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A Fast-Moving Copper-Based Molecular Shuttle: Synthesis and Dynamic Properties

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Abstract: The present report deals with the synthesis of a two-station [2]rotaxane consisting of a dpbiiq-incorporating macrocycle (dpbiiq: 8,8′-diphenyl-3,3′-biisoquinoline) threaded by a coordinating fragment whose complexing units are a dpp and a terpy ligand (dpp: 2,9-diphenyl-1,10-phenanthroline; terpy: 2,2′,6′,2”-terpyridine). The [2]rotaxane was prepared in 11 steps from commercially available or easy-to-make molecules, without taking into account the preparation of the dpbiiq-containing 39-membered ring, which was available in our group. The ring-incorporated bidentate chelate is at the same time endocyclic and sterically nonhindering, which is a specific property of the dpbiiq-coordinating unit. This unique feature has a profound influence on the rate of the ring-and-copper translation motion between the two stations of the axle. Based on an analogous multistep strategy, a related molecular shuttle has also been prepared that contains exactly the same axle and stoppers as the first compound but whose threaded ring incorporates the sterically hindering dpp chelate. The translation motions of this other system are several orders of magnitude slower than the corresponding movements of the dpbiiq-based compound. The motion corresponding to the rearrangement of the unstable five-coordinate copper(I) form of the compounds is relatively fast for both shuttles; the half lifetime of the five-coordinate Cu^{I} species being below 20 ms for the dpbiiq-containing system and below 1 s for the dpp-based molecule. The reverse motion corresponding to the rearrangement of the four-coordinate copper(II) complexes is much slower, especially for the dpp-based system. It is of the order of several hours for the dpp-based shuttle and only one second or less for the dpbiiq system, under exactly the same conditions. The remarkable difference between the motion rates for the two two-station shuttles demonstrates that the use of a very open chelate such as dpbiiq is extremely beneficial in the context of fast-moving molecular machines.

Keywords: biisoquinoline · copper · molecular machines · molecular shuttles · N ligands · rotaxanes

Introduction

The field of catenanes and rotaxanes[1] is particularly active, mostly in relation to the novel properties that these compounds may exhibit (electron and energy transfer,[2] controlled motions and mechanical properties,[3–9] and new “intelligent” materials[10–17]). In addition, catenanes represent attractive synthetic challenges in molecular chemistry. The creation of such complex functional molecules as well as related compounds of the rotaxane family demonstrates that synthetic chemistry is now powerful enough to tackle problems whose complexity is sometimes reminiscent of biology, although the elaboration of molecular ensembles displaying properties as complex as biological assemblies is still a long-term challenge. The most efficient strategies for making such compounds are based on template effects. The first templated synthesis relied on copper(I).[18] The use of Cu^{I} as template allows one to entangle two organic fragments around the metal center before incorporating them in the desired catenane backbone. This metal has been extensively used as a template in our group[1b,18] or in other research teams.[19–21] Other transition-metal centers have also been used successfully in the templated synthesis of various catenanes and rotaxanes.[22–26] Organic templates, assembled via formation of aromatic acceptor–donor complexes and/or hydrogen bonds, have also been very successful.[27–31] Nowadays, numerous template strategies are available that have

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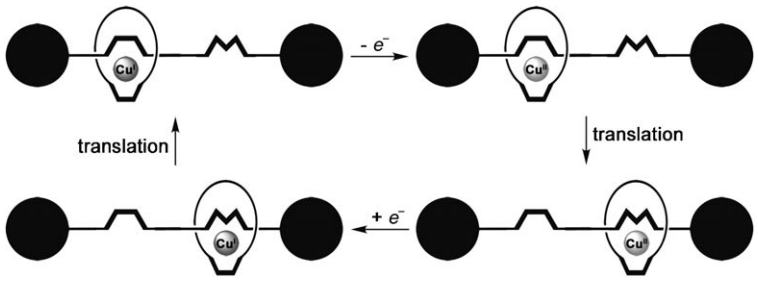
led to the preparation of a myriad of catenanes and rotaxanes incorporating various organic or inorganic fragments and displaying a multitude of chemical or physical functions. Among these functions, the ability of catenanes and rotaxanes to behave as molecular machine prototypes[3–6,28,32] is certainly the most popular, in relation to potential applications in the field of information storage and processing at the molecular level as well as the fabrication of molecular electro- or photo-mechanical devices.[33] In the course of the last 15 years, our group has proposed several molecular machine prototypes based on copper-complexed catenanes and rotaxanes.[34] The driving force for setting the molecular systems in motion is the preference of the copper(I) or copper(II) complexes for different geometries (four-coordinate for Cu^{I} and five- or six-coordinate for Cu^{II}) and thus, their rearrangement after oxidation or reduction. Critical to the elaboration of efficient machine prototypes and potential devices is the rate of the motion. The weak point of transition-metal-based dynamic systems is their relatively long response time: one of the rate-limiting steps in the rearrangement process is the substitution sphere of the metal. Exchanging ligands around a copper center can be relatively slow, especially if the metal is hindered and if its environment is congested. Herein, we describe a new approach, based on sterically non- or only slightly hindering ligands whose incorporation into catenane and rotaxane backbones is made possible thanks to their particular crescent shape. In particular, the two-station molecular shuttle[35] reported now is set in motion much faster than the previous examples from our group based on sterically hindering ligands. A preliminary account of the electrochemical and dynamic properties of the present shuttle has been reported recently.[36]



Scheme 1. Schematic representation of a metal-complexed [2]rotaxane acting as an electrochemically driven molecular shuttle. The ring contains a coordinating unit interacting with the metal center in both states. The axis incorporates two chelating units: a bidentate one and a tridentate chelate. It is attached to terminal stoppers.

Results and Discussion

Design of the two-station rotaxanes: Molecular shuttles constitute a promising class of molecular machines. A ring can glide in a controlled fashion along an axis on which it has been threaded. This motion can even be realized over large distances by playing with the length of the various fragments incorporated in the thread and the number of "stations" with which a given part of the ring is able to interact. Following the first molecular shuttle from Kaifer, Stoddart and co-workers,[35] several purely organic examples of such dynamic systems have been described,[37–44] some of them being the active components of molecular electronic memory.[45–47] The approach of our group is based on transition metals and, in particular, on Cu^{I} and Cu^{II}. The principle of a two-station molecular shuttle whose motions are driven by changing the oxidation state of the metal center is indicated in Scheme 1.

The coordination properties of the two axis ligands have to be markedly different. In this way, by oxidizing or reducing the metal center, the system will be strongly destabilized. For the system to relax, the ring and the metal will have to glide along the axis. The driving force for the rearrangement of the rotaxane (i.e., for the shuttling motion of the metal-coordinated ring between the two "stations") will be determined by the energy difference between one of the two stable states and the corresponding unstable one generated by metal oxidation or reduction.

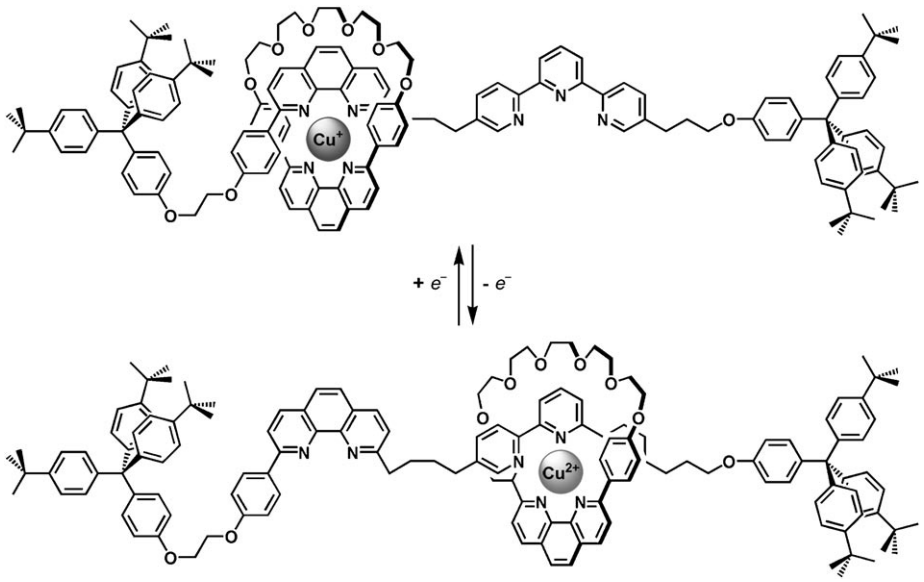
The first copper-complexed shuttle prepared and studied in our group[48] is represented in Scheme 2. In this compound, the thread is flexible, which makes it difficult to have a clear view of the geometry with, in particular, an accurate knowledge of the distance between the two stations of the shuttle. In addition, and more important in terms of function, the coordination site is highly congested in the four-coordinate situation due the presence of a 2,9-diphenyl-1,10-phenanthroline motif in the ring. This structural feature is detrimental to fast ligand exchange and thus to fast motions.

The molecular shuttle represented in Scheme 2 turned out to be kinetically very inert. The rearrangements of the unstable species Cu_5^{I} and Cu_4^{II}, described by Equations (1) and (2) take place on the minute to hour timescale (the subscripts 4 and 5 indicate the coordination number of the copper atom).

$$Cu_5^{I} \rightarrow Cu_4^{I} \quad (1)$$

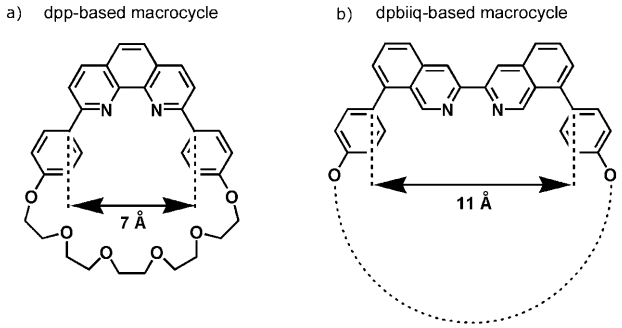
$$Cu_4^{II} \rightarrow Cu_5^{II} \quad (2)$$

As shown recently for "pirouetting" copper-complexed rotaxanes, decreasing the steric congestion around the copper center has a strong effect on the rearrangement rates of the complexes.[49] It thus seemed to be important to develop a new series of molecules whose ring-incorporated chelate would be as little hindering as possible. Conceptually, this problem is far from trivial since the chelate has to be at the same time endotopic or endocyclic so as to be incorporated in a ring in such a way that its coordination site be



Scheme 2. The two stable states of a previously reported copper-complexed bistable rotaxane: a slow moving shuttle.[48] The mobile ring is a 30-membered ring that incorporates a dpp chelate, whereas the "stations" are a 2,9-disubstituted-1,10-phenanthroline unit and a 6,6′,2′,6″-terpyridine (terpy). As in many other examples from our group, Cu^{I} is stabilized in a four-coordinate situation, that is, by interacting with two bidentate chelates of the phenanthroline family. In contrast, Cu^{II} has a strong preference for higher coordination number (5 or 6) and in the present case, its most stable coordination sphere will involve a phenanthroline and a terpy.

oriented towards the inner part of the ring in an unambiguous fashion. In this respect, the 8,8′-diphenyl-3,3′-biisoquinoline (dpbiiq) backbone seems to be ideally suited. As shown in Scheme 3, the 8,8′-diphenyl-3,3′-biisoquinoline motif is



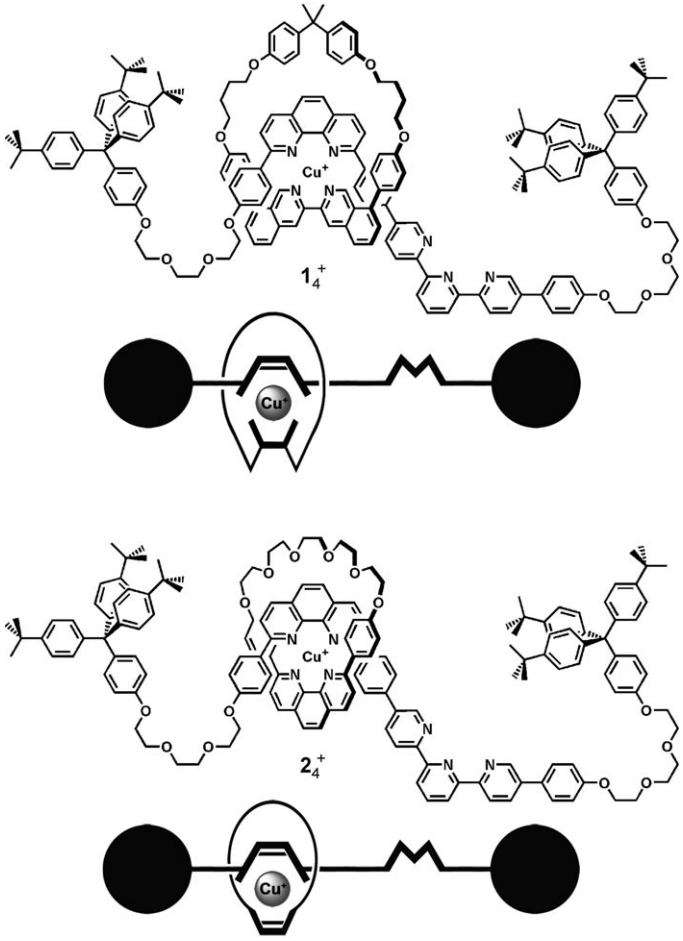
Scheme 3. a) The use of a dpp fragment as chelate induces high steric hindrance once a metal is coordinated; b) by using a 3,3′-biisoquinoline chelate, which is substituted far from the nitrogens in positions 8 and 8′, a sterically nonhindering macrocycle is obtained.

such that endocyclic coordination will be certain and, equally important, the complexed metal center will be remote from any organic group of the ligand organic backbone. In dpp (Scheme 3a), the shortest C–C distance between the phenyl rings borne by the phen nucleus at its 2- and 9-positions is around 7 Å, whereas it is around 11 Å for the two corresponding phenyl rings of dpbiiq (Scheme 3b).

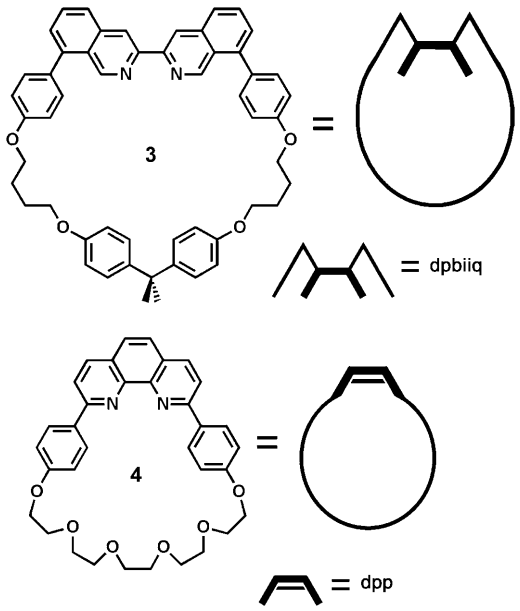
The replacement of the dpp chelate by a dpbiiq in the axis of "pirouetting" pseudo-rotaxanes turned out to have a very significant effect on the rate of the electrochemically induced rearrangement processes.[50] As described in the present report, the acceleration factor of the shuttling reaction will even be more pronounced when replacing the dpp-containing ring of the compound shown in Scheme 2 by a dpbiiq-incorporating fragment.

The chemical structure of the two rotaxanes reported in the present article and of the various constitutive components are represented in Schemes 4, 5, and 6.

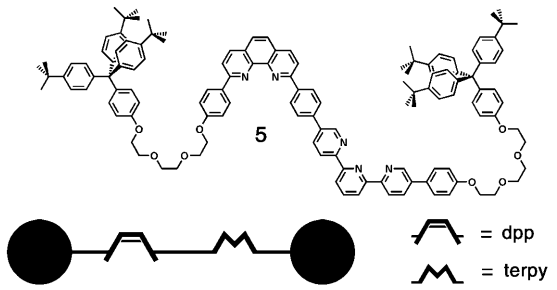
The choice of the rings was dictated by various considerations. Compound **3** incorporates the wide dpbiiq fragment and it has therefore to be relatively large to allow the macrocycle to occupy a roughly circular geometry once coordinat-



Scheme 4. Chemical formula and schematic representation of the Cu^{I} rotaxanes $\mathbf{1}_4^+$ and $\mathbf{2}_4^+$.



Scheme 5. Chemical formula and schematic representation of the rings **3** and **4**.



Scheme 6. Chemical formula and schematic representation of the axis **5**.

ed to Cu^{I} and threaded by the axis. On the other hand, its size should be adapted to that of the stopper and can not exceed 42 or 43 atoms in its periphery without relatively easy unthreading of the end-stoppered axis from the ring in the copper-free compound. The dpp-incorporating macrocycle **4** is a classical ring from our group and, in particular, it is this cyclic compound which was used in the previous shuttle of Scheme 2.

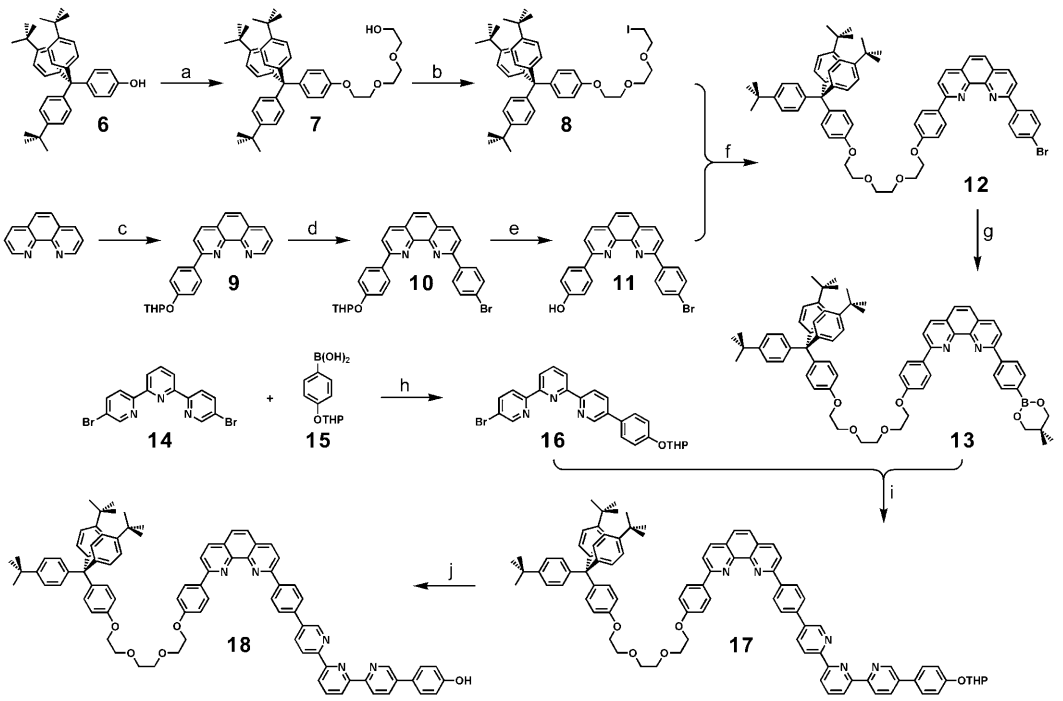
As far as the structure of the threaded fragment is concerned (Scheme 6), the stoppers are the same ones as for several other studies. For comparison purposes and to demonstrate that dpbiiq is much more efficient than dpp as an exchangeable chelate, we favored chemical structures that induced, a priori, slow motions whose kinetics can be investigated by using classical electrochemical methods. Consequently, specific to the present study is the structure of the central part, which is very rigid and composed of aromatic rings only. In this way, the axis has a limited possibility to fold up, which leads to a reasonably good estimation of the distance between the coordination sites of the two stations. In addition, the structure is such that a concerted mechanism for ligand substitution within the coordination sphere of the copper center, that is, simultaneous participation of the two stations (dpp and terpy) in the transition state of the shuttling species when the copper-complexed ring moves from one part to the other, can be totally excluded. This feature will thus make the ligand-exchange reaction particularly difficult and, as a consequence, the motion should be considerably slower than in systems where a concerted mechanism is likely to be operative such as in "pirouetting" rotaxanes.[51]

Synthesis of the copper(I) rotaxanes 1_4^+ and 2_4^+: In the present section we will detail the synthetic procedures of a) the thread and b) the full rotaxanes.

a) Synthesis of the singly stoppered axis: The axis precursor **18** is made up of three parts: the stopper, the dpp unit, and the terpyridine. Due to the complexity of this molecule, a convergent strategy of synthesis has been adopted (Scheme 7). The stopper fragment **8** is obtained in two steps from the stopper molecule **6**[52] usually used and previously synthesized (in three steps) in our group. The first step is a Williamson reaction with commercially available 2-[2-(2-chloroethoxy)ethoxy]ethanol, under classical conditions with cesium carbonate in DMF, and leads to compound **7** (90% yield). In the second step, the alcohol function of **7** is first activated with a mesyl group and then substituted with an iodide. The mesylation reaction is done under usual conditions, using mesyl chloride, dichloromethane and triethylamine with a strict control of temperature. The crude product is then allowed to react with an excess of sodium iodide in acetone to give the halogenated stopper fragment **8** in high yield (95%).

The dpp fragment **11** is obtained in three steps from commercially available 1,10-phenanthroline. The two first steps are different substitutions of the α-positions to the nitrogen atoms of the phenanthroline, by following a very efficient organometallic method developed years ago in our group by C. O. Dietrich-Buchecker.[53] In both cases, a solution of the appropriate aryl lithium compound is first prepared, under strict control of the temperature, by reaction of *tert*-butyllithium or *neo*-butyllithium with 2-(4-bromophenoxy)-tetrahydro-2*H*-pyran and 1,4-dibromobenzene, respectively. This solution is then added to a solution of the substrate, namely 1,10-phenanthroline and mono-substituted phenanthroline **9**, respectively, hydrolyzed, and finally rearomatized with MnO_2. After treatment and purification, the corresponding substituted phenanthroline is obtained, namely monosubstituted phenanthroline **9** (67% yield) and disubstituted phenanthroline **10** (80% yield), respectively. The THP protective group on the phenol function is finally removed in the presence of hydrochloric acid in methanol to give the bifunctionalized 2,9-diaryl-1,10-phenanthroline fragment **11** (90% yield).

Halogenated stopper fragment **8** and phenolic fragment **11** are coupled by using a Williamson reaction under classical conditions, in DMF with cesium carbonate as a base, to give the bromo-ended singly stoppered fragment **12** (46% yield). The bromide is then changed into a boronic ester function thanks to a palladium-catalyzed reaction involving



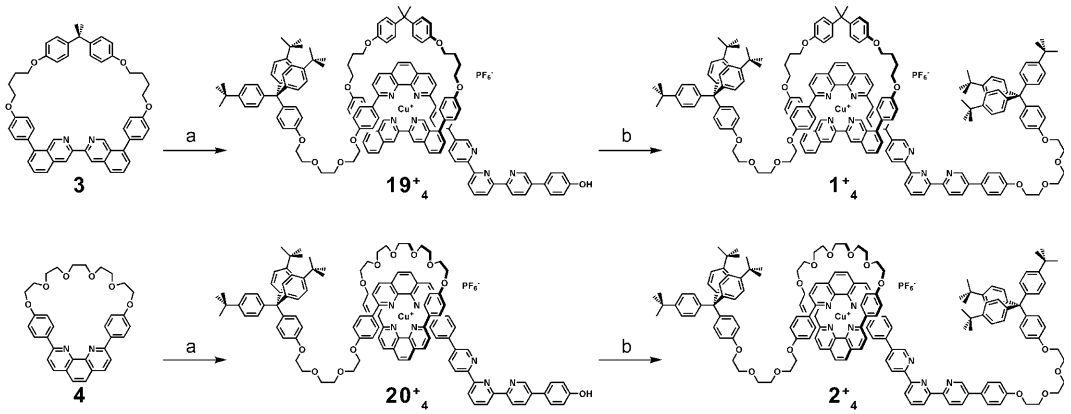
Scheme 7. Synthesis of a rigid mono-stoppered two-station axis precursor. a) Cs_2CO_3 in DMF, 90 °C, 48 h, 90 %; b) MsCl, NEt_3 in CH_2Cl_2, 0 °C, 4 h; then NaI in Me_2CO, reflux, 16 h, 95 %; c) *t*BuLi in THF, −78 °C, 30 min; then 0 °C, 2 h; then MnO_2, 25 °C, 16 h, 67 %; d) BuLi in Et_2O, 0 °C, 3 h; then MnO_2, 25 °C, 16 h, 80 %; e) HCl in MeOH, reflux, 16 h, 90 %; f) Cs_2CO_3 in DMF, 50 °C, 16 h, 46 %; g) [Pd(dppf)Cl_2], KOAc in dioxane, 80 °C, 16 h, (100 %); h) [Pd(PPh_3)$_4$], Na_2CO_3 in toluene/H_2O/EtOH, 90 °C, 2 h, 38 %; i) [Pd(PPh_3)$_4$], Na_2CO_3 in toluene/H_2O/EtOH, 90 °C, 16 h; 93 %; j) HCl in MeOH/CH_2Cl_2, reflux, 4 h, 79 %.

a diboron compound and [Pd(dppf)Cl_2] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) in dioxane. The crude product can not be purified but the boronic ester **13** seems to be obtained quantitatively.

Dibromoterpyridine **14** is synthesized following an organometallic three-step strategy from commercially available 2,6-dibromopyridine and 5-bromo-2-iodopyridine.[53] In parallel, the formation of 4-(tetrahydro-2*H*-pyran-2-yloxy)phenylboronic acid **15** is carried out in a classical way, by using butyllithium and triisopropyl borate on commercially available 2-(4-bromophenoxy)-tetrahydro-2*H*-pyran.[54] These two compounds react then in equal quantities under Suzuki coupling conditions in toluene, water, and ethanol, with [Pd(PPh_3)$_4$] as a catalyst and with Na_2CO_3 as a base. Seeing that terpyridine **14** contains two bromide functions, and since only one equivalent of boronic acid is used, a statistical mixture of nonsubstituted, mono- and disubstituted terpyridines is obtained, from which asymmetric terpyridine **16** is isolated, by chromatography, in a satisfying yield (38 %).

Finally, bromo-ended terpyridine fragment **16** and stopper-phenanthroline fragment **13**, functionalized with a boronic ester, are assembled together by a palladium-catalyzed Suzuki coupling reaction, under classical conditions. Monostoppered thread **17**, containing a dpp and a terpyridine ligand (called two-station thread), is thus obtained in a very good yield (93 %). The last step is the deprotection of the phenol function, the THP group is removed in the presence of hydrochloric acid in methanol and dichloromethane, the latter being necessary to solubilize the organic compounds. In fact, the phenol-ended two-station thread **18** is poorly soluble and therefore difficult to purify, which can also explain the non-quantitative yield (79 %) of this deprotection reaction.

b) Synthesis of the rotaxanes: The two copper(I) molecular shuttles $\mathbf{1_4}^+$ and $\mathbf{2_4}^+$ are synthesized from the same two-station thread **18** and two different chelating rings. The synthesis of these macrocycles, the recent biisoquinoline-based 39-membered ring **3**[55] and the former phenanthroline-based 30-membered ring **4**,[56] have been previously described in the literature. The formation of these two copper(I) rotaxanes follows the same threading-and-stoppering strategy and is carried out using exactly the same experimental procedure (Scheme 8). In a first step, a dichloromethane solution of macrocycle **3** or **4** and [Cu(MeCN)$_4$][PF_6] dissolved in acetonitrile are mixed to form a bright orange complex consisting of one ring and one metal center. To this solution is then added a solution of one equivalent of the thread **18** in dichloromethane. The dark red threaded complex, $\mathbf{19_4}^+$ or $\mathbf{20_4}^+$ respectively, is instantaneously formed. Under rigorously controlled stoichiometric conditions, the thermodynamic equilibrium implies that the threaded complex is the only species present in solution once the equilibrium has been reached. The solvent is then evaporated and the crude product, either $\mathbf{19_4}^+$ or $\mathbf{20_4}^+$, is then used without further purification due to the relative air- and base-sensitivity. The last stoppering reaction is a classical Williamson reaction be-



Scheme 8. Threading and stoppering reactions leading to rotaxanes $\mathbf{1_4}^+$ and $\mathbf{2_4}^+$. a) $[Cu(MeCN)_4][PF_6]$ in CH_2Cl_2/MeCN, 25 °C, 30 min; then **18** in CH_2Cl_2, 25 °C, 16 h; b) stopper **8**, Cs_2CO_3, sodium ascorbate in DMF, 50 °C, 20 h, 32 % and 31 % for $\mathbf{1}^+_4$ and $\mathbf{2}^+_4$, respectively.

tween the terminal phenol function of the threaded complex and an excess of iodo-ended stopper molecule **8**, with cesium carbonate in DMF, in the presence of sodium ascorbate to prevent oxidation of copper(I). The yield of such a reaction is generally moderate because of the sensitivity of copper(I) complexes to basic conditions. In fact, copper(I) rotaxanes $\mathbf{1_4}^+$ and $\mathbf{2_4}^+$ are obtained, after purification, with satisfactory but medium yields of 32 % and 31 %, respectively.

Since copper(I) complexes are preferably tetracoordinated, it is logical that, in rotaxanes $\mathbf{1}^+$ and $\mathbf{2}^+$, the bidentate macrocycle and the metal center are linked to the two-station thread by the means of the bidentate phenanthroline ligand. This can be proved by ^{1}H NMR spectroscopy. Concerning the example of rotaxane $\mathbf{1}^+$ (Figure 1), some protons of the copper(I) complex are highly upfield-shifted compared to their counterparts on the rotaxane's organic precursors. These protons, represented on the organic components of $\mathbf{1}^+$ in Figure 1, are all localized around the phenanthroline of the thread and around the coordination site of the macrocycle. This can be explained by the fact that they are all subjected to strong ring current effects, due to the proximity of the many aromatic fragments around the central copper(I) atom. This observation confirms that the species obtained is the four-coordinate complex, involving two bidentate units as chelates around the central metal.

Electrochemical study: Translation of the copper-complexed macrocyle between the biscoordinating dpp and tris-coordinating terpy units is perfectly reversible as described previously (Scheme 1).[36] Whereas the oxidation and reduction reactions can be considered as instantaneous in comparison with the much slower macrocycle gliding motions, the decoordination of the thermodynamically unstable complexes, and thus the translation by ligand exchange, are relatively slow. For both molecular shuttles, two different processes can be distinguished: 1) the translation motion of the ring-and-copper sub-complex in the thermodynamically unstable five-coordinate copper(I) complex and 2) the reverse motion, corresponding to the rearrangement of the unstable four-coordinate copper(II) species. The rearrangement rates were estimated by regular cyclic voltammetry. As far as the first process is concerned (movement of the ring from the terpy subunit to the dpp fragment), the electrochemical technique is not ideal and allows only to estimate a lower limit for the rate constant of the motion. The translation motion takes place within seconds or less for both systems $\mathbf{1_5}^+$ and $\mathbf{2_5}^+$, the dpbiiq-containing ring of $\mathbf{1_5}^{2+}$ being shifted from the terpy to the dpp fragment of the axle within tens

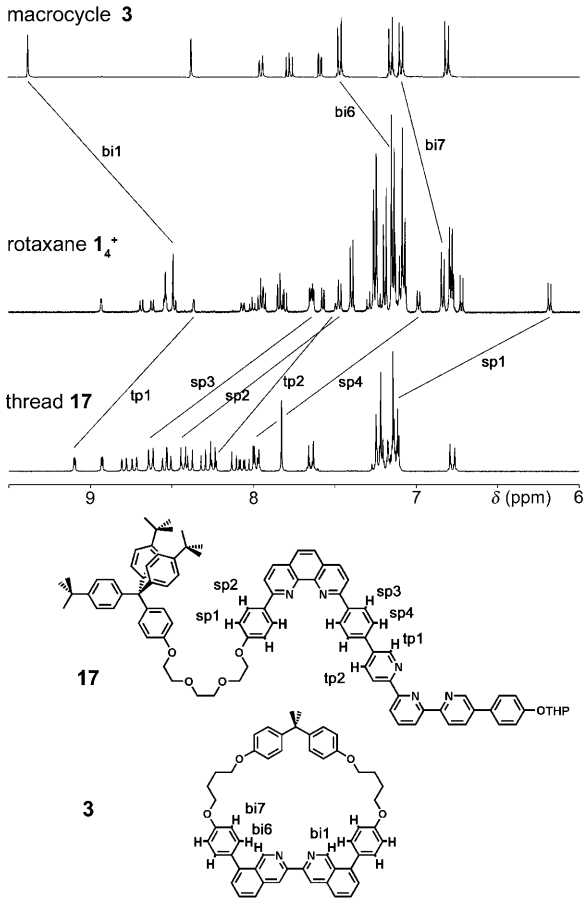


Figure 1. ^{1}H NMR spectra of $\mathbf{1_4}^+$ and its precursors **17** and **3**.

of milliseconds or even faster. As expected, the second process is much slower for both unstable species $\mathbf{1_4}^{2+}$ and $\mathbf{2_4}^{2+}$, in agreement with previous studies from our group.[34,49] By varying the potential scan rate, the speed of the translation performed by the copper-complexed ring can be estimated. Two important cyclic voltammograms (CVs) are represented in Figure 2.

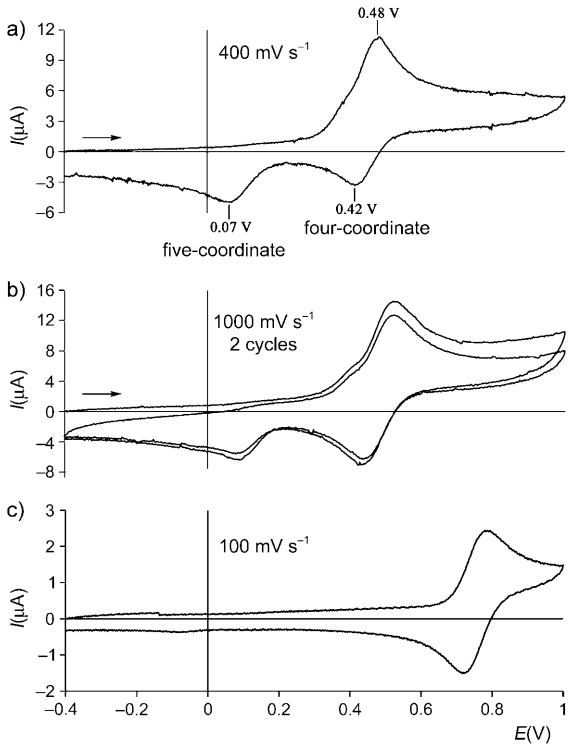


Figure 2. Cyclic voltammetry study of rotaxanes $\mathbf{1_4}^+$ and $\mathbf{2_4}^+$. a) $\mathbf{1_4}^+$: potential range: −0.4 V to 1.0 V, followed by 1.0 V to −0.4 V; b) $\mathbf{1_4}^+$: two consecutive scans; c) $\mathbf{2_4}^+$: CV of rotaxane $\mathbf{2_4}^+$ for comparison purpose. The electrochemical experiments were performed at room temperature in a 0.1 M solution of Bu_4NBF_4 in $MeCN/CH_2Cl_2$ (9:1), with a Pt working electrode, Ag wire as a pseudoreference electrode, and Pt wire as a counterelectrode.

Following the same method as in previous studies,[57] the rearrangement rate was estimated from the shape of the CV. On the CV shown in Figure 2a (400 mV s^{-1}) it appears that, after oxidation of Cu_4^+ to Cu_4^{2+} and subsequently by scanning the potential from +1.0 V to −0.4 V, almost one half of the complexes have undergone a translation to become pentacoordinated, whereas the other half stays tetracoordinated. The half reaction time corresponding to the rearrangement step, which is monomolecular (first order), can then be deduced as well as the kinetic constant. As shown by the CV in Figure 2b, whose second cycle is almost identical to the first one, and in accordance with other investigations made on previous copper-based molecular machines, the unstable five-coordinate copper(I) complex $\mathbf{1_5}^+$ rearranges much faster than the four-coordinate copper (II) complex $\mathbf{1_4}^{2+}$. As expected, ligand–exchange reactions around the singly charged metal center Cu^I are easier than around a divalent Cu^{II} center. The back and forth motion can finally be described by the Equations (3)–(6):

$$\mathbf{1_4}^+ \xrightarrow{-e^-} \mathbf{1_4}^{2+} \quad (3)$$

$$\mathbf{1_4}^{2+} \xrightarrow[\text{gliding}]{k=2\,s^{-1}} \mathbf{1_5}^{2+} \quad (4)$$

$$\mathbf{1_5}^{2+} \xrightarrow{+e^-}{}_{v}\mathbf{1_5}^{+} \quad (5)$$

$$\mathbf{1_5}^+ \xrightarrow[\text{gliding}]{k>50\,s^{-1}} \mathbf{1_4}^+ \quad (6)$$

By comparing this fast electrochemically driven shuttle with the previous system, it is clear that the biisoquinoline ligand has a pronounced kinetic effect, obviously due to its nonsterically hindering nature.

To allow a thorough comparison of the macrocycles' kinetic properties, rotaxane $\mathbf{2_4}^+$ was synthesized with the same axis and stoppers as in $\mathbf{1_4}^+$, but with the strongly shielding dpp-based macrocycle **4**, a classical building block of our research group. By contrast, after oxidation of $\mathbf{2_4}^+$ the thermodynamically unstable complex $\mathbf{2_4}^{2+}$ seems to be kinetically stable for several hours. A CV of this rotaxane in shown in Figure 2c (100 mV s^{-1}).

To confirm the coordination number of copper(II) both in thermodynamically stable (five-coordinated) and unstable (four-coordinated) states, electronic spectroscopy measurements were performed on $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$. First the dark red solution of $[\mathbf{1_4}^+][PF_6^-]$ (2×10^{-4} M) in CH_3CN/CH_2Cl_2 (9:1) was oxidized with $NO^+BF_4^-$, in a similar way to previous studies,[58] which resulted in an immediate color change to give a very pale yellow solution. The electronic spectrum shows a band maximum at $\lambda_{max}\approx640$ nm ($\varepsilon\approx150$), which is a clear indication of a five-coordinate copper(II).[59] This form of the complex was obtained quickly (mixing time), as expected from the electrochemical study. By contrast, a similar experiment done with $[\mathbf{2_4}^+][PF_6^-]$ under the same conditions gave a green solution ($\lambda_{max}\approx670$ nm, $\varepsilon\approx750$), representative of a four-coordinate copper(II) complex, as expected for the kinetically inert complex $\mathbf{2_4}^+$.

Conclusions

Using the three-dimensional template effect of copper(I), a pseudo-rotaxane containing a dpbiiq-incorporating ring and a two-coordinating station axle has been assembled. The threading step was carried out using a mono-stoppered axis and, as observed in many previous examples, it was quantitative. The second stoppering step was performed on the threaded intermediate. The yield of this key reaction was relatively mediocre (32%) and clearly represents the weak point of the whole synthetic procedure leading to the desired [2]rotaxane. An analogous [2]rotaxane was also prepared, whose chemical structure is close to that of the first compound. The only difference is that of the ring which now contains a sterically hindering chelate of the dpp family. The second stoppering reaction was not better yielding than that

of the first compound. As shown by a succinct electrochemical study, the shuttle whose ring incorporates the wide and nonsterically hindering dpbiiq chelate undergoes molecular motions which are several orders of magnitude faster than those of the dpp-based shuttle. This spectacular difference will now be exploited to construct other more sophisticated molecular machines such as muscles or presses, based on the dpbiiq-coordinating fragment.

Experimental Section

General: Some solvents were dried in the laboratory by distillation under argon, over the appropriate drying agent: tetrahydrofuran and diethyl ether over sodium and benzophenone, dichloromethane over calcium hydride, and triethylamine over potassium hydroxide. Other anhydrous solvents used (DMF and dioxane) are commercially available. Thin-layer chromatography was performed by using glass sheets coated with silica or neutral alumina. Column chromatographies were carried out on silica gel (Kieselgel 60, 0.063–0.200 mm or 0.040–0.063 mm, Merck) or alumina (Aluminiumoxid 90 standardized or acid, 0.063–0.200 mm, Merck). ^{1}H NMR spectra were acquired on either a Bruker AVANCE 300 (300 MHz) or a Bruker AVANCE 500 (500 MHz) spectrometer. The spectra were referenced to residual proton-solvent references. ^{1}H: [D$_6$]DMSO: $\delta = 2.50$ ppm, CD_2Cl_2: $\delta = 5.32$ ppm, $CDCl_3$: $\delta = 7.26$ ppm. Mass spectra were obtained by using a VG ZAB-HF (FAB) spectrometer, a VG-BIOQ triple quadrupole, positive mode, a Bruker MicroTOF spectrometer (ES-MS), or a Bruker Daltonics autoflex II TOF/TOF spectrometer with dithranol as a matrix (MALDI).

Synthesis of stopper with hydroxy-ended chain 7: 4-[Tris(4-*tert*-butylphenyl)methyl]phenol **6** (2.00 g, 3.96 mmol), cesium carbonate (2.50 g, 7.67 mmol), and 2-[2-(2-chloroethoxy)ethoxy]ethanol (1.2 mL, 1.4 g, 8.26 mmol) were mixed in dry DMF (150 mL) and stirred at 90 °C for 24 h. More 2-[2-(2-chloroethoxy)ethoxy]ethanol (1.2 mL, 1.4 g, 8.26 mmol) was added and the reaction mixture stirred for 24 h. The solvent was removed and the residue was taken up with CH_2Cl_2/H_2O. The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The combined organic phases were washed first with brine, then with distilled water. The solvent was removed and the residue purified by chromatography on silica gel by using CH_2Cl_2 as the eluent to give the title compound **7** (white solid, 2.26 g, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.22$ (d, 6H; $J = 8.7$ Hz), 7.07 (d, 8H; $J = 8.7$ Hz), 6.77 (d, 2H; $J = 9.0$ Hz), 4.11 (t, 2H; $J = 4.8$ Hz), 3.85 (t, 2H; $J = 4.8$ Hz), 3.71 (m, 6H), 3.61 (t, 2H; $J = 4.4$ Hz), 2.38 (br s, 1H), 1.30 ppm (s, 27H).

Synthesis of stopper with iodo-ended chain 8: Compound **7** (2.36 g, 3.7 mmol) was dissolved in dry CH_2Cl_2 (250 mL). The solution was cooled to about −2 °C in an ice/salt mixture, then triethylamine (8 mL) was added. The subsequent addition of methylsulfonyl chloride (0.7 g, 0.5 mL, 6.1 mmol) in CH_2Cl_2 (60 mL) was made dropwise over a period of 1 h; under an argon atmosphere. The solution was then allowed to stir at 0 °C for 3 h. Distilled water (50 mL) was then added dropwise and the mixture was allowed to warm to room temperature. The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The combined organic phases were washed with distilled water. The solvent was evaporated and the residue purified by chromatography on silica gel by using CH_2Cl_2 as the eluent to give the mesylated compound (white solid, 2.52 g, 95 %). It was then dissolved in acetone (200 mL) containing sodium iodide (10 g, 67 mmol) and heated to reflux overnight, under an argon atmosphere. A white precipitate of sodium mesylate appeared. The solvent was evaporated and the residue dissolved in CH_2Cl_2 (100 mL) and distilled water (100 mL). The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The combined organic phases were washed with distilled water. The solvent was evaporated and the residue purified by chromatography on silica gel by using CH_2Cl_2 as the eluent to give the title compound **8** (white solid, 2.50 g, 95 %). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 7.26$ (d, 6H; $J = 8.7$ Hz), 7.14 (d, 6H; $J = 8.7$ Hz), 7.13 (d, 2H; $J = 8.7$ Hz), 6.78 (d, 2H; $J = 9.0$ Hz), 4.08 (t, 2H; $J = 4.7$ Hz), 3.80 (t, 2H; $J = 4.8$ Hz), 3.73 (t, 2H; $J = 6.6$ Hz), 3.65 (m, 6H), 3.25 (t, 2H; $J = 6.6$ Hz), 1.29 ppm (s, 27H); ES-MS: m/z 769.3035 (calcd 769.3088 for $[C_{43}H_{55}IO_3+Na^+]$).

Synthesis of 2-[4-(OTHP)phenyl]phenanthroline 9: 2-(4-Lithiophenoxy)-tetrahydro-2*H*-pyran was prepared by interconversion of commercially available 2-(4-bromophenoxy)tetrahydro-2*H*-pyran with two equivalents of *t*BuLi; a solution of 2-(4-lithiophenoxy)tetrahydro-2*H*-pyran (17 mmol) in THF (50 mL) was obtained by slow addition of *t*BuLi (35 mmol) to a solution of 2-(4-bromophenoxy)-tetrahydro-2*H*-pyran (4,37 g, 17.0 mmol) in THF (25 mL) at −78 °C under argon. After being stirred for 30 min at −78 °C, this solution was slowly added to a degassed solution of 1,10-phenanthroline (3.0 g, 16.6 mmol) in THF (70 mL) maintained at −2 °C. The phenanthroline solution turned dark red instantaneously and was stirred under argon at 0 °C for 2 h. Thereafter the reaction was quenched by addition of water (30 mL) and the resulting mixture was evaporate to dryness. The 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 organic phase was then rearomatized by successive additions of batches of MnO_2 (25 g). The rearomatization was monitored by TLC (compound **9** can be recognized by a blue luminescence under UV light). The solution was then dried by addition of $MgSO_4$ and the black $MnO_2/MgSO_4$ slurry was filtered through sintered glass with celite. After evaporation of the solvent, the crude product was purified by column chromatography over silica gel, with CH_2Cl_2 as the eluent, to give the title compound **9** (pale yellow glassy solid, 3.98 g, 67 %). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 9.22$ (dd, 1H; $J = 4.2$, 1.8 Hz), 8.34 (d, 1H; $J = 8.4$ Hz), 8.32 (dd, 1H; $J = 8.1$, 1.8 Hz), 8.31 (d, 2H; $J = 9.0$ Hz), 8.12 (d, 1H; $J = 8.4$ Hz), 7.87 (d, 1H; $J = 8.7$ Hz), 7.82 (d, 1H; $J = 8.7$ Hz), 7.69 (dd, 1H; $J = 8.1$, 4.2 Hz), 7.26 (d, 2H; $J = 9.0$ Hz), 5.57 (t, 1H; $J = 3.3$ Hz), 3.96 (m, 1H), 3.67 (m, 1H), 2.07 (m, 2H), 1.94 (m, 2H), 1.74 ppm (m, 2H); ES-MS: m/z 357.1631 (calcd 357.1603 for $[C_{23}H_{20}N_2O_2+H^+]$).

Synthesis of 2-[4-(OTHP)phenyl]-9-(4-bromophenyl)phenanthroline 10: A 6.9 mL portion (11 mmol) of a 1.6 M *n*BuLi solution in hexane was rapidly added to a degassed solution of *p*-dibromobenzene (2.9 g, 12 mmol) in distilled diethyl ether (20 mL) at 0 °C and allowed to warm at room temperature. The *p*-bromophenyllithium solution thus obtained was slowly added, by the means of a double-ended needle, to a degassed suspension of phenanthroline compound **9** (2.14 g, 6 mmol) in distilled diethyl ether (70 mL) kept at 0 °C. After the resulting dark red solution was stirred for 3 h under argon at 0 °C, it was hydrolyzed with water (25 mL) at 0 °C. The ether layer was decanted and the aqueous layer extracted three times with CH_2Cl_2. The combined organic layers were thereafter rearomatized by addition of MnO_2 (15 g, 170 mmol) under effective stirring overnight. The rearomatization was monitored by TLC (compound **10** can be recognized by a blue luminescence under UV light). After the mixture was dried over Na_2SO_4, the black slurry could easily be filtered on a sintered glass with celite, washed with CH_2Cl_2, and the filtrate evaporated to dryness. The crude product was purified by column chromatography over silica gel, with CH_2Cl_2 as the eluent, to give the title compound **10** (pale yellow glassy solid, 2.44 g, 80 %). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 8.38$ (d, 2H; $J = 9.0$ Hz), 8.34 (d, 2H; $J = 9.0$ Hz), 8.32 (d, 1H; $J = 8.4$ Hz), 8.29 (d, 1H; $J = 8.4$ Hz), 8.11 (d, 1H; $J = 8.4$ Hz), 8.10 (d, 1H; $J = 8.4$ Hz), 7.80 (d, 1H; $J = 8.7$ Hz), 7.77 (d, 1H; $J = 8.7$ Hz), 7.74 (d, 2H; $J = 8.7$ Hz), 7.25 (d, 2H; $J = 8.7$ Hz), 5.55 (t, 1H; $J = 3.2$ Hz), 3.95 (m, 1H), 3.65 (m, 1H), 2.03 (m, 2H), 1.92 (m, 2H), 1.69 ppm (m, 2H); ES-MS: m/z 511.0992 (calcd 511.1021 for $[C_{29}H_{23}BrN_2O_2+H^+]$).

Synthesis of 2-(4-hydroxyphenyl)-9-(4-bromophenyl)phenanthroline 11: Phenanthroline compound **10** (2.44 g, 4,77 mmol) was dissolved in methanol (200 mL) in the presence of a catalytic amount of a 37 % solution of HCl (10 drops). The mixture was heated to reflux overnight (ca. 18 h). The solvent was removed and the product was dispersed in distilled water (100 mL) and CH_2Cl_2 (200 mL). The aqueous layer was neutralized with a 1 M solution of NaOH and the two layers were separated (a precipitate was in suspension in CH_2Cl_2). Pentane (200 mL) was then added to the organic phase and the precipitate was filtered to give the title product

11. This product was not soluble enough to be more purified and was therefore used without further purification (yellow solid, 1.84 g, 90%). ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25°C, TMS): δ=8.55 (d, 1H; J=8.7 Hz), 8.53 (d, 1H; J=9.3 Hz), 8.41 (d, 2H; J=8.4 Hz), 8.34 (d, 1H; J=8.7 Hz), 8.30 (d, 2H; J=8.4 Hz), 8.27 (d, 1H; J=9.3 Hz), 7.96 (s, 2H), 7.81 (d, 2H; J=8.4 Hz), 7.00 ppm (d, 2H; J=8.7 Hz); ES-MS: m/z 429.0344 (calculated 429.0423 for [$C_{24}H_{15}BrN_2O$+H$^+$]).

Synthesis of mono-stoppered and bromo-ended phenanthroline fragment 12: Phenanthroline compound **11** (550 mg, 1.29 mmol), cesium carbonate (840 mg, 2.58 mmol), and stopper with iodo-ended chain **8** (1.93 g, 2.58 mmol) were mixed in dry DMF (150 mL) and stirred at 50°C for 5 h. More stopper with iodo-ended chain **8** (960 mg, 0.65 mmol) was added and the reaction mixture stirred at 50°C overnight. The solvent was removed and the residue was taken up with CH_2Cl_2/H_2O. The organic phase was separated and the aqueous phase extracted twice with CH_2Cl_2. The solvent was removed and the residue purified by chromatography on silica gel by using CH_2Cl_2/MeOH (0.5%) as the eluent to give the title compound **12** (yellowish glassy solid, 620 mg, 46%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): δ=8.39 (d, 2H; J=8.7 Hz), 8.35 (d, 1H; J=8.1 Hz), 8.34 (d, 2H; J=8.7 Hz), 8.29 (d, 1H; J=8.4 Hz), 8.13 (d, 1H; J=8.4 Hz), 8.10 (d, 1H; J=8.4 Hz), 7.82 (d, 1H; J=8.7 Hz), 7.79 (d, 1H; J=8.7 Hz), 7.74 (d, 2H; J=8.7 Hz), 7.25 (d, 6H; J=8.8 Hz), 7.14 (d, 6H; J=8.8 Hz), 7.13 (d, 4H; J=9.0 Hz), 6.78 (d, 2H; J=9.0 Hz), 4.24 (dd, 2H; J=4.6, 6.0 Hz), 4.09 (dd, 2H; J=4.6, 6.0 Hz), 3.90 (dd, 2H; J=3.3, 4.8 Hz), 3.82 (dd, 2H; J=3.4, 4.9 Hz), 3.73 (s, 4H), 1.28 ppm (s, 27H); MALDI-MS: m/z 1047.375 (calcd 1047.450 for [$C_{67}H_{69}BrN_2O_4$+H$^+$]).

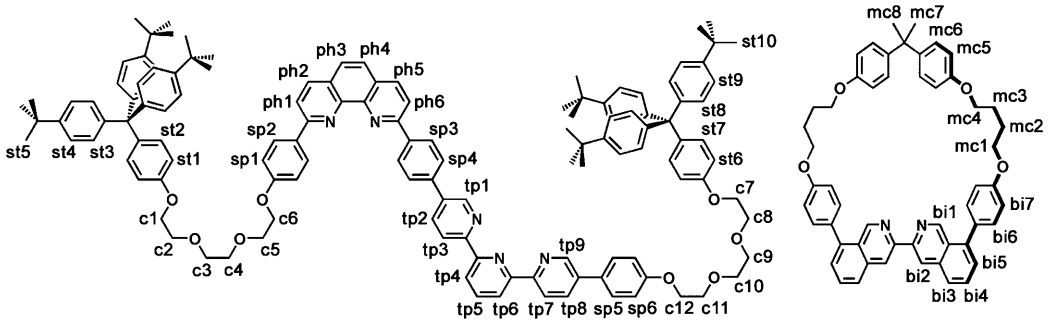
Synthesis of mono-stoppered and boronic ester-ended phenanthroline fragment 13: Brominated phenanthroline fragment **12** (660 mg, 0.63 mmol), bis(neopentyl glycolato)diboron (157 mg, 0.70 mmol), potassium acetate (186 mg, 1.90 mmol), and [Pd(dppf)Cl$_2$] (16 mg, 0.02 mmol) were dissolved in dry dioxane. The mixture was stirred under argon at 80°C overnight. After the solution was cooled down at room temperature, water (50 mL) and CH_2Cl_2 (100 mL) were added. The organic layer was then decanted and the aqueous layer was extracted two times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and evaporated. The title product obtained was used without further purification (dark brown solid, 681 mg, 100%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): δ=8.43 (d, 2H; J=8.4 Hz), 8.40 (d, 2H; J=8.9 Hz), 8.34 (d, 1H; J=8.4 Hz), 8.29 (d, 1H; J=8.5 Hz), 8.19 (d, 1H; J=8.5 Hz), 8.10 (d, 1H; J=8.5 Hz), 8.00 (d, 2H; J=8.4 Hz), 7.80 (s, 2H), 7.26 (d, 2H; J=8.8 Hz), 7.24 (d, 6H; J=8.8 Hz), 7.14 (d, 6H; J=8.8 Hz), 7.12 (d, 2H; J=9.0 Hz), 4.24 (m, 2H), 4.09 (m, 2H), 3.89 (m, 2H), 3.82 (m, 2H), 3.82 (s, 4H), 3.74 (s, 4H), 1.28 (s, 27H), 1.05 ppm (s, 6H).

Synthesis of 5-bromo-5″-[4-(OTHP)phenyl]-2,2′:6′-2″-terpyridine 16: 5,5″-Dibromo-2,2′:6′-2″-terpyridine **14** (800 mg, 2.05 mmol), boronic acid **15** (455 mg, 2.05 mmol), and Na_2CO_3 (2.16 g, 20.4 mmol) were dissolved in toluene (120 mL), water (40 mL), and ethanol (20 mL). The solution was degassed three times, [Pd(PPh$_3$)$_4$] (120 mg, 0.1 mmol) was added under an argon stream and the mixture was degassed three times again. The solution was heated at 90°C for 2 h. The organic layer was then decanted and the aqueous layer was extracted two times with CH_2Cl_2. The combined organic layer was washed with water and evaporated. The crude product was purified by chromatography on aluminum oxide by using pentane/ethyl acetate (2%) as the eluent to give the title compound **16** (white solid, 386 mg, 38%). ^{1}H NMR (300 MHz, CD_2Cl_2, 25°C, TMS): δ=8.91 (dd, 1H; J=2.4, 0.8 Hz), 8.75 (dd, 1H; J=2.4, 0.7 Hz), 8.64 (dd, 1H; J=8.3, 0.8 Hz), 8.57 (dd, 1H; J=8.5, 0.7 Hz), 8.50 (dd, 1H; J=7.9, 1.1 Hz), 8.42 (dd, 1H; J=7.9, 1.1 Hz), 8.04 (dd, 1H; J=8.4, 2.4 Hz), 8.01 (dd, 1H; J=8.6, 2.4 Hz), 7.97 (t, 1H; J=7.9 Hz), 7.63 (d, 2H; J=8.9 Hz), 7.17 (d, 2H; J=8.9 Hz), 5.48 (t, 1H; J=3.4 Hz), 3.90 (m, 1H), 3.61 (m, 1H), 2.00 (m, 2H), 1.87 (m, 2H), 1.67 ppm (m, 2H); ES-MS: m/z 488.0992 (calcd 488.0968 for [$C_{26}H_{22}BrN_3O_2$+H$^+$]).

Synthesis of OTHP-ended two stations thread 17: Boronic ester phenanthroline fragment **13** (340 mg, 0.315 mmol), brominated terpyridine **16** (130 mg, 0.266 mmol), and Na_2CO_3 (282 mg, 2.66 mmol) were dissolved in toluene (45 mL), water (15 mL), and ethanol (8 mL). The solution was degassed three times, [Pd(PPh$_3$)$_4$] (16 mg, 0.013 mmol) was added under an argon stream and the mixture was degassed three times again. The solution was heated at 90°C overnight (about 18 h). The organic layer was then decanted and the aqueous layer was extracted three times with CH_2Cl_2. The combine organic layer was washed with distilled water and evaporated. The crude product was purified by chromatography on aluminium oxide by using CH_2Cl_2 as the eluent to give the title compound **17** (colorless glassy solid, 340 mg, 93%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ=9.10 (dd, 1H; J=2.3, 0.7 Hz, tp1), 8.93 (dd, 1H; J=2.4, 0.8 Hz, tp9), 8.79 (dd, 1H; J=8.3, 0.7 Hz, tp3), 8.73 (dd, 1H; J=8.3, 0.7 Hz, tp7), 8.63 (d, 2H; J=8.6 Hz, sp3), 8.55 (dd, 1H; J=7.9, 1.1 Hz, tp6), 8.51 (dd, 1H; J=7.9, 1.0 Hz, tp4), 8.43 (d, 2H; J=8.9 Hz, sp2), 8.38 (d, 1H; J=8.5 Hz, ph5), 8.31 (d, 1H; J=8.5 Hz, ph2), 8.25 (d, 1H; J=8.4 Hz, ph6), 8.24 (dd, 1H; J=8.4, 2.5 Hz, tp2), 8.12 (d, 1H; J=8.5 Hz, ph1), 8.07 (dd, 1H; J=8.3, 2.4 Hz, tp8), 8.00 (t, 1H; J=7.9 Hz, tp5), 7.98 (d, 2H; J=8.5 Hz, sp4), 7.83 (s, 2H; ph3–4), 7.65 (d, 2H; J=8.9 Hz, sp5), 7.23 (d, 6H; J=8.7 Hz, st4), 7.19 (d, 2H; J=8.9 Hz, sp6), 7.16 (d, 2H; J=8.8 Hz, sp1), 7.13 (d, 6H; J=8.8 Hz, st3), 7.12 (d, 2H; J=8.9 Hz, st2), 6.78 (d, 2H; J=9.0 Hz, st1), 5.49 (t, 1H; J=3.1 Hz, pr1), 4.25 (dd, 2H; J=6.0, 4.5 Hz, c6), 4.09 (dd, 2H; J=6.1, 4.6 Hz, c1), 3.91 (m, 1H; pr2), 3.90 (dd, 2H; J=4.6, 3.4 Hz, c5), 3.83 (dd, 2H; J=4.9, 3.4 Hz, c2), 3.73 (s, 4H; c3–4), 3.65 (m, 1H; pr3), 2.01 (m, 2H; pr5), 1.89 (m, 2H; pr6), 1.66 (m, 2H; pr4), 1.27 ppm (s, 27H; st5); ES-MS: m/z 1374.7122 (calcd 1374.7048 for [$C_{93}H_{91}N_5O_6$+H$^+$]).

Synthesis of OH-ended two-station thread 18: OTHP-ended two stations thread **17** (340 mg, 0.247 mmol) was dissolved in CH_2Cl_2 (50 mL) and methanol (50 mL) in the presence of a catalytic amount of a 37% solution of HCl (3 drops). The mixture was heated to reflux for 4 h. The solvent was removed and the product was dispersed in distilled water (100 mL) and CH_2Cl_2 (200 mL). The aqueous layer was neutralized with an aqueous solution of NH_3 (37%). The organic layer was then decanted and the aqueous layer was extracted four times with more CH_2Cl_2. The combined organic phases were washed with distilled water. The solvent was evaporated and the crude product purified by chromatography on aluminum oxide by using CH_2Cl_2/MeOH (1%) as the eluent to give the title compound **18** (yellow glassy solid, 251 mg, 79%). ES-MS: m/z 1290.6537 (calcd 1290.6467 for [$C_{88}H_{83}N_5O_5$+H$^+$]).

Synthesis of two-station copper-based [2]rotaxane with mb-39 macrocycle 1_4^+ (via 19_4^+): A solution of [Cu(MeCN)$_4$][PF$_6$] (27.5 mg, 0.074 mmol) in degassed MeCN (10 mL) was transferred by a cannula to a stirred solution of macrocycle mb-39 **3** (54.3 mg, 0.070 mmol) in CH_2Cl_2 (5 mL) under argon, and the resulting orange solution was stirred at room temperature for 30 min. This mixture was then transferred to a degassed solution of OH-ended two-station thread **18** (90.1 mg, 0.070 mmol) in CH_2Cl_2 (10 mL) by a cannula, resulting in the immediate formation of a brown-red solution, which was stirred under argon at room temperature overnight. Solvent was evaporated to give the pseudo-rotaxane [$\mathbf{19_4}^+$]-[PF_6^-] (brown-red solid). It was then dissolved in dry and degassed DMF (8 mL) with Cs_2CO_3 (90 mg, 0.276 mmol), stopper with iodo-ended chain **8** (155 mg, 0.205 mmol), and sodium ascorbate (3 mg, 0.015 mmol). This mixture was stirred under argon at 50°C for 20 h. DMF was evaporated and the resulting crude product taken up in CH_2Cl_2 and washed with water. After evaporation of the solvent and three successive column chromatographies on alumina (CH_2Cl_2 containing 1% MeOH and 1% MeCN) the title product [$\mathbf{1_4}^+$][PF_6^-] was obtained (brown-red solid, 65 mg, 32%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25°C, TMS): δ=8.93 (d, 1H; J=2.0 Hz, tp9), 8.69 (d, 1H; J=8.3 Hz, tp3), 8.62 (d, 1H; J=8.0 Hz, tp7), 8.54 (d, 1H; J=7.0 Hz, tp6), 8.54 (s, 2H; bi2), 8.49 (s, 2H; bi1), 8.48 (d, 1H; J=8.7 Hz, tp4), 8.37 (d, 1H; J=2.0 Hz, tp1), 8.07 (dd, 1H; J=8.3, 2.3 Hz, tp8), 8.01 (t, 1H; J=7.9 Hz, tp5), 7.96 (d, 1H; J=8.3 Hz, ph2), 7.95 (d, 2H; J=7.8 Hz, bi3), 7.93 (d, 1H; J=8.1 Hz, ph5), 7.84 (d, 1H; J=8.1 Hz, ph6), 7.83 (t, 2H; J=8.2 Hz, bi4), 7.80 (d, 1H; J=8.4 Hz, ph1), 7.65 (d, 2H; J=8.7 Hz, sp5), 7.64 (d, 2H; J=8.2 Hz, sp3), 7.57 (dd, 2H; J=6.3, 0.7 Hz, bi5), 7.49 (dd, 1H; J=7.8, 2.2 Hz, tp2), 7.47 (d, 2H; J=8.6 Hz, sp2), 7.40 (d, 4H; J=8.9 Hz, mc6), 7.30 (d, 1H; J=8.9 Hz, ph3), 7.25 (d, 6H; J=8.8 Hz, st9), 7.23 (d, 1H; J=8.4 Hz, ph4), 7.19 (d, 6H; J=8.8 Hz, st4), 7.15 (d, 6H; J=8.3 Hz, st8), 7.14 (d, 4H; J=9.0 Hz, bi6), 7.13 (d, 2H; J=9.0 Hz, st7), 7.10 (d, 2H; J=8.7 Hz, st2), 7.08 (d, 6H; J=8.8 Hz, st3), 7.07 (d, 2H; J=8.8 Hz, sp6), 6.99 (d, 2H; J=8.2 Hz, sp4), 6.84 (d, 4H; J=8.7 Hz, bi7), 6.79 (d, 4H; J=8.8 Hz, mc5), 6.78 (d, 2H; J=9.0 Hz, st6), 6.72 (d, 2H; J=9.0 Hz, st1), 6.19 (d, 2H; J=8.7 Hz,



sp1), 4.19 (t, 2H; J=4.7 Hz, c12), 4.14 (t, 4H; J=6.0 Hz, mc1), 4.10 (t, 2H; J=4.7 Hz, c1), 4.08 (t, 2H; J=4.7 Hz, c7), 3.87 (t, 2H; J=4.7 Hz, c11), 3.83 (t, 2H; J=4.8 Hz, c2), 3.81 (t, 2H; J=4.8 Hz, c8), 3.79 (t, 4H; J=6.1 Hz, mc4), 3.72 (s, 8H; c3-c4-c9-c10), 3.65 (t, 2H; J=4.8 Hz, c5), 3.58 (t, 2H; J=4.8 Hz, c6), 1.89–1.81 (m, 8H; mc2-mc3), 1.76 (s, 6H; mc7-mc8), 1.29 (s, 27H; st10), 1.24 ppm (s, 27H; st5); MALDI-MS: m/z: 2749.004 (calcd 2749.344 for $[C_{184}H_{185}CuN_7O_{12}]$).

Synthesis of two-station copper-based [2]rotaxane with m-30 macrocycle 2_4^+ (via 20_4^+): A solution of $[Cu(MeCN)_4][PF_6]$ (18.2 mg, 0.049 mmol) in degassed MeCN (10 mL) was transferred by a cannula to a stirred solution of macrocycle m-30 **4** (26.3 mg, 0.046 mmol) in CH_2Cl_2 (10 mL) under argon, and the resulting orange solution was stirred at room temperature for 15 min. This mixture was then transferred to a degassed solution of OH-ended two-station thread **18** (60 mg, 0.046 mmol) in CH_2Cl_2 (10 mL) by a cannula, resulting in the immediate formation of a brown-red solution, which was stirred under argon at room temperature overnight. Solvent was evaporated to give a brown-red solid. This solid was dissolved in dry and degassed DMF (10 mL) with Cs_2CO_3 (60 mg, 184 mmol), stopper with iodo-ended chain **8** (103 mg, 138 mmol), and sodium ascorbate (2 mg, 0.010 mmol). This mixture was stirred under argon at 55 °C for 20 h. DMF was evaporated and the resulting crude product taken up in CH_2Cl_2 and washed with water. After evaporation of the solvent and four successive column chromatographies on alumina (CH_2Cl_2 containing 1% MeOH and 1% MeCN) the title product $[\mathbf{2_4}^+][PF_6^-]$ was obtained (brown-red solid, 39 mg, 31%). ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C, TMS): δ=8.93 (d, 1H; J=2.0 Hz, tp9), 8.71 (d, 1H; J=8.4 Hz, ph5), 8.71 (d, 1H; J=8.5 Hz, tp3), 8.69 (d, 1H; J=8.5 Hz, tp7), 8.66 (d, 1H; J=8.4 Hz, ph2), 8.54 (d, 1H; J=7.3 Hz, tp6), 8.53 (b, 1H; tp1), 8.50 (d, 1H; J=7.2 Hz, tp4), 8.44 (d, 2H; J=8.3 Hz, m2), 8.30 (d, 1H; J=8.9 Hz, ph4), 8.27 (d, 1H; J=8.9 Hz, ph3), 8.06 (dd, 1H; J=8.3, 2.4 Hz, tp8), 8.01 (t, 1H; J=7.8 Hz, tp5), 7.98 (d, 1H; J=8.4 Hz, ph6), 7.96 (s, 2H; m1), 7.91 (d, 1H; J=8.4 Hz, ph1), 7.83 (d, 2H; J=8.3 Hz, m3), 7.71 (dd, 1H; J=8.2, 2.3 Hz, tp2), 7.68 (d, 2H; J=8.3 Hz, sp3), 7.65 (d, 2H; J=8.7 Hz, sp5), 7.50 (d, 2H; J=8.7 Hz, sp2), 7.33 (d, 4H; J=8.7 Hz, m4), 7.25 (d, 6H; J=8.8 Hz, st9), 7.21 (d, 6H; J=8.8 Hz, st4), 7.15 (d, 6H; J=8.8 Hz, st8), 7.14 (d, 2H; J=9.0 Hz, st7), 7.14 (d, 2H; J=9.0 Hz, st2), 7.11 (d, 6H; J=8.8 Hz, st3), 7.07 (d, 2H; J=8.8 Hz, sp6), 6.92 (d, 2H; J=8.2 Hz, sp4), 6.79 (d, 2H; J=9.0 Hz, st6), 6.78 (d, 2H; J=9.0 Hz, st1), 6.11 (d, 2H; J=8.8 Hz, sp1), 6.02 (d, 4H; J=8.7 Hz, m5), 4.19 (t, 2H; J=4.7 Hz, c12), 4.11 (t, 2H; J=4.7 Hz, c1), 4.10 (t, 2H; J=4.7 Hz, c7), 3.87 (t, 2H; J=4.7 Hz, c11), 3.84 (t, 2H; J=4.7 Hz, c2), 3.82 (t, 2H; J=4.7 Hz, c8), 3.73 (t, 4H; J=4.8 Hz, m9), 3.72 (bs, 12H; c3-c4-c9-c10 m10), 3.69 (t, 2H; J=4.6 Hz, c6), 3.63 (t, 2H; J=4.9 Hz, c5), 3.62 (t, 4H; J=5.5 Hz, m8), 3.59 (t, 4H; J=5.3 Hz, m6), 3.51 (t, 4H; J=5.3 Hz, m7), 1.29 (s, 27H; st10), 1.25 ppm (s, 27H; st5); MALDI-MS: m/z: 2539.181 (calcd 2539.222 for $[C_{165}H_{171}CuN_7O_{14}]$).

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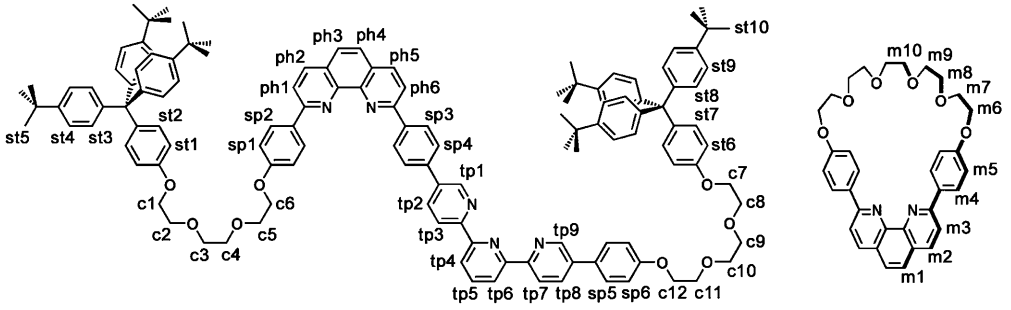

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