The key cyclization reaction is a Glaser oxidative coupling of acetylenic units forming bis-acetylenic bridges. Thus the chelate precursors are substituted with alkynes or silyl protected alkyne end groups. The synthetic route to the multi-catenand precursors **7**, **10** and **11** started by a double Skraup synthesis (figure 3, scheme a), in order to prepare the very lipophilic core, 4,7-di-(n-hexyl)-1,10-phenanthroline **3**. Condensation of o-nitroaniline and 1-chloro-nonan-3-one following the reaction conditions described by Case[12], led to 4-hexyl-8-nitroquinoline **1**, whose reduction ($SnCl_2$) to amino derivative **2** was followed by a second condensation reaction with the same ketone as before. 4,7-di-(n-hexyl)-2,9-di-(p-anisyl)-1,10-phenanthroline **4** (figure 3, scheme b), was obtained by addition of p-lithio-anisole on **3**, followed by hydrolysis and reoxidation of the adduct by activated MnO_2. This bis-methyl ether **4** was cleaved quantitatively to the corresponding bis-phenol **5**, by treatment with boiling pyridine hydrochloride (200°C).

Synthesis of **10** involves a dpp derivative (dpp= 2,9-di-phenyl-1,10-phenanthroline) bearing a reactive acetylenic group on one side, and a protected one on the other (figure 3, scheme c). The selective monosubstitution of diphenol **5** was performed by reacting **5** and propargyl bromide using DBU (DBU=1,8-diazabicyclo [5.4.0] undec-7-ene) as base, in a THF-CH_2Cl_2 solvent mixture. Using these mild reaction conditions, the selectivity of the monosubstitution is very satisfactory (**6**:**7** ~ 100:20). Besides **6** and **7**, the starting material (43%) could be easily recovered and recycled. The symmetrical and unsymmetrical diacetylenic

compounds **7** and **8** were readily obtained by reacting **5** and **6** with propargyl bromide and 3-(triisopropylsilyl)-1-bromo-2-propyne respectively, in DMF using potassium carbonate as base.

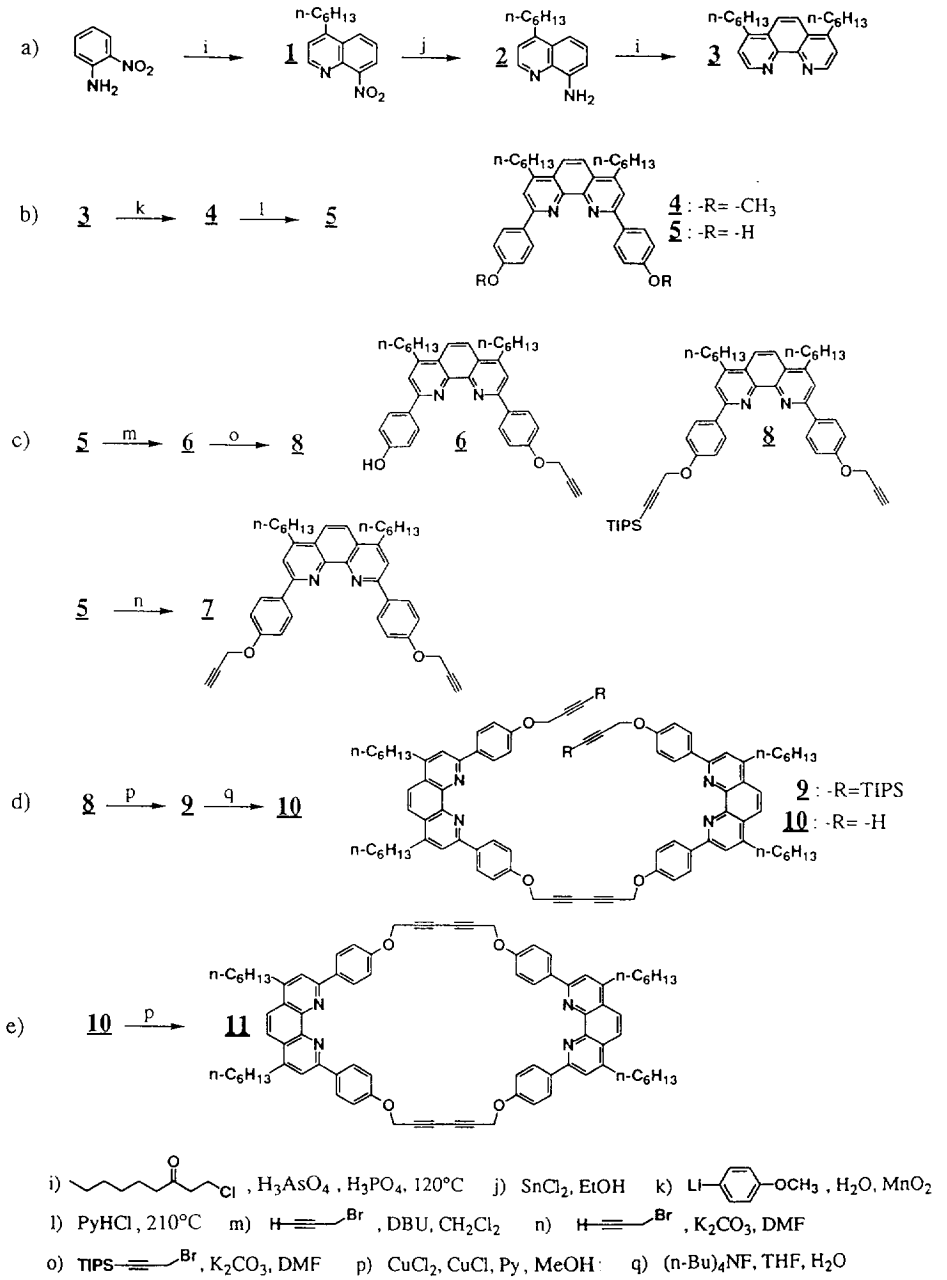


Figure 3

Homocoupling of **8** (figure 3, scheme d) was performed using one of the numerous procedures of the Glaser reaction described in the literature[13]. Reacting **8** with CuCl and $CuCl_2$ in pyridine-methanol and in the presence of air led to an intricate mixture of copper complexes, due to the large excess of copper salts used. Cu(I)-bis-(2,9-di-aryl-1,10-phenanthroline) complexes as well Cu(I)-catenates are easily demetalated by using cyanide ions[14]. Nevertheless we observed that by using this decomplexing reagent, the yields of recovered free ligand were abnormally low. Due to the sterical requirement of Cu(II) compared to that of Cu(I), the bis-(2,9-di-aryl-1,10-phenanthroline) Cu(II) complexes are much less stable than the corresponding Cu(I) species. Based on this fact, copper was removed from the dpp-containing compounds as its Cu(II) complex with pyridine by treating the reaction mixture with the strong oxidant MnO_2 in pyridine. This procedure afforded the free ligand **9** in 68% isolated yield. By desilylation of **9**, **10** was obtained nearly quantitatively. Macrocycle **11** (figure 3, scheme e) was prepared using the same procedure as for **9**, except that precursor **10** was added very slowly to the solution of copper salts. Nevertheless, due to coupling reactions of polymetallated oligomers, some of them being probably similar to those schematically represented in Figure 2, scheme c, the free macrocycle **11** was obtained in low yield (11%) as compared to that of **9** (68%). This discrepancy probably does not reflect an actual difference of the yield of the coupling reaction itself but rather the fact that a large proportion of **11** is still entrapped in non characterized mixtures of complexes containing entangled and interlocked fragments.

3. The assembling Step : Threading of Molecular Strings into Cycles via Coordination to Copper(I).

In order to compare the efficiency of the two approaches represented in Figure 2, scheme a and d, we prepared precursors $\mathbf{13}^+$ and $\mathbf{14}^{2+}$ (figure 4). Addition of **7** to complex Cu.$\mathbf{12}^+$ (prepared by adding the stoichiometric amount of $Cu(CH_3CN)_4PF_6$ to **12** in a CH_2Cl_2-CH_3CN solvent mixture) led instantaneously and quantitatively to the entwined complex $\mathbf{13}^+$. Addition of **9** to 2 equivalents of Cu.$\mathbf{12}^+$ led to $\mathbf{15}^{2+}$. Nevertheless, Cu^+-directed threading of **9** into macrocycle **12** was not quantitative (75% yield), as evidenced by ^1H NMR spectroscopy. Purification of the crude mixture containing $\mathbf{15}^{2+}$ could not be done, since reequilibration of $\mathbf{15}^{2+}$ to a mixture of the same composition as that of the crude material occurred rapidly, as shown by the poor stability of chromatographic fractions (silica) supposed to contain an enriched proportion of $\mathbf{15}^{2+}$.

$\mathbf{14}^{2+}$ was prepared in the same way as $\mathbf{15}^{2+}$ and ^1H-NMR experiments could show that, as expected, it is formed in approximately the same yield as $\mathbf{15}^{2+}$.

Despite the fact that the formation of the [3]-catenate precursor was not quantitative, we decided to undertake a [3]-catenate synthesis from this preassembled system.

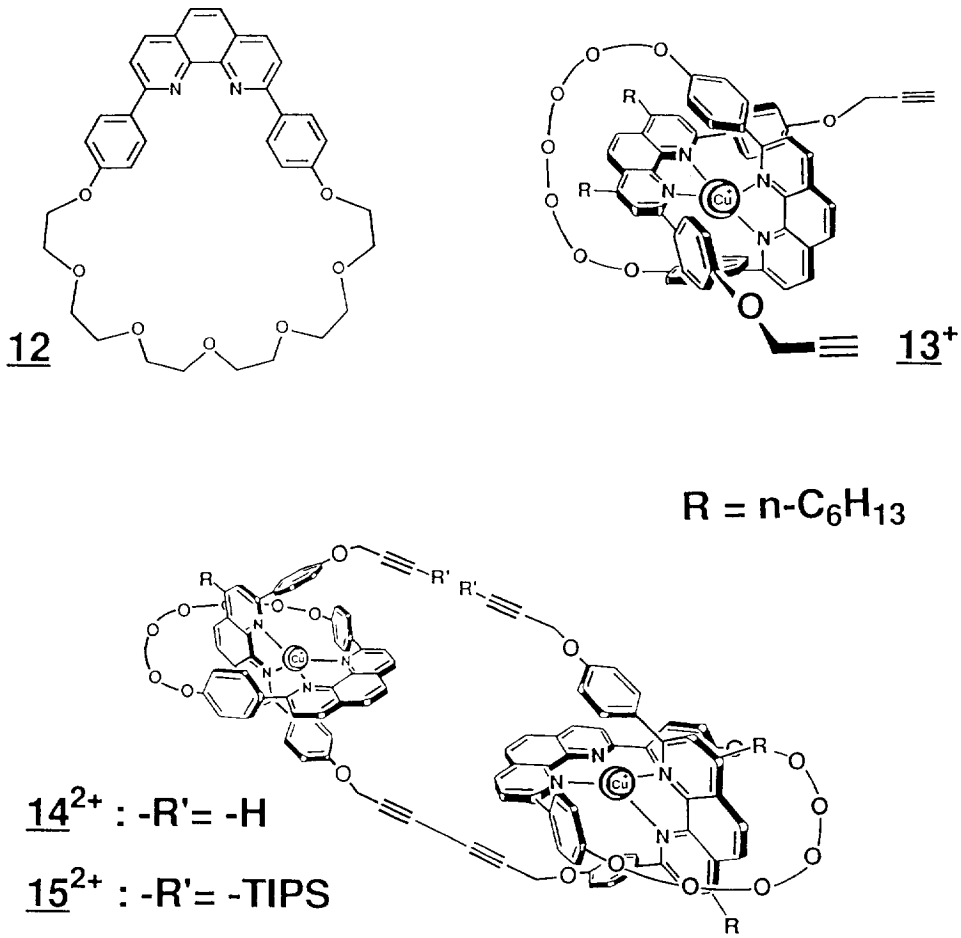


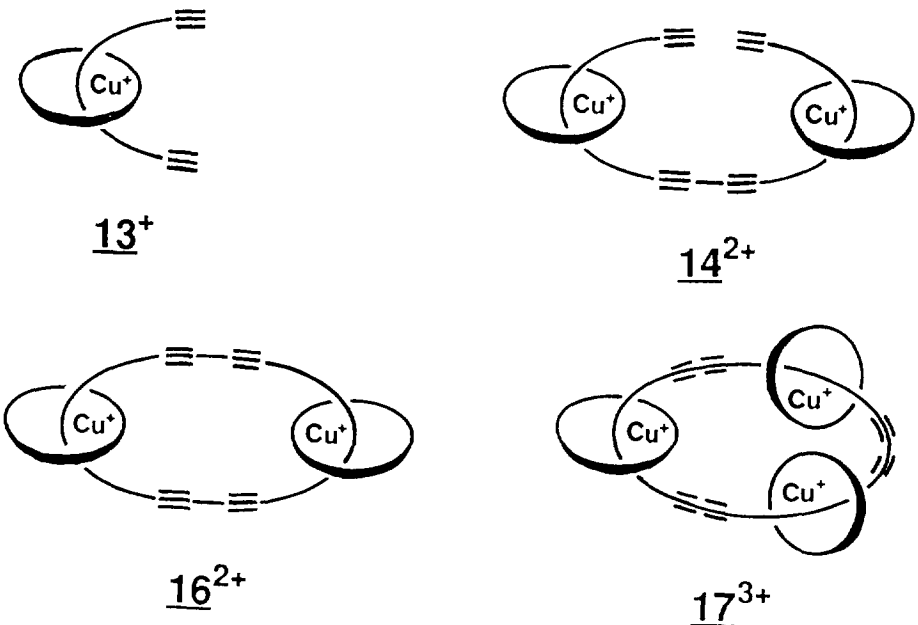
Figure 4

4. The Cyclization Step : Formation of [3]-Catenates.

The cyclization step (figure 5), based on the oxidative coupling of the acetylenic terminal groups, was done in a suspension of CuCl and $CuCl_2$ in DMF, under a dry air atmosphere. The choice of the solvent is determining. Indeed, in strongly copper-coordinating solvents such as pyridine, the pre-formed copper(I) complexes **13**$^{+}$ and **14**$^{2+}$ are destabilized, and the cyclization yields decrease dramatically. Using the coupling conditions described above afforded [3]-catenate **16**.$(PF_6)_2$ in 40% yield from precatenate **13**$^{+}$. Besides **16**$^{2+}$, a 6% yield of the cyclotrimer **17**$^{3+}$ was obtained. The intramolecular cyclization reaction of **14**$^{2+}$ (figure 5) performed in the same conditions as above, led obviously to the same [3]-catenate **16**.$(PF_6)_2$, in 48% yield based on **14**$^{2+}$. As expected, according to the strategy represented in Figure 2, scheme d, no cyclotrimer **17**$^{3+}$ was detected in the latter case. However, the yield of the intramolecular cyclisation reaction is lower than that of the intermolecular coupling (**8** → **9**). The efficiency of the Glaser reaction cannot be involved, at this stage :

^{1}H NMR analysis performed on the crude reaction mixture clearly showed the consumption of all the free terminal alkyne groups. The modest yield of the cyclization reaction has to be related to the non quantitative threading of $\underline{14}^{2+}$. $\underline{14}^{2+}$ is probably in equilibrium with oligomeric copper complexes of **10**, whose proportion is enhanced by the large excess of cuprous salt required for the Glaser reaction. Thus, during the oxidation process, the oligomeric complexes are able to react with $\underline{14}^{2+}$, lowering thus the yields of the formation of [3]-catenate.

The yield of the overall step leading to a [3]-catenate $\underline{16}^{2+}$ from a bis-chelate **10**, two coordinating macrocycles **12**, and a templating agent Cu^+ is lower than expected. One of the synthetic difficulties of the present strategy lies in the dual rôle played by copper(I) : *template* (thus able to form stable complexes with dpp units) and *reagent* in the oxidative coupling reaction. However, we have demonstrated that the procedure (represented in figure 2, scheme c), involving preassembled precursors for construction of polycatenates is conceivable.



The end macrocycles are related to **12**, *whereas, for* $\underline{16}^{2+}$, *the central macrocycle is related to* **11**.

Figure 5

Conclusion

In this work we developed an alternative approach to the synthesis of [3]-catenates with a view to making multi-interlocking rings. In this respect, we have synthesized a precursor complex, consisting of two lipophilic dpp moieties linked by a bis-acetylenic bridge and ended by two alkyne groups. The potential use of this precursor in the elaboration of multi-interlocking ring systems can be envisaged, although, at the present stage, significant synthetic improvement would be required to make the procedure truly preparative.

Experimental Section

General.

Literature methods were used to prepare $Cu(CH_3CN)_4PF_6$,[15] anhydrous $CuCl_2$,[16] and CuCl.[17] All other chemicals were of the best commercially available grade and were used without further purification.

Mass spectra were obtained either by chemical ionization (CI-MS), by positive fast atom bombardment (FAB-MS) or by electrospray (ES-MS) mass spectrometry.

4,7-di-(n-hexyl)-1,10-phenanthroline : 3.

Compound **3** was prepared in three steps as previously described by Case et al.[12] for various 4,7-di-alkyl-1,10-phenanthrolines. Starting from 37.61 g (0.272 mol) of o-nitroaniline and 69.0 g (0.346 mol) of 1-chloro-nonan-3-one,[18] 4-hexyl-8-nitroquinoline **1** was obtained by a Skraup type reaction in 42% yield. This raw quinoline **1** was then reduced ($SnCl_2$, ethanol) into 8-amino-4-hexyl-quinoline **2**, in 92% yield. A second Skraup reaction led to compound **3** in 46% yield from 8-amino-4-hexyl-quinoline, after purification by column chromatography on silica gel (eluent toluene containing 0 to 1% MeOH).

1 : Yellow solid (mp : 52°C) : ^{1}H-NMR ($CDCl_3$) : 8.94, d (J = 4.5 Hz), 1H ; 8.25, dd (J = 8.5 Hz and 1.3 Hz), 1H ; 7.98, dd (J = 7.5 Hz and 1.3 Hz), 1H ; 7.62, dd (J = 8.5 Hz and 7.5 Hz), 1H ; 7.38, d (J = 4.5 Hz), 1H ; 3.10, t (J = 7.7 Hz), 2H ; 1.75, tt (J = 7.4 Hz), 2H ; 1.50-1.20, broad, 6H ; 0.90, t (J = 6.9 Hz), 3H. Anal. calc.(%) for $C_{15}H_{18}N_2O_2$: C, 69.74 ; H, 7.02 ; N, 10.84 ; found (%) : C, 69.85 ; H, 7.01 ; N, 11.07.

2 : Black oil ; ^{1}H-NMR ($CDCl_3$) : 8.64, d (J = 4.4 Hz), 1H ; 7.34, m, 2H ; 7.20, d (J = 4.4 Hz), 1H ; 6.91, m, 1H ; 5.00, broad s, 2H ; 3.01, t (J = 7.8 Hz), 2H ; 1.75, tt (J = 7.5 Hz), 2H ; 1.50-1.20, broad, 6H ; 0.89, t (J = 7.0 Hz), 3H.

3 : Gray brown crystals (mp : 68°C) ; ^{1}H-NMR ($CDCl_3$) : 9.05, d (J = 4.5 Hz), 2H ; 8.05, s, 2H ; 7.44, d (J = 4.5 Hz), 2H ; 3.13, t (J = 7.8 Hz), 4H ; 1.80, tt (J = 7.4 Hz), 4H ; 1.55-1.25, broad, 12H ; 0.90, t (J = 7.0 Hz), 6H. CI-MS, M/z found : 348.0 $[\mathbf{3}]^{+\cdot}$, (calc. : 348.5).

4,7-di-(n-hexyl)-2,9-di-(p-anisyl)-1,10-phenanthroline : 4.

Compound **4** was prepared as previously reported for 2,9-di-(p-anisyl)-1,10-phenanthroline[19]. Starting from 15 g (43.1 mmol) of **3**, 7.47 g (13.3 mmol, 31% yield) of purified **4** were obtained. The purification was performed by column chromatography on silica gel (eluent CH_2Cl_2 containing 0 to 2% MeOH). Beside compound **4**, 9.57 g (21.0 mmol) monoarylated phenanthroline, 4,7-di-(n-hexyl)-2-(p-anisyl)-1,10-phenanthroline, was isolated in 49% yield. This monoarylated phenanthroline could be transformed into **4** using the same arylation procedure.

4 : Light yellow crystals (mp : 134°C) ; ^{1}H-NMR ($CDCl_3$) : 8.43, d (J = 8.9 Hz), 4H ; 7.99, s, 2H ; 7.90, s, 2H ; 7.11, d (J = 8.9 Hz), 4H ; 3.92, s, 6H ; 3.18, t (J = 7.7 Hz), 4H ; 1.85, tt (J = 7.5 Hz), 4H ; 1.60-1.25, broad, 12H ; 0.90, t (J = 7.1 Hz), 6H. Anal. calc. (%) for $C_{38}H_{44}N_2O_2$: C, 81.39 ; H, 7.91 ; N, 5.00 ; found (%) : C, 81.23 ; H, 7.96 ; N, 4.98.

4,7-di-(n-hexyl)-2,9-di-(p-hydroxyphenyl)-1,10-phenanthroline : 5.

Compound **5** was obtained quantitatively from compound **4**, following the procedure previously reported for 2,9-di-(p-hydroxyphenyl)-1,10-phenanthroline[19].

5 : Orange solid (mp : 155-160°C) ; ^{1}H-NMR ($CDCl_3$) : 8.24, d (J = 8.2 Hz), 4H ; 7.93, s, 2H ; 7.80, s, 2H ; 6.99, d (J =8 .6 Hz), 4H ; 3.12, t (J = 7.8 Hz), 4H ; 1.81, unresolved tt, 4H ; 1.60-1.20, broad, 12H ; 0.90, t (J = 7.0 Hz), 6H. Anal. calc. (%) for $C_{36}H_{40}N_2O_2$, H_2O : C, 78.51 ; H, 7.69 ; N, 5.09 ; found (%) : C, 78.5 ; H, 7.6 ; N, 5.1.

4,7-di-(n-hexyl)-9-(p-hydroxyphenyl)-2-[4-(2-propynyloxy)phenyl]-1,10-phenanthroline : 6.

Propargyl bromide (13.56 g, 114 mmol) dissolved in 20 ml CH_2Cl_2 was added within 20 mn to a refluxing solution of 300 ml CH_2Cl_2, 14 ml THF, 3.0 g (5.63 mmol) of **5** and 1.03 g (6.77 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene. After 3 h refluxing and stirring, the reaction mixture was washed 3 times with water, dried over $MgSO_4$ and the solvents evaporated. Column chromatography on silica gel of the residue (eluent CH_2Cl_2 containing 0.25 to 2% MeOH) allowed separation of **6** (1.34 g, 2.35 mmol, 42% yield) and compound **7** (0.278 g, 0.456 mmol, 8% yield). By increasing the polarity of the eluent (CH_2Cl_2 containing 2 to 5% MeOH), 1.30 g (43% yield) of the starting compound **5** were recovered.

6 : Red solid (mp : 74°C) ; ^{1}H-NMR ($CDCl_3$) : 8.41, d (J = 8.9 Hz), 2H ; 8.30, d (J = 8.7 Hz), 2H ; 8.00, s, 2H ; 7.89, s, 1H ; 7.86, s, 1H ; 7.16, d (J = 8.9 Hz), 2H ; 7.01, d (J = 8.7 Hz), 2H ; 4.79, d (J = 2.4 Hz), 2H ; 3.18, t (J = 7.7 Hz), 4H ; 2.56, t (J = 2.4 Hz), 1H ; 1.84, unresolved tt, 4H ; 1.55-1.20, broad, 12H ; 0.90, t (J = 7.0 Hz), 6H. FAB-MS, M/z found : 571.3 $[\mathbf{6}+H^+]^+$, (calc. : 571.8). Anal. calc. (%) for $C_{39}H_{42}N_2O_2$: C, 82.07 ; H, 7.42 ; N, 4.91 ; found (%) : C, 81.94 ; H, 7.24 ; N, 4.92.

4,7-di-(n-hexyl)-2,9-bis[4-(2-propynyloxy)phenyl]-1,10-phenanthroline : 7.

Compound **7** was prepared as previously described for 2,9-di-[4-(2-propynyloxy)phenyl]-1,10-phenanthroline[8]. Starting from 4.00 g (7.5 mmol) of **5**, 4.11 g (90% yield) of purified **7** (silica gel, eluent CH_2Cl_2 containing 0 to 0.5% MeOH) were obtained.

7 : Light yellow solid (mp : 161°C) ; ^{1}H-NMR ($CDCl_3$) : 8.43, d (J = 8.9 Hz), 4H ; 8.00, s, 2H ; 7.90, s, 2H ; 7.18, d (J = 8.9 Hz), 4H ; 4.81, d (J = 2.4 Hz), 4H ; 3.18, t (J = 7.7 Hz), 4H ; 2.57, t (J = 2.4 Hz), 2H ; 1.85, tt (J = 7.6 Hz), 4H ; 1.60-1.20, broad, 12H ; 0.90, t (J = 6.9 Hz), 6H. Anal. calc. (%) for $C_{42}H_{44}N_2O_2$: C, 82.86 ; H, 7.28 ; N, 4.60 ; found (%) : C, 83.08 ; H, 7.50 ; N, 4.22

4,7-di-(n-hexyl)-9-[4-(3-triisopropylsilyl-2-propynyloxy)phenyl]-2-[4-(2-propynyloxy)phenyl]-1,10-phenanthroline : 8.

To a degassed solution of **6** (2.00 g, 3.5 mmol) in 250 ml DMF containing K_2CO_3 (1.94 g, 14 mmol) in suspension and heated at 50°C were added, in 30 mn, 1.25 g (4.55 mmol) of 1-bromo-3-(triisopropyl-silyl)-2-propyne[20] dissolved in 20 ml DMF. After stirring and heating at 50°C for 19 h, the solvent was removed under vacuum, and the residue taken up in 100 ml CH_2Cl_2. The organic phase was washed with H_2O and dried over $MgSO_4$. After filtration and evaporation of the solvent, the raw product was dried 3 h under high vacuum. Purification was performed by column chromatography on silica gel (the polarity of the eluent was progressively

varied from CH_2Cl_2-nC_5H_{12} (1/1, v/v), to CH_2Cl_2 containing 0.4% MeOH) to yield 2.56 g (3.35 mmol, 96%) of pure **8**.

8 : Light yellow solid (mp : 108°C) ; ^{1}H-NMR ($CDCl_3$) : 8.44, d (J = 8.8 Hz), 2H ; 8.41, d (J = 8.8 Hz), 2H ; 8.00, s, 2H ; 7.90, s, 2H ; 7.21, d (J = 8.8 Hz), 2H ; 7.17, d (J = 8.8 Hz), 2H ; 4.84, s, 2H ; 4.81, d (J = 2.4 Hz), 2H ; 3.18, t (J = 7.7 Hz), 4H ; 2.57, t (J = 2.4 Hz), 1H ; 1.85, unresolved tt, 4H ; 1.60-1.20, broad, 12H ; 1.07, s, 21H ; 0.90, t (J = 7.1 Hz), 6H. FAB-MS, M/z found : 765.3 [**8**+H^+]$^+$, (calc. : 766.2). Anal. calc. (%) for $C_{51}H_{64}N_2O_2Si$: C, 80.06 ; H, 8.43 ; N, 3.66 ; found (%) : C, 80.19 ; H, 8.55 ; N, 3.59.

Preparation of 9.

A solution of pyridine-methanol (3/1, v/v, 20 ml) containing 100 mg (0.13 mmol) of **8**, 400 mg of $CuCl_2$ (2.97 mmol) and 500 mg of CuCl (5.05 mmol) was stirred 20 h, under a dry air atmosphere. H_2O (100 ml) was added, and the aqueous layer extracted six times with 50 ml portions of CH_2Cl_2 ; combined organic layers were carefully washed with water and evaporated to dryness. The red residue was taken up in 10 ml of pyridine and 116 mg (1.33 mmol) of MnO_2 were added. After 20 mn stirring, the reaction mixture was diluted with 100 ml H_2O and extracted six times with 50 ml portions of CH_2Cl_2. Combined organic layers were washed with water and treated with Na_2SO_4 ; after filtration and evaporation of the solvent, the raw product was dried 2 h under high vacuum. Column chromatography on silica gel (eluent CH_2Cl_2 containing 0 to 1% MeOH) yielded 68 mg (0.044 mmol, 68%) of **9**.

9 : Yellow crystals (mp : 90°C) ; ^{1}H-NMR ($CDCl_3$) : 8.44, d (J = 8.7 Hz), 4H ; 8.40, d (J = 8.6 Hz), 4H ; 7.99, s, 4H ; 7.89, s, 4H ; 7.20, d (J = 8.9 Hz), 4H ; 7.14, d (J = 8.8 Hz), 4H ; 4.87, s, 4H ; 4.82, s, 4H ; 3.17, t (J = 7.8 Hz), 8H ; 1.84, unresolved tt, 8H ; 1.70-1.20, broad, 24H ; 1.06, s, 42H ; 0.90, 2 superimposed unresolved t, 12H. FAB-MS, M/z found : 1528.9 [**9**+H^+]$^+$, (calc. : 1529.3). Anal. calc. (%) for $C_{102}H_{126}N_4O_4Si_2$: C, 80.16 ; H, 8.31 ; N, 3.67 ; found (%) : C, 80.28 ; H, 8.48 ; N, 3.75 .

Preparation of 10.

A solution of 57 ml THF and 3 ml H_2O, containing 394 mg (0.258 mmol) of **9** and 1627 mg (5.16 mmol) of $(n\text{-}Bu)_4NF,3H_2O$, was heated at 50°C for 8 hours. The solvents were removed and the white residue taken up in CH_2Cl_2. The resulting organic layer was washed three times with water and dried over Na_2SO_4. Filtration and evaporation of the solvent yielded 307 mg (0.253 mmol, 98%) of compound **10**. The raw product was pure enough to be used without further purification. (Chromatographic purification is not adequate, adsorption on silica gel leading to some decomposition of the substrate). Compound **10** is stable for weeks when stored in the darkness and in the refrigerator.

10 : Bright brown solid (mp : 197°C) ; ^{1}H-NMR ($CDCl_3$) : 8.43, d (J = 8.8 Hz), 8H ; 7.99, s, 4H ; 7.89, s, 4H ; 7.17, d (J = 8.8 Hz), 4H ; 7.15, d (J = 8.8 Hz), 4H ; 4.88, s, 4H ; 4.79, d (J = 2.4 Hz), 4H ; 3.17, t (J = 7.7 Hz), 8H ; 2.56, t (J = 2.3 Hz), 2H ; 1.84, unresolved tt, 8H ; 1.65-1.20, broad, 24H ; 0.90, t, 12H. FAB-MS, M/z found : 1215.2 [**10**+H^+]$^+$, (calc. : 1216.6).

Preparation of macrocycle 11.

A solution of **10** (131 mg, 0.108 mmol) in pyridine-methanol (3/1, v/v, 75 ml) was added dropwise within 10 h under efficient stirring to a mixture of anhydrous $CuCl_2$ (332 mg, 2.47 mmol) and CuCl (488 mg, 4.96

mmol) in 25 ml of the same solvents, kept at 40°C. After the end of the addition, stirring and heating were continued for 8 h, then the solution was concentrated to about 10 ml and 100 ml of water were added. The aqueous layer was extracted six times with 30 ml portions of CH_2Cl_2 ; combined organic layers were washed with water and evaporated to dryness. The dark red residue was taken up in 20 ml of pyridine and 280 mg (3.31 mmol) of MnO_2 were added. After 1 h stirring, 100 ml of water was added and the aqueous layer was again extracted three times with 30 ml portions of CH_2Cl_2. Combined organic layers were washed with water, dried over Na_2SO_4 and evaporated to dryness. Column chromatography on silica gel (eluent CH_2Cl_2 containing 0 to 1% MeOH) yielded 16 mg (0.0132 mmol, 12%) of macrocycle **11**.

11 : Bright yellow solid ; ^{1}H-NMR ($CDCl_3$) : 8.45, d (J = 8.7 Hz), 8H ; 7.98, s, 4H ; 7.89, s, 4H ; 7.18, d (J = 8.7 Hz), 8H ; 4.90, s, 8H ; 3.17, t (J = 7.8 Hz), 8H ; 1.83, unresolved tt, 8H ; 1.70-1.20, broad, 24H ; 0.90, t, 12H. FAB-MS, M/z found : 1213.5 [**11**+H$^+$]$^+$, (calc. : 1214.6).

Preparation of macrocycle 12.

A solution of 2,9-di-(p-hydroxyphenyl)-1,10-phenanthroline[19] (2.09 g, 5.735 mmol) and I-$CH_2(CH_2OCH_2)_5$-CH_2-I (3.17 g, 6.313 mmol) in DMF (150 ml) was added dropwise within 24 h under efficient stirring to an argon flushed suspension of Cs_2CO_3 (6 g, 18.4 mmol) in 800 ml DMF kept at 55-60°C. At the end of addition, stirring and heating were continued for 24 h. DMF was removed under high vacuum and the residue taken up in H_2O-CH_2Cl_2. Decantation, extraction with CH_2Cl_2 and drying over Na_2SO_4 left, after the solvent was removed, 5.62 g of crude yellow product. It was purified by column chromatography on silica gel (eluent CH_2Cl_2 containing 0.5 to 1% MeOH) giving pure macrocycle **12** (1.997 g, 3.27 mmol, 57% yield).

12 : Pale yellow solid (mp : 129°C) ; ^{1}H-NMR ($CDCl_3$) : 8.44, d (J = 8.8 Hz), 4H ; 8.26, d (J = 8.4 Hz), 2H ; 8.07, d (J = 8.4 Hz), 2H ; 7.74, s, 2H ; 7.16, d (J = 8.8 Hz), 4H ; 4.31, t (J = 5.3 Hz), 4H ; 3.90, t (J = 5.3 Hz), 4H ; 3.85-3.55, broad, 16H. ES-MS, M/z found : 611.2 [**12**+H$^+$]$^+$, (calc. : 611.7). Anal. calc. (%) for $C_{36}H_{38}N_2O_7$: C, 70.80 ; H, 6.27 ; N, 4.59 ; found (%) : C, 70.70 ; H, 6.18 ; N, 4.49.

Preparation of the copper(I) complex 13.PF_6.

By the double-ended needle transfer technique, 10.9 mg (0.0292 mmol) of $Cu(CH_3CN)_4PF_6$ in degassed acetonitrile (10 ml) were added under argon and at room temperature to a stirred degassed solution of **12** (17.0 mg, 0.0278 mmol) in CH_2Cl_2 (10 ml). Instantaneous appearance of a deep yellow coloration of the solution was related to the formation of **Cu.12**$^{+}$[19]. After 0.5 h stirring at room temperature, 16.9 mg (0.0278 mmol) **7** in 10 ml CH_2Cl_2 were added. The solution turned dark red immediately. After the solution was stirred overnight under argon at room temperature, the solvents were evaporated to dryness. NMR spectrum of crude **Cu(12,7).PF_6** showed that the complex was at least 90% pure ; it was subsequently used without further purification.

13.PF_6 : Dark red solid (mp : 79°C) ; ^{1}H-NMR (CD_2Cl_2) : 8.45, d (J = 8.4 Hz), 2H ; 8.39, s, 2H ; 8.00, s, 2H ; 7.85, d (J = 8.4 Hz), 2H ; 7.67, s, 2H ; 7.40, d (J = 8.7 Hz), 8H ; 6.12, d (J = 8.6 Hz), 4H ; 6.02, d (J = 8.7 Hz), 4H ; 4.36, d (J = 2.4 Hz), 4H ; 3.80-3.50, broad, 24H ; 3.31, t (J = 7.7 Hz), 4H ; 2.57, t (J = 2.4 Hz), 2H ; 1.93, tt, 4H ; 1.70-1.20, broad, 12H ; 0.95, t (J = 7.0 Hz), 6H.

Preparation of the dicopper(I) complex 14.$(PF_6)_2$.

Complex $\mathbf{14}^{2+}$ was prepared using the same procedure as above, starting from 24.4 mg (0.04 mmol) of **12**, 14.9 mg (0.04 mmol) of $Cu(CH_3CN)_4PF_6$ and 24.3 mg (0.02 mmol) of **10**. The ^{1}H-NMR spectrum of the crude product showed a mixture of complexes, in which $\mathbf{14}^{2+}$ was present at least in 70% yield. This crude product was used without further purification, owing to the difficulty encountered to isolate pure **14**.$(PF_6)_2$ due to the possible re-equilibration of **14**.$(PF_6)_2$ into various copper complexes.

14.$(PF_6)_2$: Dark red solid ; ^{1}H-NMR (CD_2Cl_2) : 8.46, d (J = 8.4 Hz), 4H ; 8.38, s, 4H ; 7.99, s, 4H ; 7.84, d (J = 8.3 Hz), 4H ; 7.64, broad s, 4H ; 7.39, 2 superimposed unresolved d, 16H ; 6.11, 2 superimposed unresolved d, 8H ; 6.01, d (J = 8.1 Hz), 8H ; 4.48, s, 4H ; 4.37, d (J = 2.3 Hz), 4H ; 3.80-3.50, broad, 48H ; 3.30, 2 superimposed t, 8H ; 2.56, t (J = 2.3 Hz), 2H ; 1.91, unresolved tt, 8H ; 1.70-1.20, broad, 24H ; 0.95, 2 superimposed t (J = 7.0 Hz), 12H. ES-MS, M/z found : 1280.9 [**14**]$^{2+}$, (calc. : 1282.1).

Preparation of the dicopper(I) complex 15.$(PF_6)_2$.

Prepared as described for $\mathbf{13}^+$, starting from 28.5 mg (0.047 mmol) of **12**, 17.4 mg (0.047 mmol) of $Cu(CH_3CN)_4PF_6$ and 34.0 mg (0.022 mmol) **9**. The ^{1}H-NMR spectrum of the crude product showed a mixture of complexes, in which $\mathbf{15}^{2+}$ was present at least in 75% yield. This crude product was used without further purification, for the same reasons as described for **14**.$(PF_6)_2$.

15.$(PF_6)_2$: Dark red solid ; ^{1}H-NMR ($CDCl_3$) : 8.49, d (J = 8.4 Hz), 4H ; 8.35, s, 4H ; 7.99, s, 4H ; 7.84, d (J = 8.3 Hz), 4H ; 7.61, broad s, 4H ; 7.55-7.30, 2 superimposed unresolved d, 8H ; 7.35, d (J = 8.5 Hz), 8H ; 6.30-6.05, 2 superimposed unresolved d, 8H ; 6.00, d (J=8.5 Hz), 8H ; 4.54, s, 4H ; 4.39, s, 4H ; 3.90-3.40, broad, 48H ; 3.29, 2 superimposed t (J = 7.6 Hz), 8H ; 1.89, unresolved tt, 8H ; 1.70-1.10, broad, 24H ; 1.10-0.70, broad, 54H. ES-MS, M/z found : 1438.1 [**15**]$^{2+}$, (calc. : 1438.4).

[3]-catenate 16.$(PF_6)_2$ and [4]-catenate 17.$(PF_6)_2$ starting from 13.PF_6.

163.8 mg (0.1147 mmol) of crude **13**.PF_6 was added to a stirred mixture of anhydrous $CuCl_2$ (370 mg, 2.75 mmol) and CuCl (1550 mg, 15.66 mmol) in DMF (30 ml) at room temperature, under a dry air atmosphere. After the solution was stirred for 48 h at room temperature, the solvent was evaporated to dryness and the residue taken up in CH_2Cl_2. The dark red solution was washed several times with 1 mol.L^{-1} HCl solution until the aqueous layer became colourless. The remaining dark red CH_2Cl_2 layer was washed three times with water and thereafter treated (12 h) with a large excess of KPF_6 dissolved in a minimum of water. By the means of this exchange reaction, $\mathbf{16}^{2+}$ and $\mathbf{17}^{3+}$ originally formed as PF_6^- and chloride salts, were obtained exclusively as their PF_6^- salts. The resulting organic layer, washed once with an aqueous solution of L-(+)-ascorbic acid and twice with water, was dried over Na_2SO_4, evaporated to dryness to yield 145 mg of a dark red solid. Column chromatography on silica gel gave 65 mg of **16**.$(PF_6)_2$ (40% yield, eluent CH_2Cl_2 containing 0 to 1% MeOH) and 10 mg **17**.$(PF_6)_3$ (6% yield, eluent CH_2Cl_2 containing 1 to 4% MeOH).

16.$(PF_6)_2$: Dark red solid (mp : 184°C) ; ^{1}H-NMR (CD_2Cl_2) : 8.45, d (J = 8.4 Hz), 4H ; 8.31, s, 4H ; 8.05, s, 4H ; 7.67, d (J = 8.4 Hz), 4H ; 7.59, broad s, 4H ; 7.40-7.20, broad unresolved d, 8H ; 7.19, d (J = 8.6 Hz), 8H ; 6.03, d (J = 8.3 Hz), 8H ; 5.79, d (J = 8.6 Hz), 8H ; 4.51, s, 8H ; 3.85-3.35, broad, 48H ; 3.25, t (J = 7.7 Hz), 8H ; 1.87, unresolved tt, 8H ; 1.70-1.10, broad, 24H ; 0.95, t (J = 6.9 Hz), 12H. ES-MS, M/z found : 1280.9 [**16**]$^{2+}$, 2705.4 [**16**+PF_6]$^+$, (calc. : 1281.1 and 2707.1).

17.$(PF_6)_3$: Dark red solid ; ^{1}H-NMR (CD_2Cl_2) : 8.50, d (J = 8.4 Hz), 6H ; 8.37, s, 6H ; 8.02, s, 6H ; 7.85, d (J = 8.4 Hz), 6H ; 7.65, broad s, 6H ; 7.50-7.30, 2 superimposed unresolved d, 24H ; 6.11, d (J = 8.3 Hz), 12H ; 6.00, d (J = 8.7 Hz), 12H ; 4.50, s, 12H ; 3.80-3.35, broad, 72H ; 3.27, t (J = 7.6 Hz), 12H ; 1.88, unresolved tt, 12H ; 1.70-1.10, broad, 36H ; 0.94, t (J = 6.8 Hz), 18H. ES-MS, M/z found : 1280.0 $[\mathbf{17}]^{3+}$, 1992.5 $[\mathbf{17}+PF_6]^{2+}$, (calc. : 1281.1 and 1994.1).

[3]-catenate 16.$(PF_6)_2$, starting from 14.$(PF_6)_2$.

165 mg (0.0578 mmol) of crude **14**.$(PF_6)_2$ was added to a stirred mixture of anhydrous $CuCl_2$ (190 mg, 1.413 mmol) and CuCl (800 mg, 8.081 mmol) in DMF (25 ml) at room temperature, under a dry air atmosphere. After the solution was stirred for 44 h at room temperature, the [3]-catenate $\mathbf{16}^{2+}$ was purified and isolated as its PF_6^- salt using the same work-up as described above. Yield : 56 mg, 48% yield, based on pure **14**.$(PF_6)_2$.

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