Chemically Induced Contraction and Stretching of a Linear Rotaxane Dimer

Maria Consuelo Jimenez-Molero,[b] Christiane Dietrich-Buchecker,[a] and Jean-Pierre Sauvage*[a]

Abstract: Copper(I)-induced assembly of two self-complementary identical units, which consist of a ring that incorporates a 1,10-phenanthroline group attached to a small filament containing a second 1,10-phenanthroline (phen) group, leads quantitatively to a doubly threaded complex. Each copper(I) center is four-coordinate and is located inside a ring and bound to a phen from the macrocyle. The two other coordination sites are occupied by a phen from the filament connected to the other ring. An X-ray structure of the dicopper(I) complex unambiguously demonstrates the doubly threaded nature of the system. The molecule has C_2 symmetry in the crystal. This is an extended form with a $Cu\cdots Cu$ separation of 18.3 Å and an overall length close to 40 Å. Further synthetic work, which utilizes the two terminal phenolic functions of the previous dicopper(I) complex, gives rise to a more complex system in which both filaments have been prolonged in opposite directions by 2,2′:6′,2″-terpyridine (terpy) motifs and bulky stoppers. The organic backbone is that of a rotaxane dimer. Although redox cycling of Cu^{I} to Cu^{II} did not lead to intramolecular rearrangement, simple chemical reactions induced large conformational changes. The rotaxane dimer was set in motion as follows. The dicopper(I) complex, which is in an extended conformation, was demetallated by using KCN. From the free ligand, the dizinc complex was formed quantitatively at room temperature. ^{1}H NMR data show that a new conformation is obtained: each Zn^{II} is five-coordinate (phen + terpy), and the molecule is in a contracted conformation. This process is reminiscent of biological muscles in the sense that the two filaments of this system can be moved along one another in a gliding motion that keeps the whole system together, but which converts a stretched compound (overall length ≈83 Å) into a contracted species (overall length ≈65 Å, according to CPK models). The motion is quantitatively reversed by the addition of an excess of copper(I) to the dizinc complex; this regenerates the extended starting form. Although the motivation of the present contribution was to illustrate that a musclelike molecule may be stretched or contracted using electrochemistry and coordination chemistry, the main body of the work is organic synthesis. This is testified by the fact that the dicopper(I) rotaxane dimer was obtained in 23 steps from commercially available compounds.

Keywords: copper · dimerization · rotaxanes · zinc

Introduction

Molecular motors are universally present in living systems, either to ensure mechanical properties or to fulfill important chemical functions. Rotary motors, for instance, are found in bacterial flagellae[1] and are responsible for the mobility of these organisms. ATPase is certainly the most important rotary motor in biology due to the ubiquitous nature of ATP-dependent processes and of the enzyme which converts ADP and inorganic phosphate to ATP and vice versa.[2]

Linear motors are also important, as demonstrated by recent work on kinesin or dynein motors, and are able to travel in a controlled fashion along microtubules to fulfill a transport function.[3] The most-studied linear motors are probably the striated muscles, whose function has been investigated for several decades.[4]

Synthetic molecular systems that can mimic biological motors are still primitive but they have experienced a spectacular developement over the course of the last few years. Some recent molecular machines and motors consist of interlocking or threaded rings (catenanes and rotaxanes),[5] but other organic compounds have also been proposed.[6] In particular, rotary motors have been reported,[7, 8] of which an impressive example is that of sterically hindered olefins whose rotary motion can be induced by a series of photochemical and thermal steps that perfectly control the directionality of the process.[8]

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Molecular shuttles consist of a ring threaded by a two-station axle.[9] As a result of an electrochemical or photoredox signal, the ring glides from a given station to another. The process is reversible, and the ring returns to its original position when given another signal. Interestingly, such a two-station rotaxane and the corresponding catenane have recently been proposed as switches in molecular electronic devices.[10, 11] In order to mimic a biological muscle, the molecular system should be more or less rod-shaped, with the ability to undergo contraction or extension in a controlled fashion. Keeping in mind the way a muscle functions, shown in an over-simplified representation in Figure 1, it is important to design a multicomponent system in which one filament can glide along another.

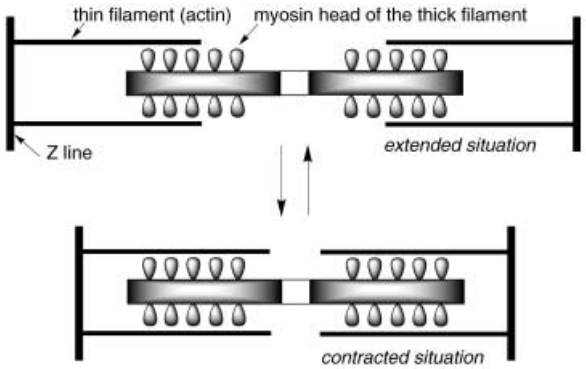

Figure 1. Schematic representation of the myosin–actin complex in skeletal muscles.

Our experience in the field of transition metal-based catenanes and rotaxanes[12] prompted us to synthesise and investigate rotaxane dimers, in which acyclic components ("filaments") can glide along one another under the action of a chemical signal. Two preliminary reports on this work have recently been published.[13, 14]

Results and Discussion

Design and principle of motion of the assembly: A multicomponent molecular assembly, which presents a symmetrical doubly threaded topology as shown in Figure 2, should fulfill the necessary requirements to mimic the behavior of a muscle at the molecular level.

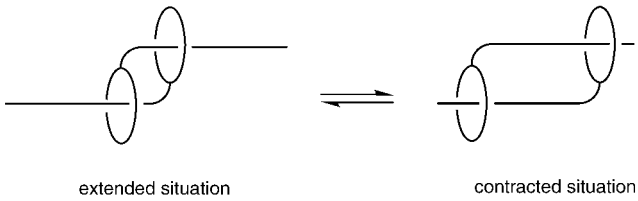

Figure 2. The topology and shape of a linear pseudorotaxane dimer is adapted to a contracting/stretching motion.

In the double-threaded object of Figure 2, the motion is easily visualized: under the action of an external stimulus both strings (mimicking the muscle filaments) can move along one another, but the assembly will stay together thanks to the rotaxane nature of the system. Analogous doubly threaded topologies were obtained by Stoddart and co-workers in the solid state by the dimerization of a self-complementary monomer, although in solution single-threading processes led to the formation of various pseudo-oligomeric rotaxane topologies.[15a, b]

Many of our machine-like compounds were obtained by copper(I)-induced template syntheses, with the motions being triggered by an electrochemical signal (Cu^{I}/Cu^{II}).[16–18] By contrast, in the here reported system, which also contains copper(I) as the assembling and templating metal, the motion will be triggered by a **chemical signal** corresponding merely to a metal exchange. The doubly threaded molecular assembly envisaged can bind simultaneously two metal centers, either in a four- or five-coordinate geometry (Figure 3). The four-coordinate situation results from the coordination of a copper(I) ion with two bidentate phenanthroline units and corresponds to an extended geometry (left Figure 3, left), whereas the five-coordinate situation results from the coordination of a divalent ion **M** with one bidentate phenanthroline and one terdentate terpyridine and has a contracted geometry (Figure 3, right).

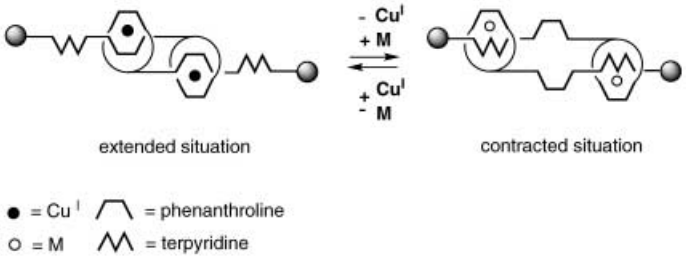

Figure 3. The principle of function of the unimolecular synthetic "muscle". The two-component rotaxane dimer contains identical ring-and-string conjugates. Each component consists of a bidentate chelate (U-shaped symbol) embedded in a ring, which is covalently attached to a filament-like part. This string contains another bidentate ligand, a terdentate-coordinating unit (schematically represented by a W-shaped symbol), and a bulky stopper (sphere on the drawings), whose function is to prevent dethreading of the filaments from the rings. The four-coordinate situation (shown on the left-hand side) is such that the metal (black disk) is coordinated to two bidentate chelates. If the bidentate chelate belonging to the string is replaced by a terdentate fragment, a five-coordinate situation is achieved, which corresponds to an overall contracted situation (shown on the right-hand side). The contracted situation is obtained by replacing the four-coordinate metal of the compound represented on the left (copper(I)) by a five-coordinate center (white disk; M = zinc(II)).

To synthesise such a rotaxane dimer, in which each monomeric subunit is a multisite ligand, we followed the general strategy that is shown in Figure 4.

A macrocycle that contains a bidentate 1,10-phenanthroline (phen) group is covalently linked to a linear rigid phen group that terminates in a phenolic function which will enable the attachment of the stopper. Synthesis of the dinuclear doubly threaded central core is performed by copper(I) which acts as a gathering and threading element between two of the bis-bidentate phen ligands. After the separate synthesis of a functionalized terdentate 2,2′:6′,2″-terpyridine bearing a

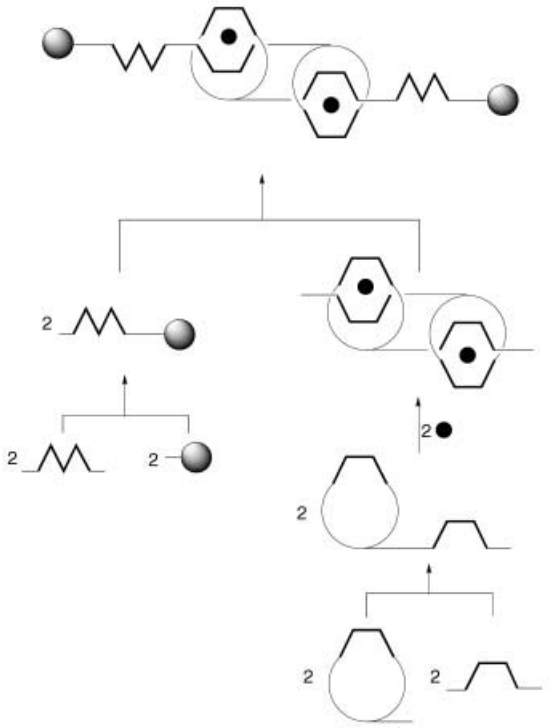

Figure 4. Synthetic strategy used for the synthesis of the rotaxane dimer.

bulky stopper, these units are connected to the extremities of the doubly threaded dicopper(I) complex. This last reaction not only allows the introduction of terdentate sites into the molecular assembly, but also gives access to a real rotaxane structure in which any dethreading process is prohibited by the presence of the two bulky stoppers.

Once the principles of motion and design were defined, Corey–Pauling–Koltun (CPK) atomic models were used to define the chemical nature of the fragments required for construction of an appropriate monomeric ligand (Figure 5a).

The models suggest that a 31-membered macrocycle would have the optimum size. It should be large enough to allow the threading of a phenanthroline belonging to an opposite rod, but also small enough to avoid intramolecular copper(I) complexation between the two phenanthrolines of the same unit. In fact, such intramolecular complexation could occur by the folding of a large flexible macrocycle. For the rod, a tetrasubstituted phenanthroline is used. Substitution in the 2- and 9-positions is necessary for the formation of a stable diphenanthroline copper(I) complex, but here the size was also critical: even though substituents are necessary, they should not be so bulky that they inhibit the threading process for steric reasons. Methyl groups fulfill this requirement. Finally, the 3- and 8-positions are substituted by aromatic groups so that the rod will be as linear as possible and that the formation of an intramolecular copper(I) complex between two adjacent phenanthrolines from the same subunit is avoided. A 5,5″-dimethylterpyridine, which can be connected to the other fragments after functionalization of the methyl groups, was chosen as terdentate site. The bulky tris(*tert*-butylphenyl)methane derivative stoppers should prevent dethreading. Connection of the various fragments gives the appropriate monomeric multisite ligand shown in Figure 5b.

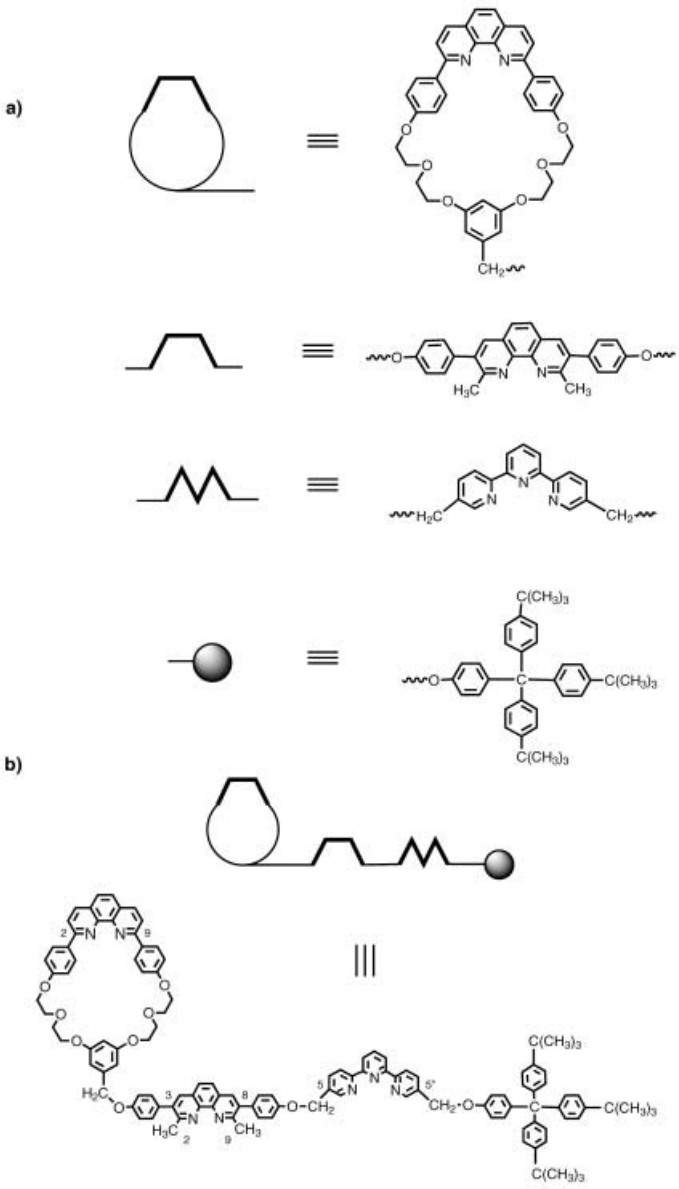

Figure 5. a) Chemical structure of the various symbolic fragments. b) Chemical content of monomeric self-complementary multisite ligand contained in the doubly threaded assembly.

Synthesis of the dinuclear doubly threaded central core: 3,8-Dibromo-1,10-phenanthroline (**2**) was prepared in 75% yield by the reaction of 1,10-phenanthroline (**1**) with Br_2, S_2Cl_2, and pyridine (Scheme 1).[19, 20] Reaction of **2** with 2.2 equivalents of the ester of *p*-methoxyphenylboronic acid under Suzuki cross-coupling conditions gave 3,8-dianisyl-1,10-phenanthroline (**3**) in 84% yield.[21] The 2,3,8-trisubstituted-1,10-phenanthroline **4** was obtained in 95% yield by the addition of a small excess of CH_3Li to **3** at a temperature of 0–5 °C. Introduction of a second methyl group in the 9-position of the phenanthroline to give **5** (97% yield) was performed by addition of CH_3Li under monosubstitution conditions to a solution of **4** in toluene.[20] Deprotection of the phenolic functions to give the diphenol **6** in almost quantitative yield was achieved with pyridinium hydrochloride at 200 °C, according to a method previously described.[22]

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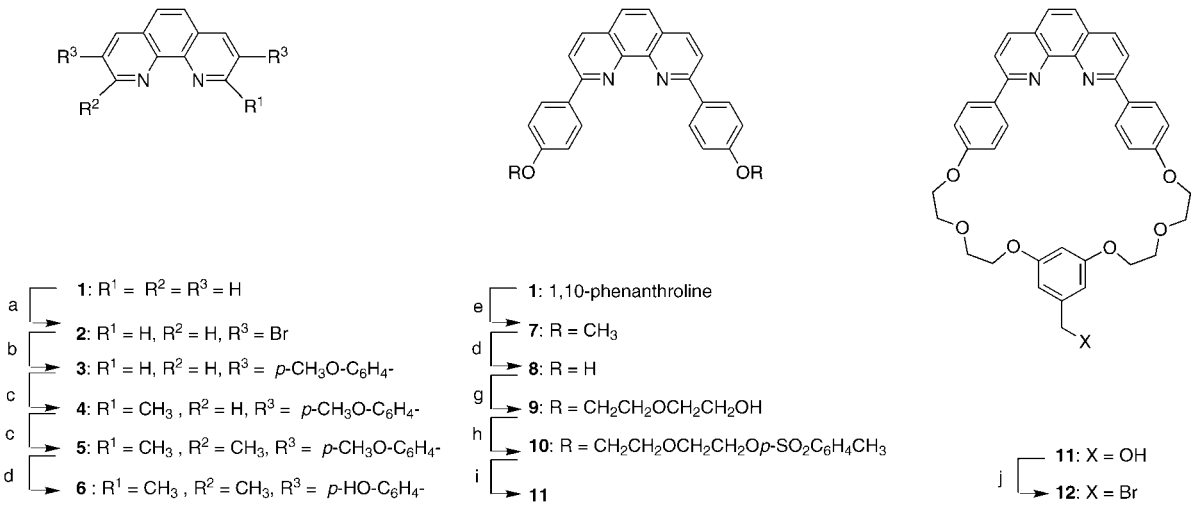
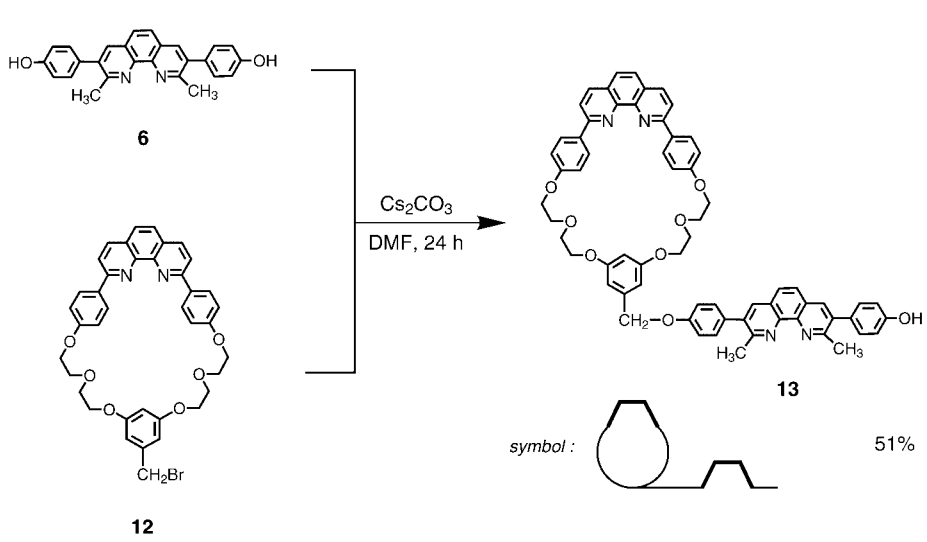


Scheme 1. The various phenanthroline-containing precursors, reagents and conditions. a) S_2Cl_2, Br_2, C_5H_5N, 1-chlorobutane, 80 °C, 24 h, 75%; b) 4-methoxyphenylboronic acid, 10% $Pd[P(C_6H_5)_3]_4$, toluene, 2 M Na_2CO_3, 80 °C, 12 h, 84%; c) 1) CH_3Li/toluene at 0–5 °C, 4 h, 2) H_2O, 3) MnO_2, 95% for **3**, 97% for **4**; d) C_5H_5N.HCl, 210 °C, 4 h, 95%; e) 1) *p*-lithioanisole, THF/toluene, room temperature, 12 h, 2) H_2O, 3) MnO_2, 60%; g) HO-$CH_2CH_2OCH_2CH_2$-Cl, DMF, 55 °C, 24 h, 80%; h) 1) TosCl, Et_3N, CH_2Cl_2, –5–20 °C, 90%, 2) 3,5-dihydroxybenzylic alcohol, Cs_2CO_3, DMF, 55 °C, 48 h, 50%; j) PBr_3/CH_2Cl_2, 25 °C, 48 h, 76%.



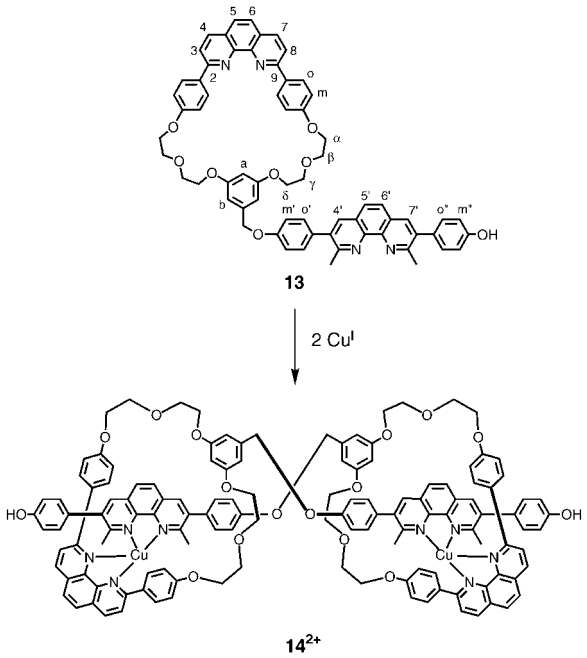
Scheme 2. Synthesis of the conjugate **13** between the ring and the phenanthroline unit.

The functionalized macrocycle **12** was prepared in several steps starting from 2,9-diphenol-1,10-phenanthroline (**8**), which was synthesised according to the literature.[23] Reaction of **8** with 2-(2-chloroethoxy)ethanol in the presence of Cs_2CO_3 in DMF at 60 °C afforded diol **9** (80% yield), which was subsequently converted into ditosylate **10** (90% yield) by treating it with *p*-toluenesulphonyl chloride in CH_2Cl_2/Et_3N (–5 °C to 20 °C).[24] The ring closure reaction, which affords the 31-membered macrocycle **11** in 50% yield, was achieved by reacting **10** with 3,5-dihydroxybenzyl alcohol under standard high-dilution conditions (Cs_2CO_3, DMF, 60 °C).[23, 24] Ring **11** was subsequently converted into the bromo derivative **12** (76%) by treatment with PBr_3 (CH_2Cl_2, 25 °C).[25]

The connection between macrocycle **12** and diphenol **6** was performed in basic medium (Cs_2CO_3, DMF, 50 °C) and led to the bis-chelating target ligand **13** in 51% yield (Scheme 2). Finally, reaction of **13** with a stoichiometric amount of $[Cu(CH_3CN)_4]PF_6$ in CH_3CN/CH_2Cl_2 at room temperature led quantitatively to $\mathbf{14}^{2+}$ as its PF_6^- salt (Scheme 3).

Interestingly, ^{1}H NMR studies and thin-layer chromatography show that the initial mixture of the kinetic copper(I) complexes, which is obtained immediately after addition of the copper(I) salt to ligand **13**, reequilibrates. The various cyclic or linear oligomers apart from $\mathbf{14}^{2+}$, which are initially present in the reaction mixture, spontaneously convert to the thermodynamically more stable dimer $\mathbf{14}^{2+}$ in quantitative yield over a period of 48 hours at room temperature. The very strong upfield chemical shift observed for the aromatic protons H_o and H_m as well as the various interfragment interactions which are observed by two-dimensional ROESY NMR experiments (e.g., strong interactions were observed between CH_3 and H_o, H_m and $H_{o''}$, H_m and $H_{m'}$, $-OCH_2-$ and $H_{4'}$, H_m and $H_{m'}$) clearly evidence the threading of one linear rigid stick belonging to one ligand into the macrocycle of another. The dimeric nature of $\mathbf{14}^{2+}$ is shown by electrospray mass spectroscopy (ES–MS). The spectrum of the single product obtained is that expected for $\mathbf{14}^{2+}$: it not only shows a molecular ion peak at 2310.3 (calcd: 2310.3), but also displays a very large, well-resolved peak at 1082.7 (calcd *m*/2: 1082.7), which is highly characteristic of a doubly charged species.

Dimer $\mathbf{14}^{2+}$ was isolated as a deep red crystalline solid, and X-ray quality crystals were obtained from acetone/diethyl ether by diffusion. The molecular structure of the dinuclear dimer $\mathbf{14}^{2+}$, which possesses only a single C_2 axis, is given in Figure 6.



Scheme 3. Formation of the "hermaphrodite" molecular assembly $\mathbf{14}^{2+}$. $[Cu(CH_3CN)_4]PF_6$, CH_3CN/CH_2Cl_2, room temperature, argon, 48 h, quantitative.

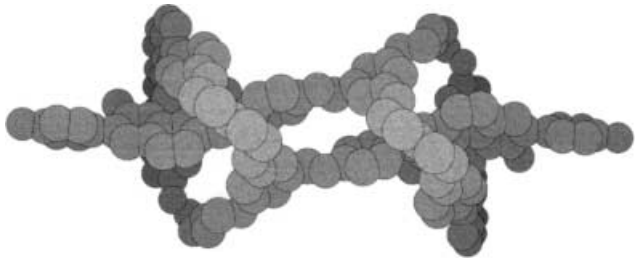


Figure 6. Crystal structure of the dicopper(I) dimer $\mathbf{14}^{2+}$: space-filling representation with the single C_2 axis shown perpendicular to the plane.

The complex contains two identical symmetry related subunits consisting each of one macrocycle, one linear 3,8-diaryl-1,10-phenanthroline rod, and one copper ion. The most striking feature of this structure is its linear extended antiparallel arrangement which locates the two terminal phenolic oxygen atoms at a distance of 36.3 Å apart. The two copper atoms are separated by 18.3 Å and are both in similar environments. The coordination tetrahedron around each copper appears distorted, with two wide angles: one opening towards the outside of the molecule (N1-Cu-N3: 125.6°) and the other towards the second copper ion of the complex (N2-Cu-N4: 137.3°). The N–Cu bond lengths range from 2.035 Å to 2.076 Å and are thus close to the values found in other copper(I) complexes of related ligands.[26]

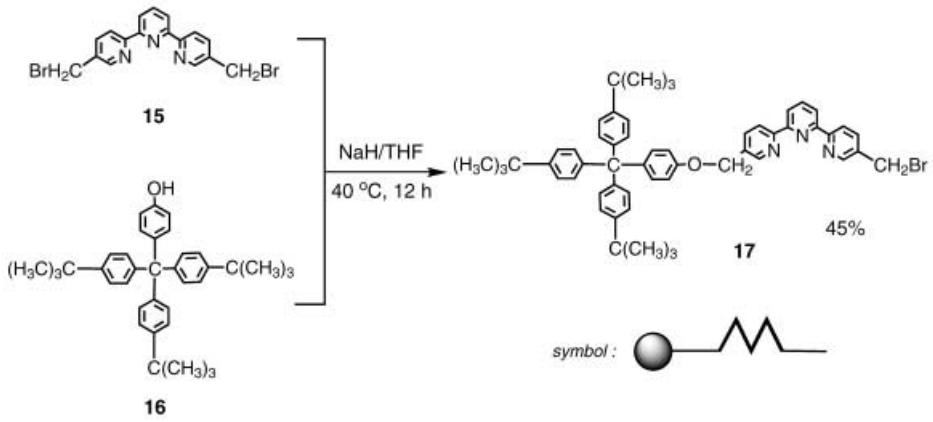
Synthesis of the stopper-bearing disymmetrical 2,2′:6′,2″-terpyridine: The two methyl groups of the 5,5″-dimethyl-2,2′:6′,2″-terpyridine, which was prepared by a double Stille cross-coupling reaction,[27] were transformed into benzylic bromides with *N*-bromosuccinimide in benzene under irradiation and reflux and gave terpyridine **15** in 48% yield.[28] Reaction of **15** with 0.68 equivalents of the bulky stopper **16**[29] in THF and in presence of NaH afforded a mixture of di- and monostoppered terpyridine (Scheme 4). After a fast chromatography over alumina, the disymmetrical terpyridine **17** was isolated in 45% yield.

Synthesis of the "muscle" $\mathbf{18}^{2+}$ in an extended form: The last connection step between the hermaphrodite dicopper(I) precursor $\mathbf{14}^{2+}$ and two equivalents of stoppered terpyridine **17** was performed in DMF at 40 °C; the base and the bromide **17** were both progressively added to the solution $\mathbf{14}^{2+}$ in DMF over a period of 5 hours. After chromatography over alumina, complex $\mathbf{18}^{2+}$ was obtained as a dark red solid in 60% yield (Scheme 5).

Extensive ^{1}H NMR studies showed that the stoppering procedure leading to $\mathbf{18}^{2+}$ occured without significant dethreading. In particular, there are striking analogies between the spectra of the doubly threaded precursor $\mathbf{14}^{2+}$ and those of the stoppered complex $\mathbf{18}^{2+}$. Indeed, as shown in Figure 7, both complexes are characterized by almost identical strong upfield chemical shifts for several of their aromatic protons with respect to those of the precursor ligand **13**. This similarity provides clear evidence that the relative spatial arrangement of the various protons is almost identical in both complexes $\mathbf{14}^{2+}$ and $\mathbf{18}^{2+}$.

The large interfragment interactions observed in two-dimensional ROESY NMR experiments, as well as the high-resolution mass spectrometry (FAB), confirm the doubly threaded topology of $\mathbf{18}^{2+}$: the expected molecular ion peak at 3834.2 (calcd 3834.3) is observed as well as a large well-resolved peak at m/z 1844.7 (calcd for $m/2$: 1844.6), corresponding to a doubly-charged species.

Chemically triggered contraction–stretching motion: Treatment of $\mathbf{18}^{2+}$ with a large excess of KCN at room temperature gives the free ligand **19** in quantitative yield, which after remetallation with $Zn(NO_3)_2$ gives the colorless dizinc com-



Scheme 4. Synthesis of the stopper-bearing terpyridine fragment **17**.

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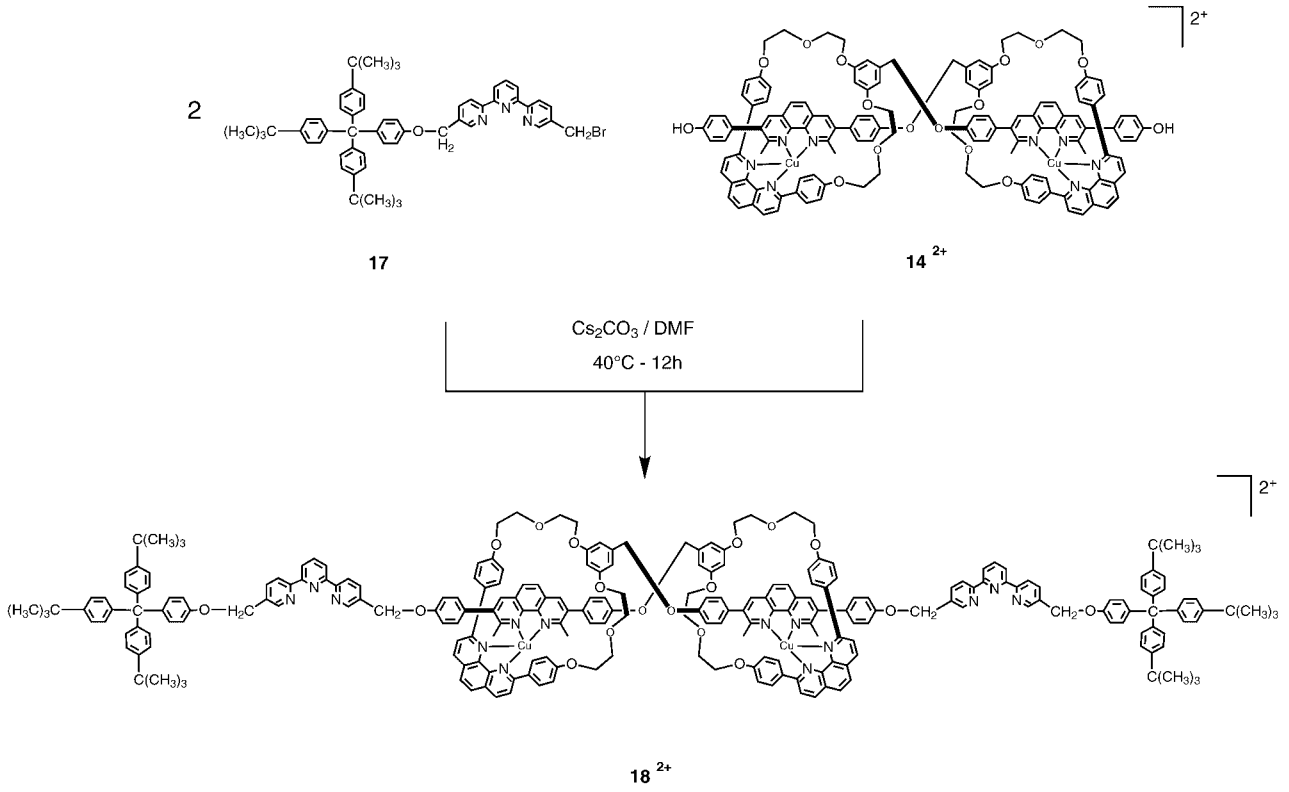


Scheme 5. Synthesis of the "muscle" $\mathbf{18}^{2+}$ in the extended form.

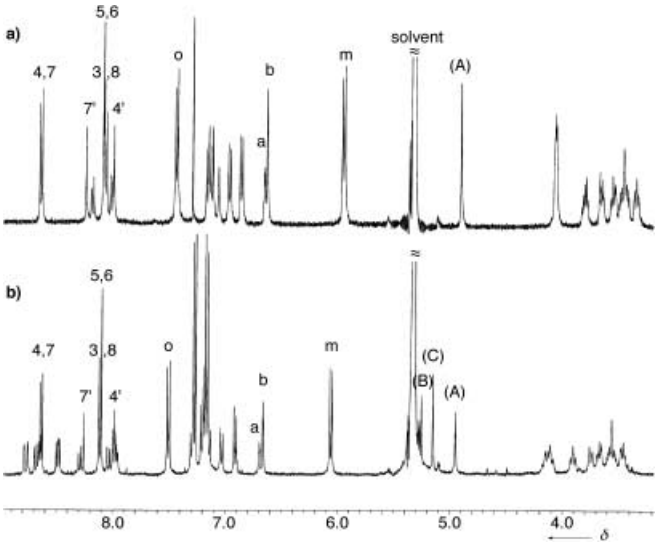


Figure 7. ^{1}H NMR spectra (400 MHz in CD_2Cl_2) (aromatic part) of the complex $\mathbf{14}^{2+}$ (top) and $\mathbf{18}^{2+}$ (bottom).

plex $\mathbf{20}^{4+}$ quantitatively in a contracted form (Scheme 6). The extended dicopper(I) dimer $\mathbf{18}^{2+}$ may be regenerated by the reaction of $\mathbf{20}^{4+}$ with an excess of $[Cu(CH_3CN)_4]PF_6$ at room temperature.

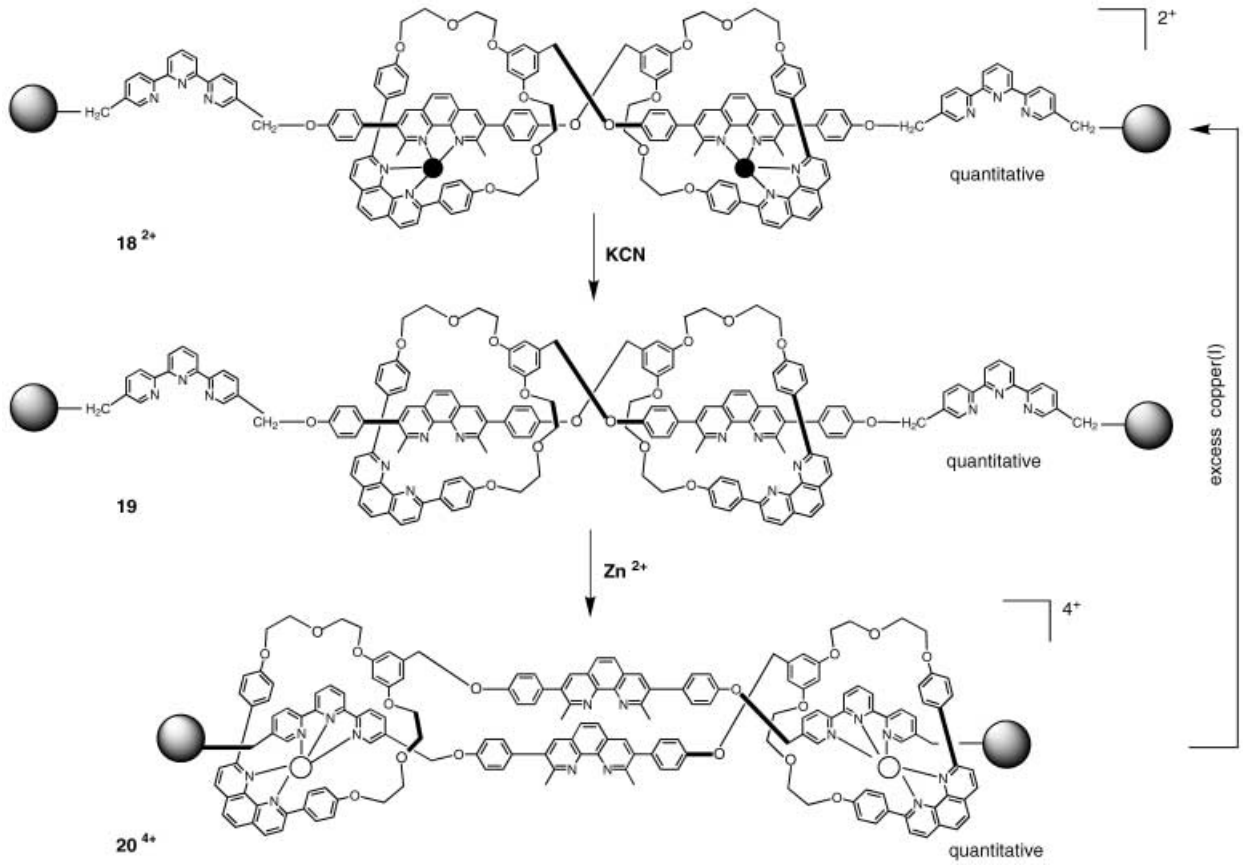
Mass spectrometry (FAB or ES) was used to confirm the dimeric nature of $\mathbf{18}^{2+}$, **19**, and $\mathbf{20}^{4+}$. Characteristic multicharged signals were observed at m/z 1844.7 for $\mathbf{18}^{2+}$ (calcd for $m/2$: 1844.6) and at m/z 1251.8 for $\mathbf{20}^{4+}$ (calcd for $m/3$: 1251.7) as well as the expected molecular ion peaks (Figure 8).

In the absence of X-ray quality crystals for both copper complex $\mathbf{18}^{2+}$ and zinc complex $\mathbf{20}^{4+}$, the alternate switching between the extended and contracted forms could only be evidenced by the careful analysis of their respective two-dimensional NMR spectra. Unambiguous chemical shifts of some aromatic protons (from either the phenanthroline or the terpyridine moities) along with numerous interfragment interactions observed in two-dimensional ROESY experiments provide the proof that the exchange process, copper(I)/zinc(II)/copper(I), generates the expected stretching–contraction motion. Indeed, it is clear from previous studies on the doubly threaded dicopper(I) precursor $\mathbf{14}^{2+}$, whose structure was fully confirmed by X-ray analysis, that $\mathbf{18}^{2+}$ contains two pseudotetrahedral complexes, in which each metal center is coordinated to a 2,9-diphenyl-1,10-phenanthroline (dpp) motif that is embedded in the ring and to a 2,9-dimethyl-1,10-phenanthroline (dmp) fragment from the filament. In Table 1, various NMR probes are considered.

1) H_o and H_m are indicative of the dpp environment. The chemical shifts of the two protons from a free dpp are in the expected range for an aromatic group attached to a 1,10-phenanthroline (phen) nucleus ($\delta = 7-8.5$). On the other

Table 1. ^{1}H NMR spectroscopy (400 MHz, CD_2Cl_2, 25 °C): chemical shifts of a few selected protons (δ).

	H_o	H_m	CH_3	6_{terpy}	$6''_{terpy}$	$4'_{terpy}$
17	–	–	–	8.68	8.72	7.96
$\mathbf{18}^{2+}$	7.48	6.04	2.09, 2.21	8.79	8.75	7.97
19	8.44	7.17	2.66, 2.72	8.80	8.71	7.97
$\mathbf{20}^{4+}$	6.85	6.29	2.71, 2.75	7.39	8.13	8.58



Scheme 6. Reversible chemically induced motions between extended $\mathbf{18}^{2+}$ and contracted $\mathbf{20}^{4+}$.

hand, when coordinated to a metal center in a 2-aromatic polyimine complex, H_o and H_m undergo a strong upfield shift characteristic of "entwined" compounds, as reported previously.[30] From Table 1, it is evident that dpp is coordinated in both complexes $\mathbf{18}^{2+}$ and $\mathbf{20}^{4+}$. For instance, H_m undergoes an upfield shift with respect to the free ligand of $\Delta\delta = -1.13$ and -0.88 ppm for $\mathbf{18}^{2+}$ and $\mathbf{20}^{4+}$ respectively. The shift is even larger for H_o in $\mathbf{20}^{4+}$ ($\Delta\delta = -1.59$ ppm) probably due to the strong ring current exerted by the terpyridine (terpy) on this proton.

2) The CH_3 groups of the phen chelate included in the filament are also shifted upfield by complexation, due to a similar "entwining" effect as observed for H_o and H_m. The chemical shifts are strikingly similar in the spectra of **19** and $\mathbf{20}^{4+}$, but they are significantly different from those of $\mathbf{18}^{2+}$: $\Delta\delta \approx -0.6$ ppm for $\mathbf{18}^{2+}$ with respect to **19** or $\mathbf{20}^{4+}$. This suggests that the dmp unit of $\mathbf{20}^{4+}$ is free.

3) H_6, $H_{6''}$, and $H_{4'}$ of the terpy moiety undergo substantial chemical shift changes upon complexation. Whereas the corresponding chemical shift values are similar in **17**, $\mathbf{18}^{2+}$ and **19** ($\delta = 8.76 \pm 0.08$ for H_6; 8.73 ± 0.02 for $H_{6''}$ and 7.97 ± 0.01 for $H_{4'}$), they are noticiably different in $\mathbf{20}^{4+}$ (strong upfield shift for H_6 and $H_{6''}$, a relatively strong downfield shift for $H_{4'}$). These observations are consistent with the "entwining" effect, and place H_6 and $H_{6''}$ in the shielding region of the dpp unit belonging to the ring for a {(dpp)(terpy)} complex. These shifts also demonstrate that both Zn^{2+} centers in $\mathbf{20}^{4+}$ coordinate to the terpy fragments, that is, the molecule is in a contracted form.

The present rotaxane dimer represents the first example of a unimolecular linear array able to stretch and contract at will under the action of a chemical stimulus. From CPK model calculations, the length of the compound changes from 83 Å in the dicopper complex $\mathbf{18}^{2+}$ to 65 Å in the dizinc complex $\mathbf{20}^{4+}$.

Conclusion

A strategy has been developed to make a doubly-threaded molecule, similar to a rotaxane dimer, and subsequently, a linearly arranged system which can contract or stretch under the action of a chemical signal. In this respect the present molecular assembly is reminiscent of natural muscles, although the principle of function is evidently remote from biological systems.

The key reaction of the multistep synthetic procedure is the double-threading step. It demonstrates the power of copper(I) as a gathering and threading center. From a ring-and-string conjugate, which consists of a dpp unit that is incorporated in the macrocycle and a 2,9-dimethyl-1,10-phenanthroline fragment that is attached as a pendent group to the ring, a doubly threaded species is quantitatively obtained by simple addition of stoichiometric amounts of copper(I). The "muscle" is then prepared by the addition of the second chelate (terpy) and the stoppers to each thread. The musclelike compound is set in motion by exchanging the metal, the copper(I) complex being extended and the zinc(II)-containing species being contracted. This process illustrates the ability of transition metal centers

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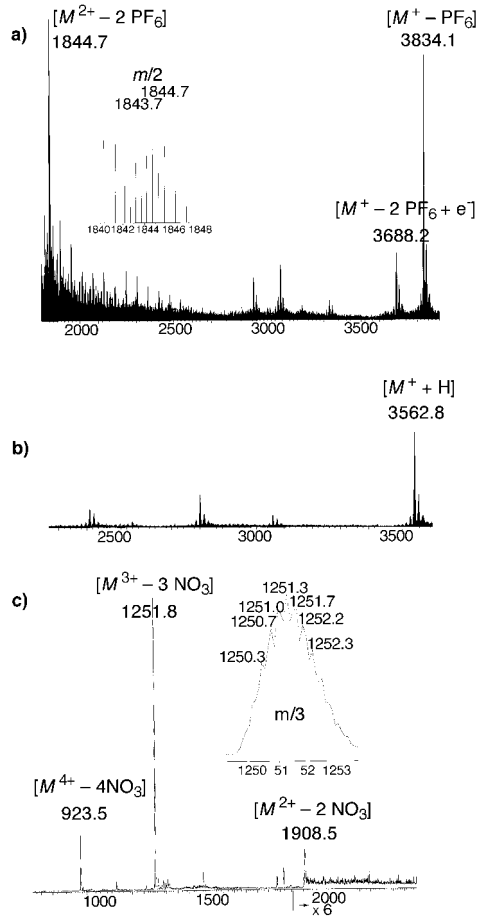

Figure 8. Mass spectra for the three states of the "muscle": a) FAB – MS of dicopper complex $\mathbf{18}^{2+}$, b) FAB-MS of free ligand **19**, c) ES – MS of dizinc complex $\mathbf{20}^{4+}$.

to govern the geometry of relatively complex molecular assemblies.

This system needs to be substantially improved before one can seriously envisage applications, in relation to stretchable/contractible organic polymers, nano- or micromachines, and artificial muscles. In particular, the chemical reaction originating in the motion (metal exchange) will have to be replaced by a simpler process (electrochemical or photochemical among many other stimuli). Finally, it is important to study both single molecules and polymers that are able to contract and stretch.

Experimental Section

General: The following compounds were prepared according to the literature: 3,8-dibromo-1,10-phenanthroline (**2**),[19, 20] 2,9-bis(4-methoxyphenyl)-1,10-phenanthroline (**7**),[23] 2,9-bis(4-hydroxyphenyl)-1,10-phenanthroline (**8**),[23] 2,9-bis{4-{2-[2-hydroxyethoxy(ethoxy)]}}phenyl-1,10-phenanthroline (**9**),[24] 2,9-bis{4-{2-[2-(4-toluenesulphonyl)ethoxy(ethoxy)]}}-phenyl-1,10-phenanthroline (**10**),[24] the 5,5″-dimethyl-2,2′:6′,2″-terpyridine,[27] stopper **16**,[29] $[Cu(CH_3CN)_4]PF_6$.[31] All other chemicals were of the best commercially available grade and were used without further purification. Dry solvents were distilled from suitable dessicants (DMF from CaH_2 under reduced pressure, CH_2Cl_2 from P_2O_5, THF 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). The purity of the new compounds made was checked by thin-layer chromatography on silica or alumina. UV/Vis spectra were recorded on a Kontron Instruments UVIKON 860 spectrophotometer. ^{1}H NMR spectra were recorded on either Bruker WP 200 SY (200 MHz) or WP 400 SY (400 MHz) spectrometers with the deuterated solvent as the lock and residual solvent as the internal reference. Fast atom bombardment mass spectra (FAB – MS) were recorded in the positive ion mode, with 3-nitrobenzyl alcohol as matrix, on a ZAB – HF mass spectrometer. Electrospray mass spectra (ES – MS) were recorded with a VG BIOQ triple quadrupole spectrometer and the electronic impact mass spectra (EI – MS) with a Waters Integrity TM System coupled with a Thermabeam TM mass detector. Melting points were measured with a Büchi SMP 20 apparatus and are uncorrected.

3,8-Bis-(4-methoxyphenyl)-1,10-phenanthroline (3): A degassed solution of Na_2CO_3 (2 M, 230 mL) and subsequently a degassed solution of the *p*-methoxyphenyl boronic ester (10 g, 45 mmol) in a $C_6H_5CH_3/CH_3OH$ (60/10 mL) were added, through a canula, to a degassed solution of **2** (7.6 g, 22 mmol) and $Pd(PPh_3)_4$ (2.5 g, 2.15 mmol) in toluene (400 mL).. After 24 h under reflux, the reaction mixture was cooled to room temperature, during which process, a precipitate appeared. This was filtered on a sintered disk funnel (porosity 4) and washed with cold toluene. Fast filtration over alumina ($CHCl_3$ as eluent) gave 7.40 g of **3** in 84% yield. Pale yellow powder, m.p.: 271–273 °C; UV/Vis (CH_2Cl_2): $\lambda_{max} = 279, 338$ nm ; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 9.40$ (d, $^4J(H,H) = 2.3$ Hz, 2H), 8.32 (d, $^4J(H,H) = 2.3$ Hz, 2H), 7.83 (s, 2H), 7.72 (d, $^3J(H,H) = 8.8$ Hz, 4H), 7.08 (d, $^3J(H,H) = 8.8$ Hz, 4H), 3.90 (s,6H); ^{13}C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 159.9, 149.2, 144.6, 135.2, 132.5, 129.9, 128.8, 128.4, 127.0, 114.7, 55.4$; MS (EI): *m*/*z*: 392.0 [M^+] (calcd: 392.15).

3,8-Bis-(4-methoxyphenyl)-2-methyl-1,10-phenanthroline (4): Compound **3** (4.00 g, 9,9 mmol) was suspended in toluene (200 mL) and maintained at 5 °C. After flushing with argon, CH_3Li (1.6 M in Et_2O, 25 mL, 40 mmol) was added slowly by means of an addition funnel at a rate such that the temperature did not exceed +5 °C. The reaction mixture was maintained at this temperature for 6 h and hydrolized by careful addition of distilled water (50 mL). The yellow toluene layer was decanted. The aqueous layer was extracted with $CHCl_3$ (3 × 100 mL). The organic layers were combined and rearomatized by succesive additions of MnO_2 (MnO_2 Merck 805958) under stirring. The reoxidation was monitored by TLC: MnO_2 was added until disapearance of the yellow color. $MgSO_4$ (5 g) was added to this mixture and stirred for 30 mins. The black slurry was filtered on a sintered disk filter (porosity 4) and subsequently thoroughly washed times with $CHCl_3$. Evaporation of the solvent yielded 3.92 g (95%) of **4** as a yellow solid. M.p.: 242–244 °C; UV/Vis (CH_2Cl_2): $\lambda_{max} = 279, 329$ nm ;^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta =$ 9.42 (d, $^4J(H,H) = 2.3$ Hz, 1H), 8.28 (d, $^4J(H,H) = 2.3$ Hz, 1H), 7.99 (s, 1H), 7.74 (s,2H), 7.70 (d, $^3J(H,H) = 8.8$ Hz, 2H), 7.40 (d, $^3J(H,H) = 8.7$ Hz, 2H), 7.05 (m,4H), 3.88 (s, 6H), 2.89 (s, 3H); ^{13}C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 159.8, 159.2, 157.8, 149.1, 144.3, 136.7, 136.2, 134.8, 132.5, 132.0, 130.3, 128.4, 126.9, 126.7, 125.9, 114.8, 113.0,55.3, 24.9$; MS (EI): *m*/*z*: 406.0 [M^+] (calcd: 406.17).

3,8-Bis-(4-methoxyphenyl)-2,9-dimethyl-1,10-phenanthroline (5): Compound **4** (3.00 g, 7.42 mmol) was suspended in toluene (150 mL) and treated with a solution of CH_3Li (1.6 M in Et_2O, 18 mL, 30 mmol) at +5 °C. The reaction conditions and the treatment were similar to those used for the preparation of **4**. The final yellow crude was purified by filtration on alumina, affording 3.10 g of **5** (97% yield). M.p.: 251–252 °C; UV/Vis (CH_2Cl_2): $\lambda_{max} = 277, 320$ nm; ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 8.04$ (s,2H), 7.74 (s, 2H), 7.41 (d, $^3J(H,H) = 8.8$ Hz, 4H), 7.04 (d, $^3J(H,H) = 8.8$ Hz, 4H), 3.91 (s, 6H), 2.91 (s, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta = 159.2, 157.7, 143.9, 136.7, 136.0, 132.1, 130.4, 127.0, 125.5, 113.6, 55.8, 25.2$; MS (EI): *m*/*z*: 420.0 [M^+] (calcd: 420.18).

3,8-Bis-(4-hydroxyphenyl)-2,9-dimethyl-1,10-phenanthroline (6): Technical grade pyridine (16 mL) was placed in a 100 mL three-necked round-bottomed flask which was equipped for distillation and fitted with a thermometer and a magnetic stirrer. Concentrated hydrochloric acid (17.6 mL) was added with rapid stirring. Water was distilled from the mixture until its internal temperature rose to 210 °C. After cooling to 140 °C, compound **5** (3.1 g, 7.4 mmol) was added as a solid in one batch, and the reaction flask was fitted with a reflux condenser connected to a source of argon. The yellow mixture was stirred under reflux for 3 h (190 °C < θ <

220 °C). The hot reaction mixture was then diluted with hot water (10 mL) and then with 60 mL of warm water. After cooling overnight, the bright yellow suspension was filtered over paper and washed with cold water. Crude acidic diphenol **6** was suspended (partially dissolved) in an ethanol/water mixture(250/90 mL) and neutralized with a dilute NaOH solution. After this pH-monitored neutralization (end-point: pH = 7.32), the suspension was diluted with hot water (150 mL) and cooled in an ice bath. Compound **6** precipitaded as a beige solid. It was filtered on paper, washed with cold water and dried overnight in air on a porous dish. Further drying (high vacuum in presence of P_2O_5) afforded **6** as a beige powder (2.6 g, 87% yield). It was used without further purification. M.p. > 260 °C ; UV/Vis (CH_2Cl_2): $\lambda_{max} = 277$, 322 nm ; ^{1}H NMR (200 MHz, [D$_6$]DMSO, 25 °C): $\delta =$ 9.68 (s,2H), 8.23 (s,2H), 7.93 (s,2H), 7.42 (d, ^3J(H,H) = 8.8 Hz, 4H), 6.96 (d, ^3J(H,H) = 8.8 Hz, 4H), 2.79 (s,6H); ^{13}C NMR (50.32 MHz, [D4]CH_3OH, 25 °C): $\delta =$ 158.6, 156.1, 144.1, 139.0, 137.5, 137.0, 131.5, 128.6, 127.0, 116.4, 24.8 ; MS (EI): *m/z*:392.0 [$M^+ - H$] (calcd: 392.15).

Macrocycle (11): A degassed mixture of the tosyl derivative **10** (1.29 g, 1.52 mmol) and 3,5-dihydroxybenzyl alcohol (0.190 g, 1.35 mmol) in DMF (150 mL) was added over 48 h to a stirred suspension of Cs_2CO_3 (2.0 g, 6.08 mmol) in DMF (400 mL) under argon at 55 °C. After an additional 24 h, the DMF was evaporated by using a vacuum pump. The residue was taken up in CH_2Cl_2/H_2O mixture (100/50 mL). The organic phase was separated and the aqueous phase was washed with CH_2Cl_2 (3 × 100 mL). The organic phases were collected and dried over $MgSO_4$, and the solvent was evaporated in vaccuo. After column chromatography on SiO_2 (CH_2Cl_2-CH_3OH 0% to 2%), compound **11** was obtained in 50% yield (0.478 g). UV/Vis (CH_2Cl_2): $\lambda_{max} = 281$, 321 nm ; ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C): $\delta = 8.34$ (m,6H), 8.12 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.81 (s, 2H), 7.12 (d, ^3J(H,H) = 8.8 Hz, 4H), 6.41 (brs, 1H), 6.33 (brs, 2H), 4.31 (m, 4H), 4.20 (s, 2H), 4.10 (m, 4H), 3.93 (m, 8H); ^{13}C NMR (50.32 MHz, $CDCl_3$, 25 °C): $\delta =$ 160.1, 159.5, 156.7, 136.9, 132.9, 129.1, 127.7, 125.7, 119.8, 115.6, 105.3, 103.8, 99.4, 66.9, 66.8, 66.8, 66.0, 32.3; MS (EI): *m/z*: 645.0 [M^+] (calcd: 644.7).

Macrocycle (12): A solution of **11** (1.00 g, 1.55 mmol) and PBr_3 (0.3 mL, 31 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature for 48 h. After addition of water (20 mL), the suspension reached pH 7 by addition of small portions of a dilute solution of NaOH (pH monitored). The organic phase was decanted, and the aqueous phase washed with CH_2Cl_2 (3 × 50 mL). The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated to afford crude macrocycle **12**. Chromatography on SiO_2 (CH_2Cl_2-CH_3OH 0% to 1%) afforded 1.10g of **12** (76% yield) as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 8.42$ (d, ^3J(H,H) = 8.8 Hz, 4H), 8.27 (d, ^3J(H,H) = 8.6 Hz, 2H), 8.08 (d, ^3J(H,H) = 8.6 Hz, 2H), 7.76 (s, 2H), 7.15 (d, ^3J(H,H) = 8.8 Hz, 4H), 6.56 (m,3H), 4.37 (s,2H), 4.34 (m, 4H), 4.18 (m, 4H), 3.95 (m, 8H); ^{13}C NMR (50.32 MHz, CD_2Cl_2, 25 °C): $\delta =$ 159.2, 158.6, 157.5, 136.7, 132.8, 129.1, 127.6, 125.6, 119.2, 115.6, 107.7, 102.7, 101.2, 70.0, 69.7, 67.8, 67.7, 33.9; MS (FAB$^+$): *m/z*: 708.20 [M^+] (calcd: 708.62).

Ligand (13): A degassed solution of bromide **12** (0.405 g, 0.57 mmol) in DMF (50 mL) was slowly added (over 10 h) to a well stirred suspension of diphenol **6** (0.674 g, 1.71 mmol) and Cs_2CO_3 (1.00 g, 3.07 mmol) in DMF (100 mL) at 55 °C under argon. After additional stirring at 55 °C (12 h), the DMF was evaporated and the residue taken up in CH_2Cl_2/H_2O (50/50 mL). The organic phase was decanted, and the aqueous phase extracted with CH_2Cl_2 (3 × 50 mL). The collected organic phases were dried over $MgSO_4$ and the resulting residue submitted to column chromatography (Al_2O_3). At $CHCl_3$/hexane (4/1), 0.298 g of pure **13** were obtained (51% yield) as a pale-yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 8.43$ (d, ^3J(H,H) = 8.8 Hz, 4H), 8.32 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.12 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.07 (s,1H), 7.98 (s, 1H), 7.80 (s,2H), 7.76 (s,1H), 7.75 (s,1H), 7.41 (d, ^3J(H,H) = 8.8 Hz, 2H), 7.29 (d, ^3J(H,H) = 8.7 Hz, 2H), 7.19 (d, ^3J(H,H) = 8.8 Hz, 4H) 7.02 (d, ^3J(H,H) = 8.8 Hz, 2H), 6.99 (d, ^3J(H,H) = 8.8 Hz, 2H), 6.65 (d, ^4J(H,H) = 2.2 Hz, 2H), 6.63 (t, ^4J(H,H) = 2.2 Hz, 1H), 5.05 (s,2H), 4.35 (m, 4H), 4.23 (m, 4H), 3.98 (m, 8H), 2.85 (s, 3H), 2.77 (s, 3H); MS (FAB$^+$): *m/z*: 1020.5 ([M^+H] (calcd: 1020.4).

Compound (14^{2+}): A degassed solution of $[Cu(CH_3CN)_4]PF_6$ (7.5 mg, 20 mmol) in CH_3CN (10 mL) was transfered through a canula to a degassed solution of **13** (20.4 mg, 20 mmol) in CH_2Cl_2 (10 mL). The solution of **13**, initially pale yellow, turned dark brown-red upon the addition of the copper(I) salt. The solution was stirred for 48 h at room temperature under argon, the solvents were then evaporated and the product analyzed by ^{1}H NMR spectroscopy, which showed that $\mathbf{14}^{2+}$ was present in at least 95% yield. It was used for the following synthesis without further purification. Suitable single crystals were obtained by the diffusion technique (acetone/diethyl ether). ^{1}H NMR (400 MHz, CD_2Cl_2/CD_3CN, 25 °C): $\delta = 8.64$ (d, ^3J(H,H) = 8.3 Hz, 4H; $H_{4,7}$), 8.24 (s, 2H; $H_{7'}$), 8.18 (d, ^3J(H,H) = 8.6 Hz, 2H; $H_{5'}$), 8.09 (s, 4H; $H_{5,6}$), 8.06 (d, ^3J(H,H) = 8.5 Hz, 4H; $H_{3,8}$), 8.01 and 8.18 (2d, ^3J(H,H) = 8.6 Hz, 4H; $H_{5'}$ and $H_{6'}$), 7.99 (s, 2H; $H_{4'}$), 7.43 (d, ^3J(H,H) = 8.6 Hz, 8H; H_a), 7.15 (d, ^3J(H,H) = 8.5 Hz, 4H; $H_{o''}$), 7.06 (s, 2H; OH), 6.96 and 7.12 (2d, ^3J(H,H) = 8.2 Hz, 8H; $H_{m'}$ and $H_{o'}$), 6.85 (d, ^3J(H,H) = 8.8 Hz, 4H; $H_{m''}$), 6.65 (t, ^4J(H,H) = 2.2 Hz, 2H; H_a), 6.62 (d, ^4J(H,H) = 2.2 Hz, 4H; H_b), 5.94 (d, ^3J(H,H) = 8.6 Hz, 8H; H_m), 4.96 (s, 4H; $ArOCH_2Ar$), 3.35 – 3.89 (m, 32H; H $_{\alpha,\beta,\gamma,\delta}$), 2.00 and 2.09 (2s, 12H; $-CH_3$) ; MS (ES$^+$): *m/z*: 2310.3 [$M^+ - PF_6^-$] (calcd: 2310.3), 1082.7 [$M^{2+} - PF_6^-$] (calcd for *m*/2: 1082.7).

X-ray crystallography of 14^{2+}: Suitable dark red single crystals of $\mathbf{14}^{2+} \cdot 2PF_6^- \cdot 2CH_3OH$ were obtained by the diffusion technique (acetone/diethyl ether). $C_{67}H_{61}O_{10}N_4PF_6Cu$, $M_W = 1290.76$, monoclinic, $a =$ 25.543(1), $b = 20.870(1)$, $c = 27.869(1)$ Å, $\beta = 116.96(2)°$, $V = 13242(2)$ Å^3, space group $C2/c$, $Z = 4$, $\rho_{calcd} = 1.295$ g cm^{-3}, $\mu = 4.296$ mm^{-1}. Data were collected at −100 °C on a Nonius Kappa CCD diffractometer using the standard data collection procedures ($2.5 < \theta < 30°$) and $Mo_{K\alpha}$ graphite monochromated radiation ($\lambda = 0.71073$ Å) on a crystal of dimensions $0.30 \times 0.30 \times 0.20$ mm^3. 21423 data collected, 7329 with $I > 3\sigma(I)$. The structure was solved by using direct methods. The diffraction power of the crystals was poor despite the collection of four samples; the same results were obtained. It was not possible to fully resolve the disorder of one of the PF_6^- anions or to locate all solvent molecules even by refining on F^2 and using all data with $I > 2\sigma(I)$. Neverless, the core of the molecule is correct and refines normally. Final results: $R = 0.142$, $wR = 0.193$.

CCDC-135902 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

5,5″-Bis(bromomethyl)-2,2′:6′,2″-terpyridine (15): A mixture of 5,5″-dimethyl-2,2′:6′,2″-terpyridine [27] (0.500 g, 1.91 mmol) and NBS (*N*-bromosuccinimide) (1.70g, 9.55 mmol) in benzene (50 mL) was heated under reflux for 30 mins and subsequently irradiated for 20 mins (diapo projector). During the irradiation, NHS precipitated as a white solid, the solvent then was evaporated to dryness, and the crude solid dissolved in CH_2Cl_2 (100 mL). The organic solution was washed with water (100 mL) and then with a $Na_2S_2O_3$ solution (2M, 100 mL), dried over $MgSO_4$, filtered, and evaporated to dryness. The product was dissolved in a minimum of CH_2Cl_2 and cooled overnight in a refrigerator. The white precipitated solid was filtered on a sintered disk funnel. Three successive such dissolution – precipitation procedures yielded 0.385 g (48% yield) of the pure dibromo derivative **15**. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 8.71$ (d, ^4J(H,H) = 1.7 Hz, 2H), 8.61 (d, ^3J(H,H) = 8.4 Hz, 2H), 8.47 (d, ^3J(H,H) = 7.9 Hz, 2H), 7.97 (t, ^3J(H,H) = 7.9 Hz, 1H), 7.90 (dd, ^3J(H,H) = 8.12 Hz, ^4J(H,H) = 2.2 Hz, 2H), 4.56 (s, 4H).

Stoppered terpyridine (17): NaH (50% in mineral oil, 0.034 g, 0.71 mmol) was added to the phenolic blocking group **16** (0.200 g, 0.39 mmol) in dry THF (10 mL) under argon at room temperature and stirred for 1h. A degassed solution of dibromide **15** (0.500 g, 0.58 mmol in 20 mL THF) was then transfered through a canula to the phenolate solution and stirred at room temperature under argon for 24 h. A few drops of water were added to destroy excess NaH. The solvent was evaporated, and the residue dissolved in CH_2Cl_2. This organic phase was washed with water(3 × 50 mL) and dried over $MgSO_4$. Fast chromatography of the crude solid over alumina [hexane/CH_2Cl_2 (70/30 v/v) as eluent] gave the stoppered terpyridine **17** in 45% yield (0.152 g). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 8.72$ (d, ^4J(H,H) = 1.6 Hz, 1H), 8.68 (d, ^4J(H,H) = 1.9 Hz, 1H), 8.63 (d, ^3J(H,H) = 7.8 Hz, 1H), 8.61 (d, ^3J(H,H) = 7.5 Hz, 1H), 8.47 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.0 Hz, 1H), 8.45 (dd, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.0 Hz, 1H), 7.96 (t, ^3J(H,H) = 7.8 Hz, 1H), 7.94 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.2 Hz, 1H), 7.90 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 2.3 Hz, 1H), 5.15 (s,2H), 4.57 (s,2H), 1.31 (s, 27H).

Extended "muscle" (18^{2+}): A degassed solution of the dimer complex $\mathbf{14}^{2+}$ (0.120 g, 0.049 mmol) in DMF (20 mL) was heated to 40 °C. A degassed solution – suspension of the stoppered terpyridine **17** (0.143 g, 0.166 mmol in 10 mL DMF) and a degassed suspension of Cs_2CO_3 (0.178 g, 0.55 mmol) in DMF (10 mL) were in two other separate Schlenk flasks, respectively.

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Both these last two flasks were maintained at room temperature and connected to the three-necked round bottom flask containing $\mathbf{14}^{2+}$ (maintained at 40 °C) through two canula. A small batch of the Cs_2CO_3 was added to $\mathbf{14}^{2+}$ followed a few minutes later by the addition of a small batch of the terpyridine **17** solution. Successive additions were performed at the rate of one each per hour for 5 h. This protocol has the advantage of minimizing both the basic hydrolysis of benzylic bromide **17** and the partial demetallation of dimer complex $\mathbf{14}^{2+}$. The resulting mixture was stirred at 40 °C under argon for 5 h and at room temperature overnight. The dark red crude solid obtained after evaporation of the DMF was redissolved in CH_2Cl_2 (50 mL) and stirred overnight in the presence of a saturated KPF_6 solution (30 mL). The organic phase was decanted and dried over $MgSO_4$, filtered, and evaporated to dryness. Column chromatography over alumina (eluent: CH_2Cl_2/MeOH 0.2 % to 0.5 %) yielded 0.117 g of complex $\mathbf{18}^{2+}$ as a dark red solid (60 % yield). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 8.79$ (d, $^4J(H,H) = 1.6$ Hz, 2H; H_{6T}), 8.75 (d, $^4J(H,H) = 1.6$ Hz, 2H ; $H_{6''T}$), 8.68 (d, $^3J(H,H) = 8.0$ Hz, 2H ; H_{3T}), 8.65 (d, $^3J(H,H) = 8.5$ Hz, 2H; $H_{3''T}$), 8.64 (d, $^3J(H,H) = 8.5$ Hz, 4H ; $H_{4,7}$), 8.48 (m, 4H ; $H_{3'T}$ and $H_{5'T}$), 8.29 (d, $^3J(H,H) = 9.0$ Hz, 2H; $H_{5'}$), 8.26 (s, 2H ; $H_{7'}$), 8.11 (d, $^3J(H,H) = 8.3$ Hz, 4H; $H_{3,8}$), 8.10 (s, 2H ; $H_{4'}$), 8.10 (s, 4H; $H_{5,6}$), 8.04 (d, $^3J(H,H) = 9.0$ Hz, 2H; $H_{6'}$), 8.00–7.95 (m, 6H ; $H_{4T,4''T,4'T}$), 7.48 (d, $^3J(H,H) = 8.8$ Hz, 8H; H_o), 7.29 (d, $^3J(H,H) = 8.5$ Hz, 4H; $H_{o''}$), 7.27 (d, $^3J(H,H) = 8.8$ Hz, 12H; H_{ostop}), 7.20 (d, $^3J(H,H) = 9.0$ Hz, 8H; $H_{o''}$ and $H_{m'}$), 7.16 (d, $^3J(H,H) = 8.8$ Hz, 12H; H_{mstop}), 7.14 (d, $^3J(H,H) = 9.0$ Hz, 4H; $H_{m''}$), 7.03 (d, $^3J(H,H) = 8.8$ Hz, 4H; $H_{o'}$), 6.91 (d, $^3J(H,H) = 9.0$ Hz, 4H; $H_{m''}$), 6.69 (d, $^4J(H,H) = 2.3$ Hz, 2H; H_a), 6.66 (d, $^4J(H,H) = 2.1$ Hz, 4H; H_b), 6.04 (d, $^3J(H,H) = 8.8$ Hz, 8H ; H_m), 5.25 (s, 4H; $-OCH_2B$), 5.15 (s, 4H; $-OCH_2C$), 4.96 (s, 4H; $-OCH_2A$), 4.18–4.09 (m, 8H ; $-OCH_{2\delta}$), 3.97–3.89 (m,4H ; $-OCH_{2\gamma}$), 3.76–3.74 (m, 4H; $-OCH_{2\gamma}$), 3.69–3.65 (m, 4H; $-OCH_{2\beta}$), 3.61–3.52 (m, 8H; $-OCH_{2\alpha}$ and $-OCH_{2\beta}$), 3.48–3.44 (m, 4H; $-OCH_{2\gamma}$), 2.21 (s, 6H; CH_3), 2.09 (s, 6H; CH_3), 1.30 (s, 54H; $H_{t\mathrm{Bu}}$); MS (FAB$^+$): m/z: 3834.2 [$M^+ - PF_6$] (calcd: 3834.3), 1844.8 [$M^{2+} - 2PF_6$], (calcd for m/2: 1844.7).

Free ligand (19): KCN (0.020 g, 0.31 mmol) in water (5 mL) was added to $\mathbf{18}^{2+}$ (0.040 g, 0.01 mmol) in CH_2Cl_2 (5 mL). After the mixture was stirred for 1 h at room temperature, the initial dark red color of the organic phase had disappeared. After an additional 2 h of stirring, the pale yellow organic phase was decanted, dried over $MgSO_4$, and evaporated to dryness. The free ligand **19** was obtained in quantitative yield as a colorless glass (0.036 g, 0.01 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 8.80$ (brs, 2H; H_{6T}), 8.71 (brs, 2H; $H_{6''T}$), 8.44 (brs, 8H; H_o), 8.24 (m, 8H; $H_{4,7}$,H_{3T} and $H_{3''T}$), 8.13 (m, 4H; $H_{3'T}$ and $H_{5'T}$), 7.97 (m, 6H; $H_{4T,4''T,4'T}$), 7.75 (brs, 4H; $H_{5,6}$), 7.70 (m, 8H ; $H_{4'}$,$H_{7'}$ and $H_{3,8}$), 7.54 (m, 4H; $H_{5',6'}$), 7.29–7.27 (brm, 16H; $H_{o\ stop.}$,$H_{o''}$), 7.20–7.17 (brm, 28H; H_m,$H_{m\ stop}$,$H_{o'}$ and $H_{o''}$), 7.06 (m, 4H; $H_{m''}$), 6.93 (m, 8H; $H_{m'}$,$H_{m''}$), 6.49 (brs, 6H; H_a and H_b), 5.10 (brs, 8H; $-OCH_2B$ and $-OCH_2C$), 4.32–3.85 (m, 32H; $-OCH_2$ cyclic), 2.72 (s, 6H; CH_3), 2.66 (s, 6H; CH_3), 1.31 (s, 54H; $H_{t\mathrm{Bu}}$); MS (FAB$^+$): m/z: 3562.8 [M^++H], (calcd: 3562.7).

Contracted "muscle" ($\mathbf{20}^{4+}$): $Zn(NO_3)_2 \cdot 4H_2O$ (3 mg, 0.0094 mmol) dissolved in MeOH (3 mL) was added to stirred solution of **19** (0.018 g, 0.005 mmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction was monitored by TLC and ended after 1 h. Evaporation of solvent gave $\mathbf{20}^{4+}$ quantitatively (0.019 g, 0.005 mmol) as a pale yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): $\delta = 8.85$ (d, $^3J(H,H) = 8.1$ Hz, 2H; $H_{3''T}$), 8.80 (d, $^3J(H,H) = 7.2$ Hz, 2H; H_{3T}), 8.70 (d, $^3J(H,H) = 8.5$ Hz, 4H; $H_{4,7}$), 8.58 (t, $^3J(H,H) = 8.0$ Hz, 2H; $H_{4''T}$), 8.28 (s, 4H; $H_{5,6}$), 8.27 (brd, $^3J(H,H) = 8.6$ Hz, 2H; H_{4T}), 8.16 (brd, $^3J(H,H) = 8.7$ Hz, 2H; $H_{4''T}$), 8.13 (brs, 2H; $H_{6''T}$), 7.84 (d, $^3J(H,H) = 8.0$ Hz, 2H; $H_{5''T}$), 7.77 (d, $^3J(H,H) = 8.5$ Hz, 4H; $H_{3,8}$), 7.68 (d, $^3J(H,H) = 8.2$ Hz, 2H; $H_{3''T}$), 7.62 (s, 4H; $H_{4'}$ and $H_{7'}$), 7.39 (brs,2H ; H_{6T}), 7.26–7.09 (m, 40H; $H_{o',o'',o''',m'}$ and $H_{o,m\ stop.}$), 6.93 (d, $^4J(H,H) = 2.1$ Hz, 4H; H_b), 6.85 (d, $^3J(H,H) = 8.6$ Hz, 8H; H_o), 6.81 (d, $^4J(H,H) = 2.0$ Hz, 2H; H_a), 6.79 (d, $^3J(H,H) = 8.6$ Hz, 4H; $H_{m''}$), 6.52 (d, $^3J(H,H) = 9.0$ Hz, 4H; $H_{m''}$), 6.29 (d, $^3J(H,H) = 8.7$ Hz, 8H; H_m), 5.15 (s, 4H; $-OCH_2A$), 4.95 (s, 4H; $-OCH_2B$), 4.90 (s, 4H; $-OCH_2C$), 4.30–3.80 (m, 32H; $-OCH_2$ cyclic), 2.75 (s, 6H; CH_3), 2.71 (s, 6H; CH_3), 1.27 (s, 54H; $H_{t\mathrm{Bu}}$); MS (ES$^+$): m/z: 1908.5 [$M^{2+} - 2NO_3$]$^{2+}$ (calcd for m/2: 1908.5), 1251.8 [$M^{3+} - 3NO_3$] (calcd for m/3: 1251.7), 923.5 [$M^{4+} - 4NO_3$] (calcd for m/4: 923.3).

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