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Passing Two Strings through the Same Ring Using an Octahedral Metal Center as Template: A New Synthesis of [3]Rotaxanes

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Abstract: Octahedral transition metal centers such as Fe(II), Co(II), and Co(III) have been used as templates in the construction of [3]pseudorotaxanes and [3]rotaxanes from various acyclic and macrocyclic fragments. The species obtained consist of a ring threaded by two string-like compounds. Such systems are relatively uncommon in the [3]rotaxane family, the most usual form being made up of a single axis threaded through two rings. The key structural feature of the present systems is the coordinating unit incorporated in the various organic fragments and used in conjunction with the metal to gather and thread the two filaments through the ring. This bidentate chelate is derived from 8,8'-diphenyl-3,3'-bi-isoquinoline, a very rare example of an endotopic but nonsterically hindering ligand. The stoppered [3]rotaxanes were obtained by using an open-chain fragment bearing azide groups as end functions, followed by click chemistry using a propargyl ether attached to a very bulky group. A particularly attractive X-ray structure was obtained for a cobalt(III)-complexed [3]pseudorotaxane consisting of a 41-membered ring and two crescent-shaped threaded components. The Fe(II) and Co(III) complexes were characterized by ¹H NMR and ES-MS. By taking advantage of the markedly different kinetic properties of the two oxidation states, Co(II) and Co(III), it was possible to proceed to fast coordination or decoordination reactions (for the divalent state) or, when needed, to “freeze” the complexes due to the kinetic inertness of the trivalent state and to study them by ¹H NMR. Finally, demetalation of the two stoppered compounds prepared was performed. This demetalation reaction was fast for the Co(II)-complexed [3]rotaxane, whereas decomplexation of the Fe(II) equivalent required harsh conditions which were not compatible with the stability of the metal-free rotaxane. Interestingly, the thermal stability of the free [3]rotaxane toward unthreading and formation of its constitutive elements was only limited. ¹H NMR measurements showed that the half-life of the rotaxane is about one week at room temperature in dichloromethane. A variable-temperature study revealed that the unthreading reaction leading to dissociation of the [3]rotaxane has a remarkably high entropy of activation, in agreement with the intuitive view that the unthreading process involves a highly ordered transition state.

1. Introduction

In the course of the last 20 years, the field of catenanes and rotaxanes has experienced a spectacular development. These compounds continue to attract much attention either as synthetic challenges¹ or in relation to their properties as functional

compounds and components of future “intelligent” materials.² As an extension of catenanes and rotaxanes, the field of controlled dynamic systems, often referred to as “molecular machines”, seems to be particularly important conceptually and from a more applied viewpoint. Practical applications may be discovered for these molecules or molecular assemblies as well as for non-interlocking systems,³ for example in the area of information storage and processing⁴ or in the elaboration of

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photomechanical devices.⁵ The templated synthesis of [2]catenanes and [2]rotaxanes (consisting of two components) has been remarkably successful. The most efficient strategies are based on transition metals⁶ or on organic templates.⁷ Several examples of topologically more complex molecules have also been reported, some of them being prepared in an efficient way from several precursor fragments.⁸ Among the most spectacular examples of topologically complex synthetic molecules, one can think of molecular knots, such as the trefoil knot⁹ or its derivatives,¹⁰ as well as the recently prepared Borromean rings.¹¹ Even if rotaxanes are not, strictly speaking, topologically interesting compounds due to the planarity of their molecular graphs, rotaxanes have often been considered as topologically nontrivial due to their analogy to catenanes,¹² at least in terms of synthetic approaches. This is the case for [n]rotaxanes ($n > 2$) which also represent a subclass of challenging compounds. [n]Rotaxanes generally consist of $n-1$ rings threaded on the same thread,¹³ as in the case of cyclodextrin-based rotaxanes.¹⁴ Most of the systems with more than one thread passing through the ring(s) are restricted to nonstoppered inclusion complexes,¹⁵ whereas very few real [3]rotaxanes have been reported.¹⁶

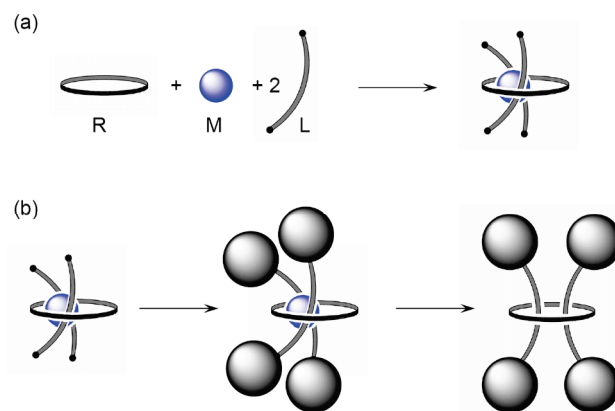


Figure 1. (a) Principle of the double-threading reaction driven by coordination of the ligands to an octahedral metal center; (b) stoppering reaction leads to a rotaxane–metal complex which, after demetalation, yields the metal-free [3] rotaxane. The ring, R, and each string-like fragment, L, contain a bidentate chelate.

In the present report, we describe the use of octahedral transition metal centers such as Fe(II) and Co(II) or Co(III) as templates. These metals allow for high-yield synthesis of two-string [3]pseudorotaxanes or [3]rotaxanes. The metal is used in a novel “gathering and threading” strategy, leading to a doubly threaded structure, which represents a generalization of the previously reported principle based on copper(I) and leading to a singly threaded complex consisting of one ring and one “string”.¹⁷ A preliminary account of this new approach has recently been published in which the template was Fe(II).¹⁸ With this metal, demetalation seemed to be highly problematic under classical conditions. This is one of the reasons why we undertook similar studies with cobalt as template since cobalt(III) is inert and will thus allow the synthesis of the rotaxanes even under relatively aggressive conditions, whereas the corresponding cobalt(II) complexes should be labile and thus lead readily to the free ligands. In the present report, the free rotaxane is thus described as well as some of its properties. In particular, the unthreading reaction has been investigated. Whereas the free rotaxane is stable at low temperature, unthreading is slow but effective at room temperature.

The principle of the presently reported double-threading process is represented in Figure 1 a. This reaction leads to an entanglement consisting of three components: a ring and two acyclic fragments. Stoppering and removing the metal template affords the free [3]rotaxane, as depicted in Figure 1 b.

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It is noteworthy that the double-threading reaction is expected to be quantitative, provided the reaction stoichiometry is respected accurately. Mixing one equivalent of ring (R), one equivalent of metal center (M), and two equivalents of acyclic ligand (L) will lead to the threaded species if the complexation reaction is done under thermodynamic control. With this 1:1:2 stoichiometry for R, M, and L, the doubly threaded complex depicted in Figure 1 represents the only situation in which neither ligands nor metal centers are "frustrated". In other words, any other state will involve uncoordinated ligands and/or coordinatively unsaturated metal centers. This principle has been applied very long ago by our group for making singly threaded species from a 1,10-phenanthroline-containing ring, copper(I), and another phenanthroline-type ligand.^{6,17} These [2]pseudorotaxanes were the precursors to various catenanes and rotaxanes. The coordination chemistry-driven formation of threaded species turned out to be virtually as efficient for making doubly threaded species as it used to be for generating copper(I)-complexed singly threaded compounds, as shown by the present study.

2. Results and Discussion

In order to prepare [3]pseudorotaxanes similar to those represented in Figure 1a and the corresponding stoppered compounds as well as the metal-free rotaxanes (Figure 1b), several steps have to be considered: (i) The double-threading reaction (Figure 1a), (ii) the stoppering reaction, and (iii) the demetalation reaction, consisting in removing the metal template so as to generate the free compound. In principle, any inert octahedral metal center will be adapted to the two first steps, provided the stoppering reaction conditions are compatible with the threaded complex. The last step is potentially more delicate, and its success will largely depend on the lability of the final metal-complexed [3]rotaxane. In this respect, the use of cobalt as a template seemed to be complementary to that of iron(II). Fe(II) complexes are normally reasonably labile although the 3d⁶ electronic configuration is expected to stabilize the corresponding complexes. As will be discussed later, we were surprised by the high kinetic inertness of the iron complexes. In order to demetalate the complexed rotaxanes more readily without decreasing the kinetic inertness of the precursors, it seemed to be judicious to use cobalt. As already demonstrated by other groups,^{19,32} cobalt(III) is sufficiently inert to stabilize precursors in the course of a template reaction. By contrast, after reduction to the divalent state, a labile complex is obtained. The strategy is thus straightforward: the formation of the doubly threaded species will be performed using the kinetically labile cobalt(II) center; subsequently, in order to "freeze" the complex in the desired geometry and with the appropriate coordination sphere, the threaded precursor will be oxidized to yield a Co(III) complex able to resist the reaction conditions of the stoppering step. The [3]rotaxane will be prepared on the Co(III) precursor complex. After reduction of the cobalt(III)-complexed [3]ro-

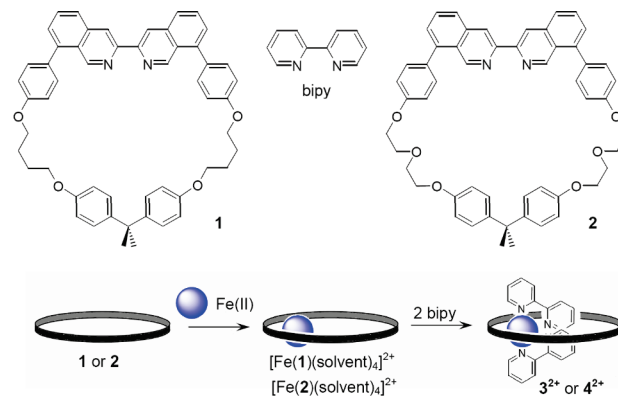


Figure 2. The macrocyclic ligands **1** and **2** used for the threading reactions and schematic representation of their heteroleptic complexes with iron(II) and 2,2'-bipyridyl (bipy): $3^{2+} = [\text{Fe}(\mathbf{1})(\text{bipy})_2]^{2+}$, $4^{2+} = [\text{Fe}(\mathbf{2})(\text{bipy})_2]^{2+}$.

taxane, the labile Co(II) species will be readily decomposed, thus producing the free rotaxane.

In the present report we will first describe the Fe(II)-complexed systems, including dynamic properties as studied by ¹H NMR spectroscopy, electrochemical, and spectrochemical parameters. The second section will be devoted to cobalt chemistry (Co(II) and Co(III)) and to the use of this metal for making rotaxanes. The interplay between the oxidation state and the kinetic properties of the complexes obtained will be discussed. In the third part, formation of the metal-free rotaxane from its Co(II) precursor will be discussed as well as the kinetic stability of the free rotaxane. In particular the unthreading reaction of the two string-like fragments from the ring will be considered, and its kinetic parameters will be given and discussed.

2.1. Iron(II) Heteroleptic Complexes of the Macrocyclic Ligands with Two bipy Units As Ancillary Ligands. A new family of endotopic or endocyclic chelates based on 8,8'-diphenyl-3,3'-bi-isoquinoline (dpbiiq) was reported recently by our group.^{20,21} Two of them are represented in Figure 2: The macrocycles **1** (39-membered) and **2** (41-membered).²¹ These macrocycles combine a large size with a nonsterically hindering nature since the two aromatic groups introduced at the 8 and 8' positions of the 3,3'-bi-isoquinoline backbone are sufficiently remote from the coordination site to sterically allow introducing a metal ion as well as other ligands inside the macrocyclic cavity.

As a preliminary study, the interaction between the macrocyclic ligands and iron(II) was investigated (see Figure 2). In a typical experiment, a dpbiiq-based macrocycle (1 equiv of **1** or **2**, dissolved in CH₂Cl₂) was added to an acetonitrile solution containing Fe(BF₄)₂·6H₂O (1 equiv). Immediate coloring of the reaction mixture to yellow-red was observed. This color originates from metal-to-ligand charge transfer (MLCT) between iron(II) and dpbiiq (λ_{max} at ~460 nm). Noteworthy, the coordination to the metal ion can be also monitored by quenching of the strong fluorescence characteristic of the free dpbiiq ligands under UV-light irradiation.²²

To characterize these complexes, a ¹H NMR study was undertaken. The experiments were carried out in a mixture of

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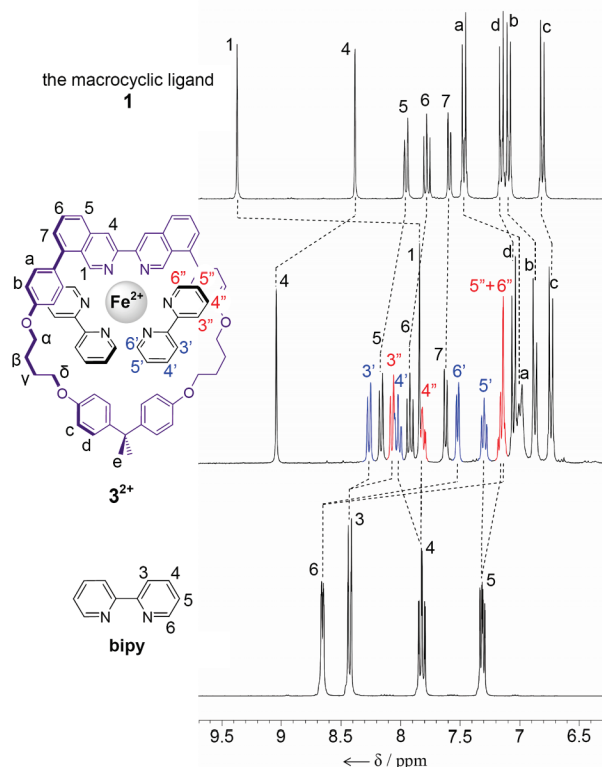


Figure 3. Comparison of ^1H NMR spectra of the heteroleptic 3^{2+} complex (solution in CD_3CN) and the ligands: **1** (CD_2Cl_2) and bipy (CD_2Cl_2); 300 MHz, 298 K.

deuterated solvents (CD_2Cl_2 and CD_3CN). Due to the high-spin nature of the iron(II) complexes prepared, the very complicated spectra observed precluded any detailed study. Assuming an octahedral coordination sphere for the transition metal,²⁴ we postulate the general formulas $[\text{Fe}(\mathbf{1})(\text{H}_2\text{O})_{4-x}(\text{CH}_3\text{CN})_x]^{2+}$ and $[\text{Fe}(\mathbf{2})(\text{H}_2\text{O})_{4-x}(\text{CH}_3\text{CN})_x]^{2+}$ ($x \leq 4$) to describe the chemical composition of the species formed at this stage.

To stabilize the iron(II) complexes in a low-spin state, additional pyridine-type ligands were necessary. 2,2'-bipyridine (bipy) chelates (2 equiv) were used for this purpose (see Figure 2). The corresponding heteroleptic complexes ($3^{2+} = [\text{Fe}(\mathbf{1})(\text{bipy})_2]^{2+}$ or $4^{2+} = [\text{Fe}(\mathbf{2})(\text{bipy})_2]^{2+}$) were obtained quantitatively.

In Figure 3, a representative part of the ^1H NMR spectrum of 3^{2+} is shown and compared with the spectra of the starting organic ligands. The complexity of the spectra reflects the C_2 symmetry of 3^{2+} and 4^{2+} which leads to splitting of the H -bipy signals: in a three-chelate octahedral complex consisting of two symmetrical and identical chelates (bipy) and a third symmetrical but different bidentate ligand (dpbiiq). As a result of the low symmetry, the two identical chelates become asymmetric. Consequently, the bipy chelates lead to two sets of signals: $3',3''$; $4',4''$; $5',5''$; $6',6''$, whereas free bipy displays only one set (3, 4, 5, 6).

The most noticeable ^1H NMR feature is the large upfield shift of the signals for the protons next to the nitrogen atoms. In analogy with related complexes previously reported by our

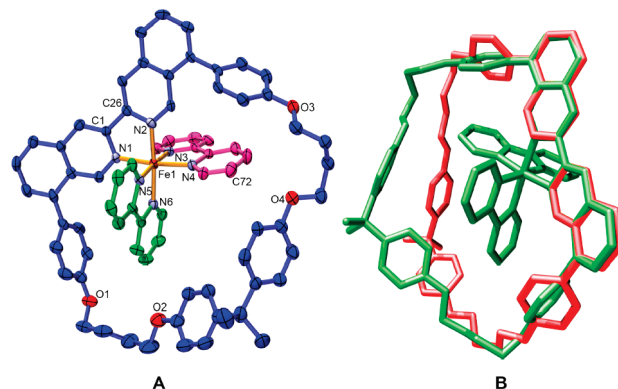


Figure 4. X-ray crystal structure of $3(\text{PF}_6)_2 \cdot 2\text{CO}(\text{CH}_3)_2$: (A) ORTEP-plot showing thermal ellipsoids at 50% probability (solvent molecules and PF_6^- anions are omitted for clarity, carbon atoms of the different ligand molecules are shown with different colors, the atoms mentioned in the text are labeled); (B) overlapping the molecular structures of 3^{2+} (green) and of the macrocycle **1** (red).²¹

group,^{22,23,29} this evidence coordination to the metal which favors close proximity between the various organic fragments and thus exposes $H^{6'}$, $H^{6''}$, and H^1 protons to the strong ring-current effects of the aromatic fragments of other ligands.

The molecular structure of 3^{2+} derived from ^1H NMR data was confirmed by X-ray crystallography (Figure 4a). The six Fe–N interatomic distances are typical for low-spin iron(II) complexes²⁴ although they are slightly longer for the coordination bonds with 3,3'-bi-isoquinoline chelate: 1.986 (N2) and 1.991 Å (N1), than for the coordination bonds to the bipy ligands. The latter are in the range 1.963 (N5) to 1.974 Å (N6).

Figure 4b shows two overlapping X-ray crystal structures: 3^{2+} and macrocycle **1**.²¹ It illustrates how the macrocycle can adapt itself to the steric demand of the $\text{Fe}(\text{bipy})_2$ fragment. For example, the aromatic substituents in 8 and 8' positions of 3,3'-bi-isoquinoline tend to stack with the neighboring bipy ligands which leads to changes in the macrocycle conformation. It must be noted, the $\text{O1} \cdots \text{O3}$ distance (see Figure 4a for labeling) is 14.83 Å, whereas the corresponding distance in the free macrocycle is 15.45 Å. This shortening is due to the coordination of the metal to the 3,3'-bi-isoquinoline chelate, which flattens this fragment significantly and thus reduces the distance between the oxygen atoms.

As expected, coordination of two bipy chelates to the iron(II) center of $[\text{Fe}(\mathbf{1})(\text{solvent})_4]^{2+}$ or $[\text{Fe}(\mathbf{2})(\text{solvent})_4]^{2+}$ with formation of the heteroleptic complexes 3^{2+} and 4^{2+} leads to three-chelate iron complexes. Although the bipy ligands are too short to be considered as “threaded” fragments, the high yield formation of 3^{2+} and 4^{2+} is a first step toward the preparation of real pseudorotaxanes from the macrocyclic complexes $[\text{Fe}(\mathbf{1})(\text{solvent})_4]^{2+}$ or $[\text{Fe}(\mathbf{2})(\text{solvent})_4]^{2+}$ provided that longer fragments are used in the complexation reaction. Derivatives of 8,8'-diphenyl-3,3'-bi-isoquinoline (dpbiiq) such as **5**²⁰ (Figure 5) are the optimal candidates as “threads”. Due to the endotopic but nonsterically hindering nature of these ligands,²³ the dpbiiq backbone is ideally suited for the generation of three-component entanglements around a metal center.²⁹

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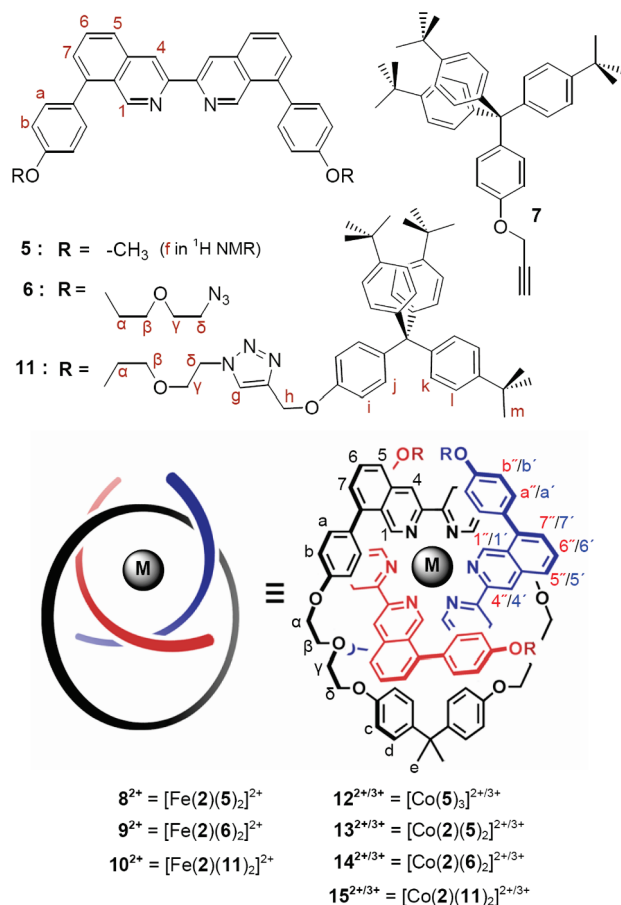


Figure 5. Ligands used for the double-threading reaction (**5** and **6**), the stoppering reagent **7**; the iron(II)- or cobalt(II/III)- [3]pseudorotaxanes: **8**²⁺ and **13**^{2+/3+}, the [3]prerotaxanes: **9**²⁺ and **14**^{2+/3+} and their stoppered analogues: **10**²⁺ and **15**^{2+/3+}; the dumbbell **11**.

2.2. Iron(II)-Driven Double-Threading of Two 3,3'-Bi-isoquinoline Derivatives and [3]Rotaxane Synthesis. The first step was the complexation reaction of the macrocycle (**1** or **2**) with stoichiometric amounts of a metal salt (e.g., Fe(BF₄)₂·6H₂O). Subsequently, two equivalents of the noncyclic reagent (**5** or **6**, Figure 5) were added. In experiments with the smaller 39-membered macrocycle **1**, the main reaction product was not the desired double-threaded species [Fe(**1**)(**5**)₂]²⁺. Instead, the homoleptic complex [Fe(**5**)₃]²⁺ was produced mainly, and minor amounts of [Fe(**1**)(**5**)₂]²⁺ were detected by mass spectrometry. In contrast, the reaction with the 41-membered macrocycle **2** led to the desired complex [Fe(**2**)(**5**)₂]²⁺ (**8**²⁺, Figure 5) in high yield (82%).¹⁸ These observations tend to indicate that two threads can be passed relatively easily through the 41-membered ring **2** by coordination to iron(II), whereas the 39-membered ring **1** is too small to comfortably accommodate two threads of the dpbiq family.

When using ligand **6** with azide functions as terminal groups in a similar Fe(II)-driven threading reaction was as effective as the double threading with **5**. It led to a heteroleptic complex **9**[PF₆]₂ (**9**²⁺ = [Fe(**2**)(**6**)₂]²⁺) which was a precursor to two-thread [3]rotaxanes. Subsequently, **9**²⁺ was reacted with an excess of propargyl derivative **7** under conditions which are typical of copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition ("click" chemistry, developed by Sharpless, Medal, and their co-workers).²⁵ **9**²⁺ and **7** were dissolved in CH₂Cl₂ and stirred with an aqueous solution of CuSO₄ using sodium ascorbate as reducing agent. The tetratriazole derivative **10**²⁺ was obtained

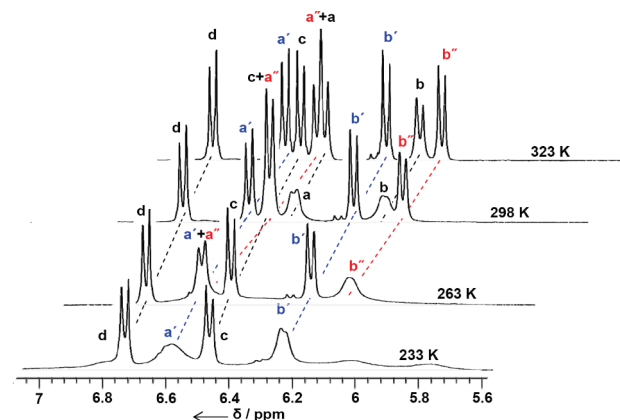


Figure 6. Temperature dependence of **8**²⁺ ¹H NMR spectra (500 MHz, CD₃CN, see Figure 5 for assignment of the signals and the text for explanations).

as its PF₆[−] salt in good yield¹⁸ after ion exchange with KPF₆ and column chromatography on silica. The iron(II) complexes were fully characterized by the classical analytical techniques.

The electrochemical behavior of the new iron(II) complexes **3**²⁺, **4**²⁺, **8**²⁺, and **10**²⁺ is very similar to that of the reference complex [Fe(bipy)₃]²⁺²⁶ (see Experimental Section). The cyclic voltammograms of all the iron complexes are characterized by two quasi-reversible redox processes, independently of the substituents attached at the periphery of the ligands: Fe^{3+/2+}, *E*_{1/2} ≈ +1.00 V (vs SCE). The second wave in the voltammogram at *E*_{1/2} ≈ −1.43 V (vs SCE) can be assigned to a ligand-centered electrochemical process.

The electronic spectra of the iron(II) complexes (see experimental section) are as expected for three-chelate complexes: (i) below 300 nm the high intensity bands are ascribed to allowed ¹ππ* transitions; (ii) in the region 300–400 nm various transitions tend to overlap:²⁷ contribution from ¹nπ* and intra-ligand charge transfer (¹ILCT) transitions are expected, the latter being due to the presence of electron-donating -RCH₂O- groups; (iii) the MLCT absorption transitions observed in the region 400–600 nm are in agreement with previous reports on related complexes.^{22,28} Noteworthy, the MLCT bands of [Fe(bipy)₃]²⁺²⁸ **3**²⁺ and **4**²⁺ (λ_{max} = 487 and 523 nm) appear at lower energy than those of **8**²⁺ and **10**²⁺ (λ_{max} = 462 nm) due to the more electron-rich nature of dabiqli compared to that of bipy.

The ¹H NMR study of the various iron(II) complexes prepared revealed rather interesting features. The chemical shifts of certain signals are unusually low compared to the corresponding signals of the free ligands. For example, the doublet corresponding to *H*^b appears at 7.08 ppm²⁰ in **5**, and after complexation in **8**²⁺ it is split and upfield shifted, appearing as two doublets at 6.29 (*H*^{b'}) and 6.14 (*H*^{b''}) ppm (Figure 6). As was already mentioned, such a large upfield shift results from the strong shielding of the aromatic groups due to formation of a three-fold symmetry set of π–π interacting rings.^{23,29} This three-component en-

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tanglement in a doubly threaded species is also responsible for the remarkable temperature-dependent dynamic behavior.

The ^1H NMR spectra of 8^{2+} in CD_3CN are strongly dependent on temperature especially in the region 5.60 – 7.00 ppm. Several representative spectra, shown in Figure 6, were recorded in the temperature range from 323 K (50 °C) to 233 K (–40 °C). At 323 K eight doublets of equal intensity are observed. Upon cooling, the signals of H^a and H^b from the macrocycle coalesce (see spectra at 298 K) and finally disappear in the baseline at 273 K (not shown in the Figure 6). In a similar way, a coalescence of analogous signals from one of the aromatic groups of **5**, $H^{a''}$ – $H^{b''}$, takes place in the range from 273 to 243 K (see spectrum at 263 K). Eventually at 233 K the coalescence of the third set of signals, $H^{a'}$ – $H^{b'}$, is detected. In addition, very broad signals appear at 6.00 and 5.75 ppm (233 K). These ^1H NMR observation are in agreement with slow conformational changes. The triply entangled nature of the complexes imposes steric constraints which prevent the organic fragments from moving fast on the ^1H NMR time scale. Thus, rotation of the aromatic rings bearing H^a and H^b is hindered by the filling of the macrocycle **2** with the metal ion and two other **5** ligands. As a result, the activation barrier is too high to be overcome even at room temperature. In fact, the rotation of the other two ligands inside of the macrocycle also becomes difficult as soon as the rotation in macrocycle is broken. Due to the asymmetric structure, one of the aromatic rings from **5** is more affected by the embracing macrocycle than the other. This leads to a stepwise coalescence of the signals with decreasing the temperature.

Interestingly, two clean doublets at 6.33 and 6.64 ppm corresponding to a small amount of homoleptic $[\text{Fe}(\mathbf{5})_3]^{2+}$ (3 mol %) are also observed. These signals are not affected at all in this temperature range. It is an additional indication that specific temperature dependence of 8^{2+} is a result of the macrocyclic structure of one of the ligands. The experiments performed tend to demonstrate that the size of macrocycle **2** is sufficient for **2** to accommodate two ligands **5**, affording a compact structure. Moreover, it can be concluded that the smaller macrocycle **1** is too small to enfold an $\text{Fe}(\mathbf{5})_2$ fragment.

2.3. Removal of the Templating Fe(II) Metal Center. Considerable difficulties were encountered when attempting to demetallate 10^{2+} so as to obtain the corresponding metal-free [3]rotaxane. The usual procedures, e.g. treatment with H_2O_2 in basic medium³⁰ or reaction with an excess of Na_3HEEDTA which were effective for the decomplexation of 3^{2+} and 4^{2+} (see the Experimental Section), were completely inefficient. According to our experience, iron(II) complexes are not stable in hot basic DMF. Thus, a diluted solution of 10^{2+} in DMF was added during 4 days to a hot solution of Cs_2CO_3 in DMF (70 °C) under argon. After chromatographic separation of the products only the starting macrocycle **2** and the strings **11** (Figure 5) were recovered in more than 90% yield, but no trace of the [3]rotaxane was detected, showing that the desired [3]rotaxane is not stable toward unthreading at elevated temperatures. Although disappointing, this result was in a good agreement with the recent data of Saito and co-workers³¹ on

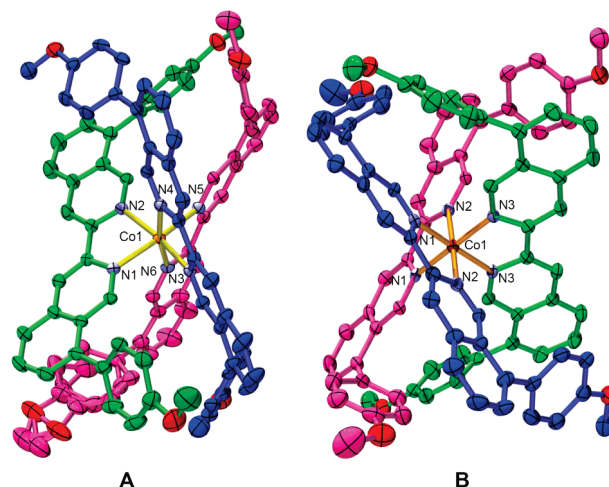


Figure 7. X-ray crystal structures of $12(\text{ClO}_4)_2 \cdot \text{CO}(\text{CH}_3)_2$ (A) and $12(\text{PF}_6)_3 \cdot 2\text{CO}(\text{CH}_3)_2$ (B). ORTEP-plots showing thermal ellipsoids at 50% probability, solvent molecules, ClO_4^- and PF_6^- anions are omitted for clarity, carbon atoms of different ligand molecules are shown with different colors; one of the phenoxy-group in $12(\text{ClO}_4)_2 \cdot \text{CO}(\text{CH}_3)_2$ is disordered.

the stability of [2]-rotaxanes. For example, it has been reported that a 37-membered ring is too large already for a tris(biphenyl)methyl stopper. Although our system is significantly different from that of Saito (we used two threads instead of one and a larger 41-membered ring), it was not too surprising to observe unthreading. In order to minimize unthreading, solvent and temperature effects were investigated. By using a saturated solution of Na_3HEEDTA in DMSO it was necessary to heat the reaction mixture which also led to unthreading. These difficulties urged us to look for a metal center other than Fe(II). The cobalt(II) complex of **5** (*vide infra*) is very sensitive to DMSO and completely decomposes in the presence of Na_3HEEDTA within several minutes at room temperature. This observation prompted us to repeat the double-threading and “click chemistry” sequence using cobalt(II) and cobalt(III) ions as octahedral templates.

2.4. Homoleptic dabiig Cobalt(II) and Cobalt(III) Complexes. Reaction of **5** with cobalt(II) ions (starting from $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$) goes smoothly with the immediate formation of the yellow paramagnetic complex 12^{2+} which can be readily crystallized as its perchlorate salt. The X-ray structure of $12(\text{ClO}_4)_2 \cdot \text{CO}(\text{CH}_3)_2$ is shown in Figure 7A. The three-fold entanglement of the organic ligands around the metal ion is analogous to the recently reported octahedral iron(II) and ruthenium(II) complexes.^{23,29} The large interatomic distances $\text{Co}-\text{N}^{32}$ (the mean value is 2.125 Å) are typical of cobalt(II) complexes. Although the complex 12^{2+} is stable in acetone, acetonitrile, and dichloromethane solutions, it decomposes on silica and undergoes fast dissociation in DMSO with release of free ligand **5**.

Oxidation of the metal ion to cobalt(III) yielded a stable (kinetically inert) complex. The relevant redox potential ($\text{Co}^{3+/2+}$ for $12^{3+/2+}$) is rather low: $E_{1/2} = +0.16$ V vs SCE. For comparison, $E_{1/2} = +0.25$ V vs SCE in $[\text{Co}(\text{bipy})_3]^{3+/2+}$. Oxidation of 12^{2+} to the cobalt(III) complex by $[\text{Ce}^{\text{IV}}(\text{NO}_3)_6]^{2+}$ was very fast and quantitative. All Co^{III} complexes reported in this work were obtained by treatment of the corresponding Co^{II} species with a small excess of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (1.1 equiv).

12^{3+} is a low-spin cobalt(III) complex. As expected, it is stable and kinetically inert. In particular, it can be readily purified by column chromatography on silica. The X-ray crystal

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structure of $\mathbf{12}(\text{PF}_6)_3 \cdot 2\text{CO}(\text{CH}_3)_2$ (shown in Figure 7b) is very similar to that of the starting cobalt(II) complex (Figure 7a). The cobalt(III) coordination bonds are shorter than those of the corresponding divalent complex: the Co–N distances are in the range of 1.923–1.941 Å, whereas those of $\mathbf{12}^{2+}$ vary between 2.099 and 2.146 Å.³² It is noteworthy that the difference in distances around the metal ion in $\mathbf{12}^{2+}$ and $\mathbf{12}^{3+}$ leads to changes at the periphery of the molecule. The O···O distances in the intrachelate cleft of $\mathbf{12}^{2+}$ are 15.23, 15.96, and 15.95 Å, whereas they are significantly shorter in $\mathbf{12}^{3+}$: 14.42, 14.42, 14.98 Å. The aromatic ligand can thus adapt its conformation to the steric demands of the metal center (see also other recently reported data for comparison^{23,29}). However, these geometrical changes are only minor, considering the large size of $\mathbf{12}^{2+}$ and $\mathbf{12}^{3+}$. Hence, the overall structures of the cobalt–dpbiiq complexes are almost completely independent of the metal oxidation state.

The electronic spectrum of the cobalt(II) complex $\mathbf{12}^{2+}$ in the region 220–400 nm is very similar to that of the corresponding iron(II) compound. Similarly to $[\text{Co}(\text{bipy})_3]^{2+}$,³³ the MLCT is observed in the region 300–400 nm. Oxidation to cobalt(III) is accompanied by the appearance of an intense LMCT band centered at 390 nm which is responsible for the orange color of the cobalt(III) complexes.^{32,33}

2.5. Cobalt(II)-Driven Double-Threading Reaction and [3]Rotaxane Synthesis. The cobalt(II)-induced threading reaction was performed analogously to the iron(II) complexes described above. It was started from the macrocycle **2** (1 equiv) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 equiv) in CH_2Cl_2 – CH_3CN solution. Without isolation of the intermediate $[\text{Co}(\mathbf{2})(\text{H}_2\text{O})_{4-x}(\text{CH}_3\text{CN})_x]^{2+}$ ($x \leq 4$) species, the string component **5** (2 equiv) was added to the reaction mixture. The paramagnetic complex $\mathbf{13}^{2+}$ ($\mathbf{13}^{2+} = [\text{Co}(\mathbf{2})(\mathbf{5})_2]^{2+}$) was obtained, and it was directly oxidized to $\mathbf{13}^{3+}$. $\mathbf{13}^{3+}$ was isolated as its PF_6^- salt (yield 89%) after chromatography and ion-exchange. Using the smaller macrocycle **1** in the same reaction turned out to be unproductive, which confirms that **1** is too small for the metal-templated double threading reaction when derivatives of **5** are utilized.

Slow diffusion of diisopropyl ether into a solution of $\mathbf{13}(\text{PF}_6)_3$ in acetone afforded crystals suitable for X-ray investigations. The molecular structure of $\mathbf{13}^{3+}$ (Figure 8A) reveals typical Co–N distances for cobalt(III) complexes with an average value equal to 1.934 Å.³² The structure clearly demonstrates threading of the two string-like components (**5**) through the dpbiiq-macrocycle (**2**). The structure is stabilized by interligand π – π interactions (Figure 8B) which are typical of all complexes with three dpbiiq ligands.^{23,29} The aromatic groups of the bis-phenol A (2,2-bis(phenyl)propane) unit (of the macrocycle **2**) also take part in the π – π staking ensemble (Figure 8B) since the interplane distance between one of its aromatic rings and the phenyl group of the neighboring threaded chelate (**5**) are comparable to those observed for other π – π contacts. Noteworthy, the torsion angles OCCO in the diethylenetrioxo-linkages (69.3°, 74.4°, 75.5°, and 69.9°) are as expected, thus reflecting the relaxed conformation of the chain. In solution, the situation is different since several conformers, corresponding to energetically close structures, are expected to be in equilibrium. This was confirmed by ^1H NMR spectroscopy (see Experimental Section) which shows spectra corresponding to a C_2 symmetry. The temperature dependence of the ^1H NMR spectrum of $\mathbf{13}^{3+}$ is analogous to what was observed for $\mathbf{8}^{2+}$.

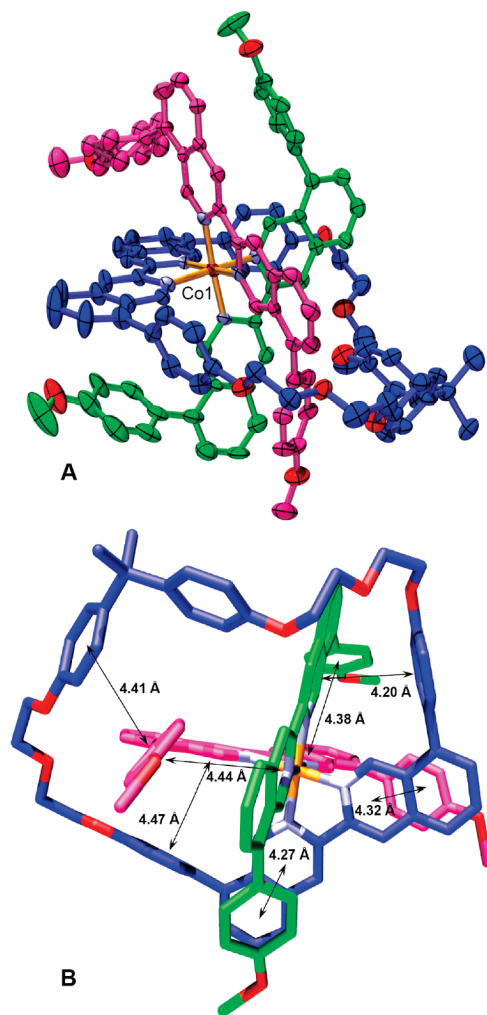


Figure 8. X-ray crystal structures of $\mathbf{13}(\text{PF}_6)_3 \cdot 2\text{CO}(\text{CH}_3)_2$: (A) ORTEP-plot showing thermal ellipsoids at 50% probability. The solvent molecules and PF_6^- anions are omitted for clarity, carbon atoms of different ligand molecules are shown with different colors. (B) Stick representation with the average distances between carbon atoms of the neighboring aromatic rings.

Use of the azide-bearing thread **6** instead of **5** in the same reaction sequence with macrocycle **2** (1 equiv) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 equiv) yields the cobalt(III) complex $\mathbf{14}^{3+}$ ($\mathbf{14}^{3+} = [\text{Co}(\mathbf{2})(\mathbf{6})_2]^{3+}$) which is a precursor of the copper(I)-catalyzed reaction with the alkyne-bearing stopper **7** (click-chemistry) (Figure 9). However, the ^1H NMR data evidenced that significant amounts (up to 10 mol %) of the homoleptic $[\text{Co}(\mathbf{6})_3]^{3+}$ was also formed. Nevertheless, the crude product was used for the next step without purification. Since it was anticipated that the stability of the pseudorotaxane precursor $\mathbf{14}^{3+}$ or the expected rotaxane $\mathbf{15}^{3+}$ would be higher than that of nonthreaded species³⁴ it was decided to perform purification after the click-reaction.

The conditions utilized for copper(I)-catalyzed terminal alkyne-azide cycloaddition between $\mathbf{8}^{2+}$ and **7**^{18,25} were also employed for the synthesis of $\mathbf{15}^{3+}$ (Figure 9). The crude cobalt(III) complex $\mathbf{14}^{3+}$ with terminal azide-functions was dissolved in CH_2Cl_2 together with a large excess (8 equiv) of the propargyl stopper **7**. It was mixed with an aqueous solution

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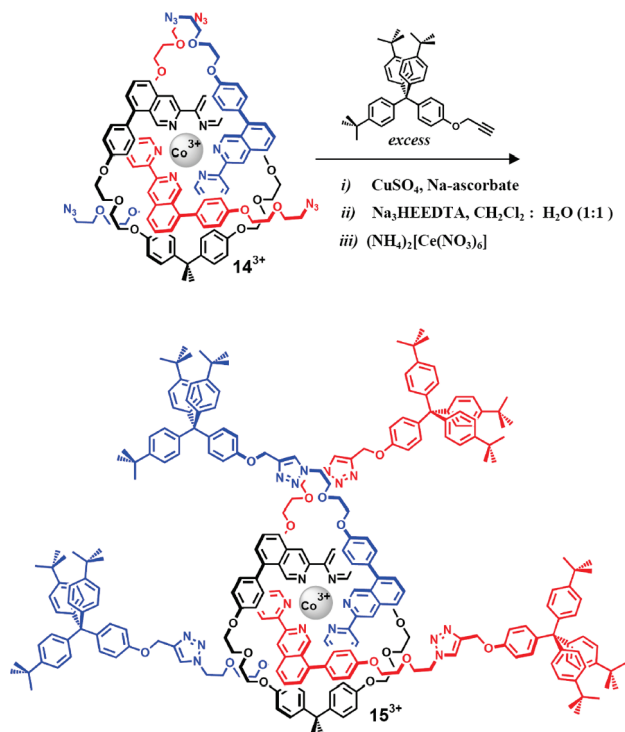


Figure 9. Synthesis of the cobalt(III) [3]rotaxane complex 15^{3+} (see explanations in text and Experimental Section).

of sodium ascorbate used in large excess (10 equiv). Aqueous KPF_6 and acetonitrile were added to the reaction mixture. Finally, an aqueous solution of $CuSO_4$ was added.

Although in classical click reactions, the function of sodium ascorbate is only to reduce divalent copper to copper(I) ions in water, in the present case it also reduces the cobalt(III) complexes contained in the organic phase. After several hours of reaction, cobalt(II) was the main oxidation state as shown by 1H NMR spectroscopy. In other words, the reaction product was 15^{2+} , contaminated by the homoleptic complex $[Co(11)_3]^{2+}$. The cobalt(II) complexes were isolated and treated at ambient temperature with a large excess of $Na_3HEEDTA$ in biphasic CH_2Cl_2 -water medium. Fortunately, 15^{2+} was stable enough in dichloromethane to resist the complexation agent, whereas $[Co(11)_3]^{2+}$ was decomposed completely. The desired [3]rotaxane cobalt(II) complex 15^{2+} was readily separated from the organic compounds by conventional column chromatography on silica.

In order to characterize the double-threaded specie by 1H NMR spectroscopy, paramagnetic 15^{2+} was oxidized, and 15^{3+} was isolated as its PF_6^- salt in good yield (70% based on macrocycle **2**). The 1H NMR spectrum of the final compound 15^{3+} is shown in Figure 10. The three singlets at 9.25 (H^a), 9.14 ($H^{a'}$), and 9.12 ($H^{a''}$) ppm are characteristic signals of the three cobalt(III)-coordinated dpbiiq-type ligands with C_2 -symmetry. The large upfield shift of the $H^{1,1',1''}$ -signals indicate the triple entanglements of the ligands around the cobalt(III) ion. No significant signals of the homoleptic $[Co(11)_3]^{3+}$ complex could be detected which indicates that 15^{2+} was purified efficiently by the treatment with $Na_3HEEDTA$. As expected, the most intense signals belong to the aromatic group of the stoppers (7.00–7.30 ppm). Their intensities are in agreement with the stoichiometry of the double-threaded species. Although the signals of the aromatic protons in the range from 6.00 to 7.00 ppm are sharp doublets at elevated temperatures (not shown in Figure 10), the

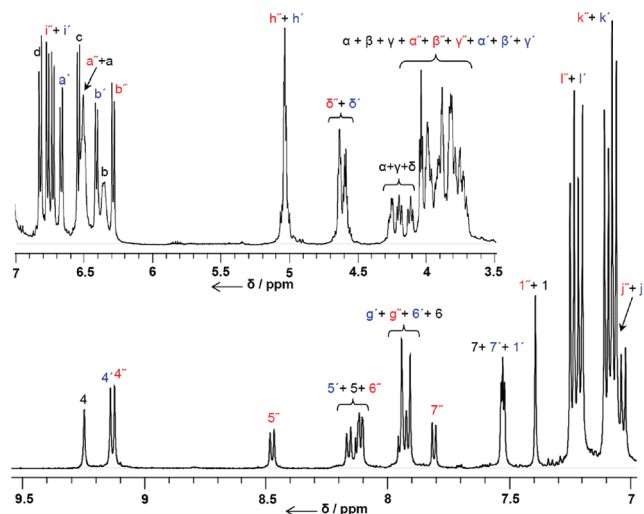


Figure 10. 1H NMR spectrum of 15^{3+} (500 MHz, CD_3CN , see Figure 5 for the assignment of the signals).

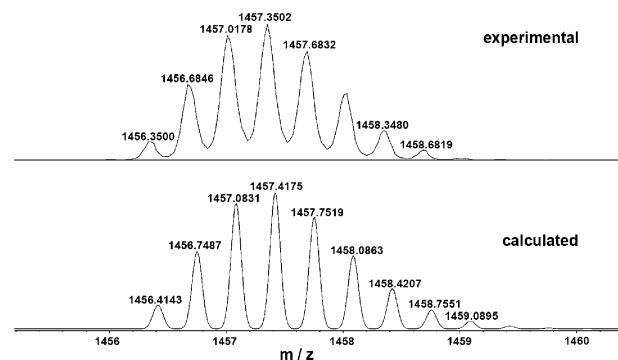


Figure 11. Experimental and calculated distribution of peak intensities for $C_{289}H_{300}CoN_{18}O_{18}$ (15^{3+}) - the molecular peak in positive ion mass spectra (ES-MS) of acetonitrile $15(PF_6)_3$ solution.

signals of H^a and H^b at 25 °C are broader than others. An analogous temperature behavior was discussed above for iron(II) [3]pseudorotaxane 8^{2+} . It shows that the aromatic group of the coordinated macrocycle **2** is prevented from rotating fast on the 1H NMR time scale. This phenomenon is caused by the interaction with aromatic groups of the two other dpbiiq-ligands (**11**) inside the macrocyclic cavity. The signals of CH_2 -groups next to the triazine cycles (H^h , $H^{h'}$, $H^{h''}$, and $H^{h'''}$) are well-separated multiplets. Remarkably, the signals of $H^{d'}$ and $H^{d''}$ are largely downfield shifted compared to the starting 14^{3+} complex (the difference is ~ 1.1 ppm) which evidence the “click” reaction between the azide (14^{3+}) and alkyne (**7**) functions.

The structure of 15^{3+} was also confirmed by mass-spectroscopy, showing the peak of the three-positive charge cobalt(III) rotaxane as the most intense peak (see Figure 11), whereas no peaks corresponding to $[Co(11)_3]^{3+}$ could be detected.

6. Formation of the metal-free [3]rotaxane. Treatment of 15^{2+} with a large excess of $Na_3HEEDTA$ in a DMSO solution (at ambient temperature) led to a quantitative yield of the metal-free [3]rotaxane **16** (see Figure 12). This certainly is in marked contrast to similar experiments conducted in dichloromethane (see previous paragraph) which emphasizes the importance of the solvent in metal decomplexation reactions. From previous experiments with the analogous iron(II) complex 10^{2+} (*vide supra*), it was expected that **16** is a metastable species, and

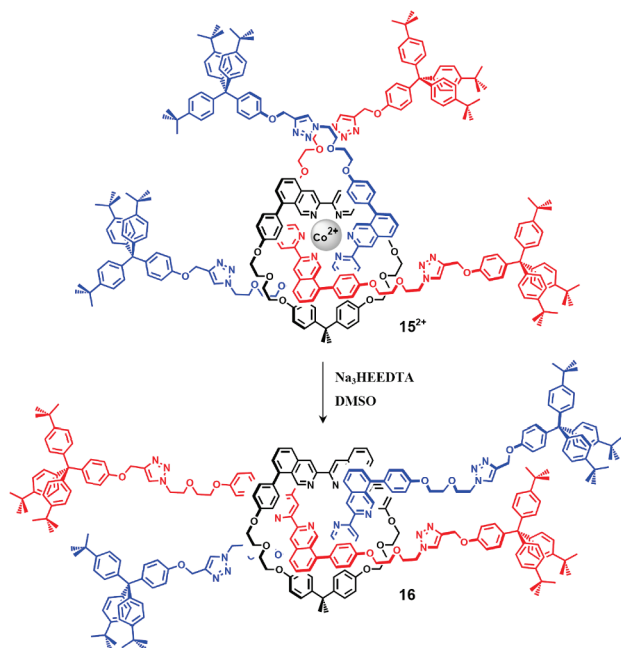


Figure 12. Synthesis of the metal-free [3]rotaxane **16**.

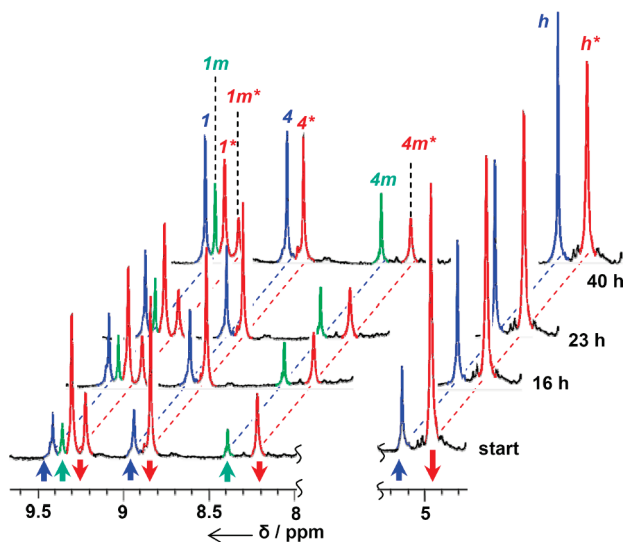


Figure 13. Representative parts of the ^1H NMR spectra of **16** (500 MHz, CD_2Cl_2) showing the kinetics of the unthreading reaction at 294 K. The signals of [3]rotaxane **16** are in red and marked with an asterisk. The homologous signals of the “free” components are in blue (**11** - the “string”, see Figure 5 for assignment of the signals) and green (**2** - the macrocycle, see Figure 2).

indeed, the ^1H NMR spectra of a freshly prepared sample (in CD_2Cl_2) evolve with time and also exhibit signals of **2** and **11**. Figure 13 shows representative ^1H NMR spectra of the metal-free [3]rotaxane **16** after several time intervals at 294 K. As expected, the corresponding signals of **11** (blue, H^1 and H^4) are more intense than those of macrocycle **2** (green, H^{1m} and H^{4m}) by a factor of 2.

To investigate unthreading of **16**, the kinetic experiment was performed in a $3 \times 10^{-3} \text{ mol L}^{-1}$ CD_2Cl_2 solution. The sample was sealed in an NMR-tube and incubated for 144 h at 274 K (0.8 °C) in a thermostat. The ^1H NMR spectra were recorded every 24 h. Then the temperature was increased to 284 K (10.9 °C) and monitoring was repeated. Finally, the same sample was kept at 294 K (20.5 °C) for 96 h, and the collected data were

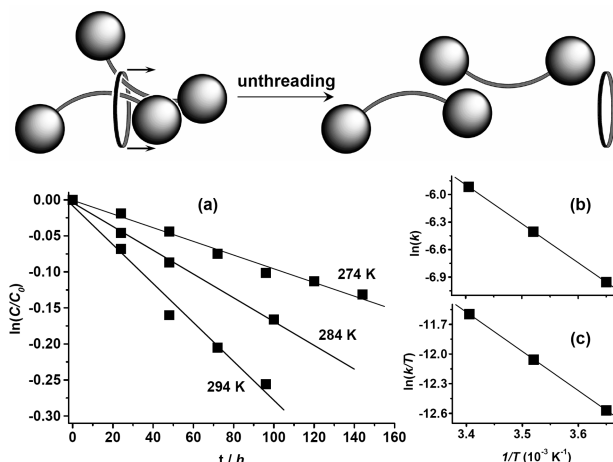


Figure 14. Schematic representation of the unthreading process as illustration of the working hypothesis and the corresponding kinetic plots for the unthreading in CH_2Cl_2 : (a) First-order dependence on time $\ln(C/C_0) = -kt$ at three different temperatures, (b) Arrhenius plot, and (c) Eyring plot.

analyzed using the standard procedure³⁵ (see also the experimental section for details).

Figure 13. Representative parts of the ^1H NMR spectra of **16** (500 MHz, CD_2Cl_2) showing the kinetics of the unthreading reaction at 294 K. The signals of [3]rotaxane **16** are in red and marked with an asterisk. The homologous signals of the “free” components are in blue (**11** - the “string”, see Figure 5 for assignment of the signals) and green (**2** - the macrocycle, see Figure 2).

It can be seen clearly (Figure 13) that the signals of [3]rotaxane **16** (marked with *) decrease while those of the free components, **11** and **2**, are increasing. In particular, the signals for the CH_2 -groups between a triazole ring and the bulky stopper (in **16** and **11**) can easily be monitored at 4.97 ppm (red, H^{h*} for **16**) and 5.13 ppm (blue, H^h for **11**) because they are nonoverlapping, intense, and sharp singlets. On the other hand, the ^1H NMR spectra do not show any signals that can be interpreted as belonging to the homologous [2]rotaxane. The stability of the [2]rotaxane specie is thus very small, and its concentration in solution is negligible, as expected from CPK model examination. In addition, MALDI-TOF mass-spectrometry measurements showed that **16**, **2**, and **11** are the only species found in the mixture. No trace of the intermediate [2]rotaxane was found. It may therefore be assumed that the unthreading reaction is a first order process. Both stoppers slide almost simultaneously through the wheel without cleaving any covalent bond (see Figure 14).

On the basis of the measurements at three different temperatures, it was possible to determine the rate constants k (Figure 14a) and evaluate the kinetic parameters. Thus, from the Arrhenius plot (Figure 14b) the frequency factor $k_\infty = 2 \text{ MHz}$ and the energy of activation $E_A = 35 \pm 3 \text{ kJ} \cdot \text{mol}^{-1}$ were obtained. In addition, the Eyring plot (Figure 14c) provides $\Delta H^\ddagger = 33 \pm 3 \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta S^\ddagger = -182 \pm 55 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, from which $\Delta G^\ddagger (298 \text{ K}) = 87 \pm 9 \text{ kJ} \cdot \text{mol}^{-1}$ and the half-lives for the [3]rotaxane ($t_{1/2} = \ln 2/k$): e.g. $t_{1/2} (298 \text{ K}) = 206 \text{ h}$, $t_{1/2} (333 \text{ K}) = 46 \text{ h}$ are deduced. Although direct comparison to other systems^{31,35} is impossible, it must be noted that the enthalpic contribution (E_A and ΔH^\ddagger) to the unthreading barrier

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is rather low, whereas the entropic component (k_{∞} and ΔS^{\ddagger}) is remarkably high. Especially the high activation entropy indicates that the unthreading reaction has a highly ordered transition state, i.e. it is strongly dependent on the relative orientation of the wheel and the two strings. For example, unthreading may be favorable if the bulky stopper of one string is placed near the axle of the other, as illustrated schematically in Figure 14. On the other hand, placing two stoppers close enough to each other would make unthreading impossible. The fact that the unthreading reaction for **16** can be described satisfactorily as a first-order process indicates that the activation barrier for unthreading of the homologous [2]rotaxane (consisting of **2** and one molecule of **11**) is very low.

Conclusion

The present report illustrates the generality of the transition metal-templated methods for making rotaxanes and, more generally speaking, interlocking and threaded species. Using an octahedrally coordinated metal center such as cobalt(II) or iron(II), in conjunction with endocyclic but nonsterically hindering bidentate chelates of the 8,8'-diphenyl-3,3'-bi-isoquinoline (dpbiq), the preparation of doubly threaded species could be carried out in good yield. A particularly attractive X-ray structure was obtained for a [3]pseudorotaxane, which consists of a dpbiq-incorporating 41-membered ring, a central cobalt(III) center, and two 8,8'-di(*p*-anisyl)-3,3'-bi-isoquinoline fragments. Cobalt is ideally adapted to the preparation of dpbiq complexes such as rotaxane-like compounds since cobalt(II) is labile enough to allow for efficient preparation of the doubly threaded species and, after oxidation, the corresponding cobalt(III) species is kinetically very stable, which facilitates handling of the complexes. Using dpbiq threads bearing terminal azide functions, a real rotaxane could be prepared from the cobalt(III) precursor. In a first step, a cobalt(II) complex was generated due to the reducing conditions of the click chemistry reaction used for introducing the stoppers. The highly stable reoxidized cobalt(III) species was fully characterized, in particular by ^1H NMR and ES-MS. On the other hand, the divalent complex was easily demetalated due to the labile nature of cobalt(II) complexes to afford a free [3]rotaxane in good yield. This rotaxane was disassembled spontaneously by unthreading of the two string-like fragments from the ring in a slow but quantitative process (half-life of the free [3]rotaxane ~ 200 h at 298 K). The kinetic of the dissociation process was investigated by ^1H NMR spectroscopy at various temperatures. Remarkably, the entropy of activation obtained is very negative, with a value of $\sim -180 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, which tends to indicate that the reaction pathway leading to the unthreaded species is very narrow, with a highly ordered transition state.

4. Experimental Section

4.1. General. ^1H NMR spectra were recorded with a Bruker AVANCE 300 (300 MHz (^1H)) or Bruker AVANCE-500 (500 MHz) spectrometer using deuterated solvent as the lock. The spectra were collected at 25 °C (unless temperature dependence was investigated), and the chemical shifts were referenced to residual solvent protons as internal standards, ^1H : CD_3CN 1.94 ppm, CD_2Cl_2 5.32 ppm. Mass spectra were obtained with a VG ZAB-HF spectrometer (FAB) and a VG-BIOQ triple quadrupole in the positive or negative mode (ES-MS). Microanalyses were performed using an Elementar Vario EL III instrument.

Single-crystal X-ray data were collected at "Service de Radiocristallographie, Institut de Chimie UMR 7177 CNRS-ULP" with a Nonius Kappa CCD.

Electrochemical measurements were performed with a three-electrode system consisting of a platinum working electrode, a platinum wire counter electrode, and a silver wire as a pseudoreference electrode (ferrocene being used as an internal reference). All measurements were carried out at room temperature under argon, in degassed spectroscopic-grade acetonitrile, using 0.1 M *n*-Bu₄NPF₆ solutions as supporting electrolyte. An EG&G Princeton Applied Research model 273A potentiostat connected to a computer was used (software from Electrochemistry Research).

Absorption spectra of diluted solutions (10^{-5} M) in acetonitrile (spectrophotometric-grade) were obtained with a UVIKON XL (Bio-TEK instruments) UV-vis spectrometer.

The following chemicals were purchased and used without further purification: potassium hexafluorophosphate (Acros), iron(II) tetrafluoroborate tetrahydrate (Aldrich), 2,2'-bipyridyl (Lancaster), *N*-(2-hydroxyethyl)ethylenediamine-*N,N'*-triacetic acid trisodium salt hydrate (Aldrich), cesium carbonate (Aldrich), bis(2-bromoethyl)ether (Alfa Aesar), sodium azide (Acros), (+)-sodium L-ascorbate (Sigma), copper(II) sulfate pentahydrate (Aldrich), cobalt(II) perchlorate hexahydrate (Aldrich), cobalt(II) nitrate hexahydrate (Aldrich), ammonium cerium(IV) nitrate (Lancaster). All silica column chromatographies were performed using Merck Silicagel 60 (0.063–0.200 mm) or Merck Silicagel 60 (40–63 μm).

8,8'-(4-Methoxyphenyl)-3,3'-bi-isoquinoline (**5**),²⁰ 8,8'-dihydroxyphenyl-3,3'-bi-isoquinoline,²¹ and 1-(prop-2-ynoxy)-4-(tris(4-tert-butylphenyl)methyl)benzene (**7**)³⁶ were synthesized as described previously. The samples of crude macrocycles **1** and **2** were obtained according to the procedures²¹ published, starting from 0.326 g (0.740 mmol) and 0.569 g (1.29 mmol) of 8,8'-dihydroxyphenyl-3,3'-bi-isoquinoline respectively. After the first run of chromatography on silica,²¹ all fractions containing the target products were collected and combined, and the compounds were used for synthesis of **3**(PF₆)₂ and **4**(PF₆)₂ without any further purification.

4.2. Note. Purification of the starting macrocycles **1** and **2** requires repeated column chromatography.²¹ In contrast to this, both **3**²⁺ and **4**²⁺ were purified as described below by a single run of conventional chromatography if samples of the crude macrocycles, an excess of the iron(II) salt, and of bipy were used as the starting materials (*vide infra*). Moreover, the samples of both **1** and **2** (obtained by decomplexation of **3**²⁺ and **4**²⁺, respectively) were of excellent purity and were used further in all experiments with iron(II) and cobalt(II) as described below. According to our experience, a "complexation–decomplexation" procedure may be considered as an alternative for the purification of the dpbiq-based macrocycles, especially if extra-pure samples (e.g., for stoichiometric setups in coordination chemistry or physicochemical investigations) are necessary.

4.3. 3(PF₆)₂·2H₂O and 4(PF₆)₂. A solution of crude **1** (0.247 g) or **2** (0.751 g, 0.93 mmol) in 40 mL of dichloromethane was added to a solution of Fe(BF₄)₂ · 6H₂O (0.189 g, 0.56 mmol for **1**, and 0.440 g, 1.30 mmol for **2**) in 40 mL of acetonitrile and 2 mL of methanol, and it was stirred for 10 min at ambient temperature. A solution of 2,2'-bipyridyl (0.175 g, 1.12 mmol for **1**, and 0.407 g, 2.61 mmol for **2**) in 200 mL of dichloromethane was added drop by drop during 1 h to the orange-red reaction mixture, and stirring was continued for about 30 min. The solvents were evaporated, and the red reaction mixture was separated by chromatography on silica using acetone/water/KNO₃ sat mixtures as an eluent. The acetone/water/KNO₃ sat ratio was initially set to 700:25:1.5. After eluting of the first red byproduct band, the content of water and KNO₃ sat was increased to 700:50:3. The major red band containing the desired pure complexes (**3**²⁺ or **4**²⁺) was collected. Aqueous KPF₆ solution (sat., approximately 10 mL) was added to the eluate, and the organic solvent was evaporated. The red precipitate was collected by filtration and copiously washed with water.

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To remove NO_3^- traces, the product was dissolved in acetone and precipitated again with an aqueous KPF_6 on evaporation. After filtration and washing with water, the resulting solid was dissolved in acetonitrile, the solution was evaporated, and the product was dried in vacuum. For purification, the dried product was dissolved in acetone (approximately 5 mL) and added drop by drop to *n*-pentane (200 mL) while stirring. The resulting microcrystalline red precipitate was collected by filtration, washed with *n*-pentane and dried in vacuum. *Note*: Three major bands were collected in total. The third band was eluted with acetone/water/ KNO_3 (70:20:1), and the compound was identified to be $[\text{Fe}(\text{bipy})_3]^{3+}$ by means of ^1H NMR spectroscopy.

Yield: 0.160 g of $3(\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ (0.11 mmol, corresponding to 15% of the starting 8,8'-dihydroxyphenyl-3,3'-bi-isoquinoline). $\text{C}_{73}\text{H}_{64}\text{F}_{12}\text{FeN}_6\text{O}_4\text{P}_2 \cdot 2\text{H}_2\text{O}$ (1471.13) calc.: C 59.60, H 4.66, N 5.71; found: C 59.58, H 4.93, N 5.39. ^1H NMR (CD_3CN , 300 MHz at 298 K): δ = 9.05 (s, 2H, H^8), 8.27 (d, 2H, J = 8.0 Hz, $H^{3'}$), 8.17 (d, 2H, J = 8.0 Hz, H^5), 8.07 (d, 2H, J = 8.0 Hz, $H^{3''}$), 8.02 (ddd, 2H, J_1 = 8.0 Hz, J_2 = 7.8 Hz, J_3 = 1.2 Hz, H^4), 7.92 (dd, 2H, J_1 = 8.0 Hz, J_2 = 7.1 Hz, H^6), 7.84 (s, 2H, H^1), 7.82 (ddd, 2H, J_1 = 8.0 Hz, J_2 = 6.3 Hz, J_3 = 2.2 Hz, $H^{4'}$), 7.62 (d, 2H, J = 7.1 Hz, H^7), 7.52 (d, 2H, J = 5.8 Hz, $H^{6'}$), 7.30 (ddd, 2H, J_1 = 7.8 Hz, J_2 = 5.8 Hz, J_3 = 1.0 Hz, $H^{5'}$), 7.16 (ddd, 2H, J_1 = 6.3 Hz, J_2 = 5.2 Hz, J_3 = 2.2 Hz, $H^{5''}$), 7.13 (dd, 2H, J_1 = 5.2 Hz, J_2 = 1.2 Hz, $H^{6''}$), 7.05 (d, 4H, J = 8.8 Hz, H^4), 7.00 (d, 4H, J = 8.8 Hz, H^a), 6.87 (d, 4H, J = 8.8 Hz, H^b), 6.74 (d, 4H, J = 8.8 Hz, H^c), 4.26 (t, 4H, J = 5.9 Hz, H^a), 4.13 (m, 4H, H^b), 2.07 (m, 8H, $H^{\beta+\gamma}$), 1.58 (s, 6H, H^c). ES-MS: m/z : 572.2196 (calculated 572.2165 for $\text{C}_{73}\text{H}_{64}\text{FeN}_6\text{O}_4^{2+}$). UV-vis, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$): 198 (1.25), 229 (0.69), 259 (0.54), 301 (0.53), 358 (0.31), 486 (0.07), 528 (0.06). Cyclic voltammetry, $E_{1/2}$ (V vs SCE): +1.08 ($\text{Fe}^{3+/2+}$), -1.19.

X-ray quality crystals of $3(\text{PF}_6)_2 \cdot 2\text{CO}(\text{CH}_3)_2$ were grown by slow diffusion of di-isopropyl ether in acetone. Crystal data: M = 1551.25, red block, $0.40 \times 0.35 \times 0.30 \text{ mm}^3$, monoclinic, space group $P2_1/c$, a = 13.5203(2) Å, b = 30.6169(6) Å, c = 17.9603(3) Å, β = 99.356(1)°, V = 7335.8(2) Å³, Z = 4, ρ_{calc} = 1.405 g·cm⁻³, F_{000} = 3216, Mo K α radiation, λ = 0.71073 Å, μ = 0.338 mm⁻¹, T = 173(2) K, θ_{max} = 27.47°, 69240 reflections collected, 16744 unique (R_{int} = 0.0655), 10216 with $I_0 > 2\sigma(I_0)$, structure solved by SHELXS-97³⁷ and refined with SHELXL-97³⁸ full-matrix least-squares on F^2 , 949 parameters, 0 restraints, GoF = 1.060, R_1 = 0.0676, wR_2 = 0.2056 (all reflections), $-1.158 < \rho < 1.268 \text{ e} \cdot \text{\AA}^{-3}$.

Yield: 0.650 g of $4(\text{PF}_6)_2$ (0.443 mmol corresponding to 34% of the starting 8,8'-dihydroxyphenyl-3,3'-bi-isoquinoline). $\text{C}_{73}\text{H}_{64}\text{F}_{12}\text{FeN}_6\text{O}_6\text{P}_2$ (1467.10) calc.: C 59.76, H 4.40, N 5.73; found: C 59.72, H 4.85, N 5.24. ^1H NMR (CD_3CN , 300 MHz at 298 K): δ = 9.02 (s, 2H, H^8), 8.40 (d, 2H, J = 8.0 Hz, $H^{3'}$), 8.26 (d, 2H, J = 8.0 Hz, $H^{3''}$), 8.16 (d, 2H, J = 8.2 Hz, H^5), 8.01 (ddd, 2H, J_1 = 8.0 Hz, J_2 = 7.3 Hz, J_3 = 1.2 Hz, H^4), 7.99 (ddd, 2H, J_1 = 8.0 Hz, J_2 = 7.3 Hz, J_3 = 1.2 Hz, $H^{4'}$), 7.92 (dd, 2H, J_1 = 8.2 Hz, J_2 = 7.3 Hz, H^6), 7.62 (d, 2H, J_1 = 7.3 Hz, H^7), 7.56 (s, 2H, H^1), 7.55 (d, 2H, J = 6.0 Hz, $H^{6'}$), 7.28 (ddd, 2H, J_1 = 7.3 Hz, J_2 = 6.0 Hz, J_3 = 1.0 Hz, $H^{5'}$), 7.15 (dd, 2H, J_1 = 6.0 Hz, J_2 = 1.0 Hz, $H^{5''}$), 7.07 (ddd, 2H, J_1 = 7.3 Hz, J_2 = 6.0 Hz, J_3 = 1.0 Hz, $H^{6''}$), 6.97 (d, 4H, J = 8.8 Hz, H^a), 6.96 (d, 4H, J = 8.8 Hz, H^d), 6.88 (d, 4H, J = 8.8 Hz, H^c), 6.67 (d, 4H, J = 8.8 Hz, H^b), 4.28 (m, 4H, H^b), 4.13 (m, 4H, H^a), 3.97 (m, 8H, $H^{\beta+\gamma}$), 1.53 (s, 6H, H^c). ES-MS: m/z : 588.2263 (calculated 588.2114 for $\text{C}_{73}\text{H}_{64}\text{FeN}_6\text{O}_6^{2+}$). UV-vis, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$): 198 (1.14), 229 (0.65), 259 (0.52), 301 (0.49), 358 (0.31), 412 (0.06), 486 (0.07), 528 (0.06). Cyclic voltammetry, $E_{1/2}$ (V vs SCE): +1.07 ($\text{Fe}^{3+/2+}$), -1.34.

4.4. Macrocycles 1 and 2 (by Decomplexation of 3^{2+} and 4^{2+} , Respectively). A solution of Na_3HEEDTA (1.0 g, 2.9 mmol) in 20 mL of water was added to a solution of the iron(II) complex

($3(\text{PF}_6)_2 \cdot 2\text{H}_2\text{O}$ (0.132 g, 0.090 mmol) or $4(\text{PF}_6)_2$ (0.274 g, 0.187 mmol)) in 50 mL of acetonitrile. The reaction mixture was stirred for about 10 min. under heating (70 °C). During this time, the initial dark red solution became pale red, and the precipitate of the product formed. The organic solvent was evaporated, and the product was collected by filtration of the cold mixture and washed with cold methanol. In this stage, the macrocycle is free of 2,2'-bipyridyl, but colored pale red by traces of iron(II) complexes which can not be destroyed upon interaction with Na_3HEEDTA . For final purification, the product was dissolved in dichloromethane, sorbed on a short silica column, and then eluted by CH_2Cl_2 : CH_3OH (99:1) giving **1** or **2** as a yellow solid after evaporation of the solvent. Yields: **1** - 0.066 g (0.085 mmol, 95%), **2** - 0.131 g (0.162 mmol, 87%). The analytical data were identical to those reported previously.²¹

4.5. 8,8'-(4-(2-(2-azidoethoxy)ethoxy)phenyl)-3,3'-bi-isoquinoline (6). A suspension of 8,8'-dihydroxyphenyl-3,3'-bi-isoquinoline (0.300 g, 0.68 mmol) and Cs_2CO_3 (1.0 g, 3.07 mmol) in 50 mL of water-free and degassed DMF (Aldrich) was stirred for 10 min at 55 °C under argon. Then, bis(2-bromoethyl)ether (2.5 mL, 4.6 g, 19.89 mmol) was added as a single portion with a syringe, the mixture was degassed, and the heating and stirring were continued for 24 h. After this time, another portion of bis(2-bromoethyl)ether (2.5 mL, 4.6 g, 19.89 mmol) was injected, the mixture was degassed again, and the reaction was run as described above for another 24 h. The reaction mixture was cooled to ambient temperature, the precipitate of the inorganic salts was filtered off, washed with dichloromethane, the solutions (DMF and CH_2Cl_2) were combined, and the solvents were removed by evaporation under reduced pressure. A mixture of the corresponding bi-isoquinoline-dibromoderivative with an excess of bis(2-bromoethyl)ether was obtained as a yellow oil. It was diluted with dichloromethane (8 mL) and added drop by drop to a large volume of *n*-pentane (200 mL) under vigorous stirring. The yellow precipitate was collected by filtration, washed with *n*-pentane, and dried on air. It was suspended in 25 mL of DMSO together with NaN_3 (0.885 g, 13.26 mmol, approximately 20 equiv) and stirred in a closed flask at 40 °C overnight (16 h). After cooling to the ambient temperature, the reaction mixture was diluted with water (150 mL), and organic products were extracted with dichloromethane (4 × 50 mL). The organic solution was washed with water and dried over MgSO_4 , and the solvent was removed under reduced pressure. The crude yellow **6** was purified by column chromatography on silica using dichloromethane and then CH_2Cl_2 : CH_3OH (99:1) as the eluents. Yield: 0.350 g (0.52 mmol, 77%) of white microcrystalline solid. ^1H NMR (CD_2Cl_2 , 300 MHz): δ = 9.42 (s, 2H, H^1), 8.94 (s, 2H, H^4), 7.97 (d, 2H, J = 8.2 Hz, H^5), 7.75 (dd, 2H, J_1 = 8.2 Hz, J_2 = 7.2 Hz, H^6), 7.53 (d, 2H, J = 8.6 Hz, H^a), 7.53 (d, 2H, J = 7.2 Hz, H^7), 7.12 (d, 2H, J = 8.6 Hz, H^b), 4.26 (t, 4H, J = 4.6 Hz, H^a), 3.93 (t, 4H, J = 4.6 Hz, H^b), 3.79 (t, 4H, J = 5.0 Hz, H^c), 3.45 (t, 4H, J = 5.0 Hz, H^d). MALDI-TOF: m/z : 667.1952 ($[\text{M} + 1]^+$, $\text{C}_{38}\text{H}_{35}\text{N}_8\text{O}_4^+$; calc. 667.2781).

4.6. Note. It is possible to isolate the intermediate 8,8'-(4-(2-(2-bromoethoxy)-ethoxy)phenyl)-3,3'-bi-isoquinoline by chromatography (silica, CH_2Cl_2). ^1H NMR (CH_2Cl_2 , 300 MHz at 298 K): δ = 9.42 (s, 2H, H^1), 8.95 (s, 2H, H^4), 7.97 (d, 2H, J = 8.2 Hz, H^5), 7.75 (dd, 2H, J_1 = 8.2 Hz, J_2 = 7.2 Hz, H^6), 7.53 (d, 2H, J = 8.6 Hz, H^a), 7.53 (d, 2H, J = 7.2 Hz, H^7), 7.12 (d, 2H, J = 8.6 Hz, H^b), 4.25 (t, 4H, J = 4.5 Hz, H^a), 3.93 (m, 8H, $H^{\beta+\gamma}$), 3.56 (t, 4H, J = 6.0 Hz, H^b). MALDI-TOF: m/z : 743.0234 ($[\text{M} + 1]^+$, $\text{C}_{38}\text{H}_{35}\text{N}_2\text{O}_4\text{Br}_2^+$; calc. 743.0963). According to our experience, however, purification of the dibromoderivative is more difficult than purification of **6**, and it is preferable to use a crude, freshly prepared sample for the reaction with NaN_3 as described above. The reaction between NaN_3 and the pure dibromoderivative quantitatively yields **6**.

4.7. $8(\text{PF}_6)_2 \cdot \text{H}_2\text{O}$. A solution of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0105 g, 0.0312 mmol) in 20 mL of acetonitrile was added to a solution of **2** (0.0280 g, 0.0346 mmol) in 20 mL of dichloromethane and stirred for 30 min at ambient temperature. A solution of **5** (0.0292 g, 0.0623

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mmol) in 200 mL of dichloromethane was added in droplets during 3 h to the orange-red reaction mixture, and stirring was continued overnight. The solvents were evaporated under reduced pressure, and the solid residue was redissolved in an acetonitrile/water mixture (5:2, mL). Saturated aqueous KPF₆ (4 mL) was added, the organic solvent was evaporated, and the precipitate was collected and copiously washed with water. Chromatography on silica (acetone/water/KNO₃ sat. - 700:50:3), ion-exchange with KPF₆, and subsequent precipitation by ether from an acetone solution afforded **8**(PF₆)₂·H₂O as a red crystalline solid. Yield: 0.0532 g (0.0252 mmol - 81% calculated to Fe²⁺). C₁₁₇H₉₆F₁₂FeN₆O₁₀P₂·H₂O (2109.84) calc.: C 66.60, H 4.68, N 3.98; found: C 66.69, H 5.04, N 3.95. ¹H NMR (CD₃CN, 500 MHz at 298 K): δ = 8.87 (s, 2H, H^{d'}), 8.79 (s, 2H, H^{d'}), 8.71 (s, 2H, H^{d'}), 8.33 (d, 2H, J = 8.3 Hz, H^{5''}), 8.05 (d, 2H, J = 8.3 Hz, H^{5''}), 7.97 (d, 2H, J = 8.3 Hz, H^{5''}), 7.95 (s, 2H, H^{1''}), 7.92 (dd, 2H, J₁ = 7.3 Hz, J₂ = 8.3 Hz, H^{6''}), 7.88 (s, 2H, H^{1''}), 7.88 (dd, 2H, J₁ = 7.3 Hz, J₂ = 8.3 Hz, H^{6''}), 7.83 (dd, 2H, J₁ = 7.3 Hz, J₂ = 8.3 Hz, H^{6''}), 7.69 (s, 2H, H^{1'}), 7.68 (d, 2H, J₁ = 7.3 Hz, H^{7''}), 7.48 (d, 2H, J₁ = 7.3 Hz, H^{7''}), 7.48 (d, 2H, J₁ = 7.3 Hz, H^{7''}), 6.83 (d, 4H, J = 8.8 Hz, H^{d'}), 6.62 (d, 4H, J = 8.7 Hz, H^{d'}), 6.56 (d, 4H, J = 8.8 Hz, H^{c'}), 6.56 (d, 4H, J = 8.4 Hz, H^{a''}), 6.48 (d, 4H, J = 6.0 Hz, H^{c'}), 6.29 (d, 4H, J = 8.7 Hz, H^{b'}), 6.19 (d, 4H, J = 6.0 Hz, H^{b'}), 6.14 (d, 4H, J = 8.4 Hz, H^{b''}), 4.34 (dd, 1H, J₁ = 5.3 Hz, J₂ = 1.6 Hz, H^{δ1}), 4.32 (dd, 1H, J₁ = 5.0 Hz, J₂ = 1.3 Hz, H^{δ2}), 4.27 (dd, 1H, J₁ = 7.1 Hz, J₂ = 1.4 Hz, H^{δ3}), 4.25 (dd, 1H, J₁ = 7.0 Hz, J₂ = 1.0 Hz, H^{δ4}), 4.21 (dd, 1H, J₁ = 6.8 Hz, J₂ = 0.8 Hz, H^{γ1}), 4.19 (dd, 1H, J₁ = 7.4 Hz, J₂ = 1.4 Hz, H^{γ2}), 4.10 (d, 1H, J₁ = 6.5 Hz, H^{α1}), 4.08 (d, 1H, J₁ = 5.0 Hz, H^{α2}), 3.97–3.91 (m, 8H, H^{α,β,γ}), 3.50 (s, 6H, H^γ), 3.47 (s, 6H, H^γ), 1.40 (s, 6H, H^ε). ES-MS: *m/z*: 900.7938 (calculated 900.8280 for C₁₁₇H₉₆FeN₆O₁₀²⁺). UV-vis, λ_{max}/nm (ε/10⁵ mol⁻¹·L·cm⁻¹): 194 (2.69), 229 (1.40), 258 (1.37), 305 (0.61), 347 (0.78), 364 (0.84), 459 (0.15). Cyclic voltammetry, E_{1/2} (V vs. SCE): + 0.99 (Fe^{3+/2+}), -1.45.

4.8. 9(PF₆)₂. A solution of Fe(BF₄)₂·6H₂O (0.0118 g, 0.0350 mmol) in 20 mL of acetonitrile was added to a solution of **2** (0.0315 g, 0.0389 mmol) in 20 mL of dichloromethane and stirred for 30 min at ambient temperature. A solution of **6** (0.0467 g, 0.0701 mmol) in 200 mL of dichloromethane was subsequently added in droplets during 3 h to the orange-red reaction mixture, and stirring was continued overnight. The solvents were evaporated under reduced pressure, and the solid residue was redissolved in an acetonitrile/water mixture (5: 2, 35 mL). Saturated aqueous KPF₆ (4 mL) was added, the organic solvent was evaporated, and the precipitate was collected and copiously washed with water. The crude product was dissolved in about 4 mL of acetone and added in droplets to 200 mL of Et₂O under stirring. The precipitate was collected by filtration, washed with Et₂O, and dried in vacuum. Yield of **9**(PF₆)₂ (red crystalline solid): 0.0733 g (0.0294 mmol - 84% calculated for Fe²⁺). C₁₂₉H₁₁₆F₁₂FeN₈O₁₄P₂ (2488.19). This compound was used for the next reaction without purification; elemental analysis was not performed. ¹H NMR (CD₃CN, 300 MHz at 298 K): δ = 8.86 (s, 2H, H^{d'}), 8.77 (s, 2H, H^{d'}), 8.70 (s, 2H, H^{d'}), 8.33 (d, 2H, J = 8.5 Hz, H^{5''}), 8.07 (d, 2H, J = 8.3 Hz, H^{5''}), 7.98–7.84 (m, 12H, H⁵, H^{5''}, H^{6''}, H^{6''}, H^{6''}, H^{6''}), 7.69 (s, 2H, H^{1'}), 7.67 (d, 2H, J₁ = 7.3 Hz, H^{7''}), 7.49 (d, 2H, J₁ = 7.1 Hz, H^{7''}), 7.49 (d, 2H, J₁ = 7.1 Hz, H^{7''}), 6.84 (d, 4H, J = 8.8 Hz, H^{d'}), 6.62 (d, 4H, J = 8.7 Hz, H^{d'}), 6.56 (d, 4H, J = 8.8 Hz, H^{c'}), 6.56 (d, 4H, J = 8.4 Hz, H^{a''}), 6.47 (d, 4H, J = 6.9 Hz, H^{c'}), 6.29 (d, 4H, J = 8.7 Hz, H^{b'}), 6.18 (d, 4H, J = 6.9 Hz, H^{b'}), 6.12 (d, 4H, J = 8.4 Hz, H^{b''}), 4.36–4.05 (m, 8H, H^{α,β,γ}), 3.98–3.90 (m, 8H, H^{α,β,γ}), 3.81–3.68 (m, 24H, H^{α,β,γ,α',β',γ',α'',β'',γ''}), 3.48 (t, 4H, J = 4.7 Hz, H^{δ'} or H^{δ''}), 3.42 (t, 4H, J = 4.8 Hz, H^{δ'} or H^{δ''}), 1.41 (s, 6H, H^ε). ES-MS: *m/z*: 1098.9099 (calculated 1098.9145 for C₁₂₉H₁₁₆FeN₈O₁₄²⁺).

4.9. 10(PF₆)₂·5H₂O. The starting reagents, **9**(PF₆)₂ (0.0700 g, 0.0281 mmol) and **7** (0.2730 g, 0.5030 mmol, ~18 equiv), were dissolved in 10 mL of dichloromethane and 0.5 mL of acetonitrile and added to a solution of sodium ascorbate (0.060 g, 0.303 mmol, ~10 equiv) in 10 mL of water under stirring. An aqueous solution

of CuSO₄ (0.1 mL (0.3 mol·L⁻¹), 0.030 mmol, ~1 equiv) was added to the degassed reaction mixture, and stirring was continued overnight (argon, ambient temperature). The reaction mixture was diluted with 50 mL of water, the organic compounds were extracted by dichloromethane (3 × 50 mL), and the combined dichloromethane phases were washed with water. The organic solvent was evaporated, and the products were separated by flash chromatography on silica: unreacted **6** was eluted by dichloromethane. Then, the eluent was changed to the mixed solvent CH₂Cl₂:CH₃OH (9: 1). The single red band containing **10**²⁺ was collected. Saturated aqueous KPF₆ (4 mL) was added, the organic solvent was evaporated. The precipitated product was collected and copiously washed with water. The crude product was dissolved in 4 mL of dichloromethane and added in droplets to 200 mL of *n*-pentane under stirring. The precipitate was collected by filtration, washed with *n*-pentane, and dried in vacuum. Yield of **10**(PF₆)₂·5H₂O (red crystalline solid): 0.1236 g (0.0265 mmol - 94%). C₂₈₉H₃₀₀F₁₂FeN₁₈O₁₈P₂·5H₂O (4749.43) calc.: C 73.08, H 6.58, N 5.31; found: C 73.28, H 6.57, N 4.90. ¹H NMR (CD₃CN, 500 MHz at 298 K): δ = 8.83 (s, 2H, H^{d'}), 8.72 (s, 2H, H^{d'}), 8.59 (s, 2H, H^{d'}), 8.28 (d, 2H, J = 8.3 Hz, H^{5''}), 7.93 (d, 2H, J = 8.3 Hz, H^{5''}), 7.90 (s, 2H, H^{1''}), 7.86–7.84 (m, 10H, H⁵, H^{5''}, H^{6''}, H^{6''}, H^{6''}, H^{6''}), 7.72–7.66 (m, 6H, H^{1'}, H^{6'}, H^{6'}), 7.58 (d, 2H, J₁ = 7.0 Hz, H^{7''}), 7.36 (d, 2H, J₁ = 7.0 Hz, H^{7''}), 7.34 (d, 2H, J₁ = 7.0 Hz, H^{7''}), 7.21 (d, 12H, J₁ = 8.6 Hz, H^{7'} or H^{7''}), 7.18 (d, 12H, J₁ = 8.6 Hz, H^{7'} or H^{7''}), 7.09 (d, 12H, J₁ = 8.6 Hz, H^{7'} or H^{7''}), 7.07 (d, 12H, J₁ = 8.6 Hz, H^{7'} or H^{7''}), 7.05 (d, 4H, J₁ = 8.6 Hz, H^{7'} or H^{7''}), 7.04 (d, 4H, J₁ = 8.6 Hz, H^{7'} or H^{7''}), 6.83 (d, 4H, J = 8.6 Hz, H^{d'}), 6.75 (d, 4H, J₁ = 8.6 Hz, H^{7'} or H^{7''}), 6.74 (d, 4H, J₁ = 8.6 Hz, H^{7'} or H^{7''}), 6.54 (d, 4H, J = 8.6 Hz, H^{c'}), 6.53 (d, 4H, J = 8.7 Hz, H^{c'}), 6.48 (d, 4H, J = 7.3 Hz, H^{a''}), 6.43 (d, 4H, J = 6.2 Hz, H^{a''}), 6.19 (d, 4H, J = 8.7 Hz, H^{b'}), 6.13 (d, 4H, J = 6.0 Hz, H^{b'}), 6.05 (d, 4H, J = 8.4 Hz, H^{b''}), 5.01 (s, 4H, H^{δ'} or H^{δ''}), 4.98 (s, 4H, H^{δ'} or H^{δ''}), 4.58 (t, 4H, J = 4.3 Hz, H^{δ'} or H^{δ''}), 4.54 (t, 4H, J = 4.3 Hz, H^{δ'} or H^{δ''}), 4.29–4.12 (m, 8H, H^{α,β,γ}), 3.98–3.54 (m, 32H, H^{α,β,γ,α',β',γ',α'',β'',γ''}), 1.39 (s, 6H, H^ε), 1.19 (s, 54H, H^{mm'} or H^{mm''}), 1.17 (s, 54H, H^{mm'} or H^{mm''}). ES-MS: *m/z*: 2184.6498 (calculated 2184.6276 for C₂₈₉H₃₀₀FeN₁₈O₁₈²⁺). UV-vis, λ_{max}/nm (ε/10⁵ mol⁻¹·L·cm⁻¹): 196 (5.45), 258 (1.40), 308 (0.68), 347 (0.78), 365 (0.83), 462 (0.15). Cyclic voltammetry, E_{1/2} (V vs. SCE): + 1.00 (Fe^{3+/2+}), -1.44.

4.10. 8,8'-(4-(2-(2-(4-((4-(Tris(4-tert-butylphenyl)methyl)phenoxy)methyl)-1H-1,2,3-triazol-1-yl)ethoxy)ethoxy)phenyl)-3,3'-biisoquinoline (11). A solution of **10**(PF₆)₂·5H₂O (0.1000 g, 0.021 mmol) in 250 mL of DMF was added for 48 h to a hot (70 °C, under argon) suspension of Cs₂CO₃ (3.0 g, 9.2 mmol) in 300 mL of DMF under vigorous stirring. When the addition of the complex was finished, the dropping funnel was rinsed with 20 mL of DMF, another portion of Cs₂CO₃ (3.0 g, 9.2 mmol) was added, and the heating under stirring was continued for 48 h. The cold reaction mixture was filtrated, the solid on the filter was rinsed with CH₂Cl₂, and the combined organic solution was evaporated until dryness, yielding reddish oil. The products were separated by chromatography on silica (CH₂Cl₂/CH₃OH, 99:1). Yields: **2** - 0.0136 g (0.0168 mmol, 78%), **11** - 0.0666 g (0.038 mmol, 89%). Analytical data for **11**: ¹H NMR (CD₂Cl₂, 300 MHz at 298 K): δ = 9.42 (s, 2H, H^{1'}), 8.97 (s, 2H, H^{4'}), 7.94 (d, 2H, J = 8.2 Hz, H^{5''}), 7.88 (s, 2H, H^{5''}), 7.70 (dd, 2H, J₁ = 8.2 Hz, J₂ = 7.2 Hz, H^{6''}), 7.50 (d, 2H, J₁ = 7.2 Hz, H^{7''}), 7.49 (d, 4H, J = 8.6 Hz, H^{a''}), 7.23 (d, 12H, J = 8.6 Hz, H^{7'}), 7.15 (d, 4H, J = 9.0 Hz, H^{7'}), 7.13 (d, 12H, J = 8.6 Hz, H^{7'}), 7.08 (d, 4H, J = 8.6 Hz, H^{b'}), 6.87 (d, 4H, J = 9.0 Hz, H^{7'}), 5.14 (s, 4H, H^{δ'}), 4.61 (t, 4H, J = 4.9 Hz, H^{δ'}), 4.19 (t, 4H, J = 4.5 Hz, H^{δ'}), 3.99 (t, 4H, J = 4.9 Hz, H^{γ'}), 3.88 (t, 4H, J = 4.5 Hz, H^{δ'}), 1.28 (s, 54H, H^{mm'}). MALDI-TOF: *m/z*: 1753.6632 ([M + 1]⁺, C₁₁₈H₁₂₇N₈O₆⁺; calc. 1752.9878).

4.11. 12(ClO₄)₂. A solution of Co(ClO₄)₂·6H₂O (0.026 g, 0.0711 mmol) in 25 mL of methanol was added to a solution of **5** (0.100 g, 0.213 mmol) in 25 mL of chloroform and stirred for 30 min at ambient temperature until crystallization of the product started. The volume of the reaction mixture was reduced to about 10 mL by

rotary evaporation, and the product was collected, washed on a filter with methanol, and dried on air. Yield: 0.106 g (0.0637 mmol, 90%). *Note:* Elemental analysis was not performed because perchlorates are *potentially explosive*. Large crystals were obtained when the reaction mixture was left without stirring in a closed vessel for several days. According to ^1H NMR data, the crystals contain CHCl_3 as solvate molecules. Crystals of $\mathbf{12}(\text{ClO}_4)_2 \cdot n\text{CHCl}_3$ are not stable—solvent molecules can be lost, and the crystals turn to powder upon drying. ^1H NMR (CD_3CN , 300 MHz, signal 7.24 ppm from crystal–solvate molecules of CHCl_3 as a reference): δ = 123.55 (s, 6H), 74.70 (s, 6H), 10.62 (d, 6H, J = 7.1 Hz, H^7), 10.10 (dd, 6H, J_1 = 8.4 Hz, J_2 = 7.1 Hz, H^9), 9.07 (d, 6H, J_1 = 8.4 Hz, H^5), 2.79 (s, 12H), 1.95 (s, 18H, H^f), 0.54 (s, 12H). ES-MS: m/z : 732.257 (calculated 732.746 for $\text{C}_{96}\text{H}_{72}\text{CoN}_6\text{O}_6^{2+}$). UV–vis, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$): 193 (1.62), 225 (0.91), 259 (1.17), 302 (0.55), 346 (0.40), 370 (0.35).

X-ray quality crystals of $\mathbf{12}(\text{ClO}_4)_2 \cdot \text{CO}(\text{CH}_3)_2$ were grown by slow diffusion of di-isopropyl ether in acetone. Crystal data: M = 1721.51, orange plate, $0.40 \times 0.30 \times 0.15 \text{ mm}^3$, triclinic, space group $P\bar{1}$, a = 13.9680(4) Å, b = 16.0410(3) Å, c = 20.7350(6) Å, α = 103.808(2)°, β = 98.2280(1)°, γ = 101.688(2)°, V = 4327.61(19) Å³, Z = 2, ρ_{calcd} = 1.321 g·cm^{−3}, F_{000} = 1790, Mo $K\alpha$ radiation, λ = 0.71073 Å, μ = 0.331 mm^{−1}, T = 173(2) K, θ_{max} = 27.51°, 41339 reflections collected, 19615 unique (R_{int} = 0.0730), 13812 with $I_0 > 2\sigma(I_0)$, structure solved by SHELXS-97³⁷ and refined with SHELXL-97³⁸ full-matrix least-squares on F^2 , 1174 parameters, 0 restraints, GoF = 1.102, R_1 = 0.0642, wR_2 = 0.1918 (all reflections), $-1.283 < \Delta\rho < 1.312 \text{ e} \cdot \text{Å}^{-3}$.

4.12. $\mathbf{12}(\text{PF}_6)_3 \cdot 3\text{H}_2\text{O}$. A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0207 g, 0.0711 mmol) in 25 mL of acetonitrile was added to the solution of **5** (0.1000 g, 0.213 mmol) in 25 mL of chloroform and stirred for 10 min at ambient temperature. A solution of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (0.0390 g, 0.0711 mmol) in 25 mL of acetonitrile was added to the clear yellow reaction mixture in droplets over a period of 15 min, and stirring was continued for 15 min. (*Note:* Precipitation of unidentified orange solid was observed.) The organic solvents were evaporated under reduced pressure, and the solid residue was redissolved in an acetonitrile/water mixture (5:2, 35 mL). Saturated aqueous solution of KPF_6 (4 mL) was added, the organic solvent was evaporated, and the precipitate of the product was collected and copiously washed with water. The complex was dissolved in an acetone/water mixture (1:1, 80 mL) containing excess of KPF_6 and KNO_3 , and the solution was left for slow evaporation at ambient temperature. Large orange crystals were collected in several days, washed with water, and dried in air. Yield: 0.125 g (0.064 mmol, 90%). $\text{C}_{96}\text{H}_{72}\text{CoF}_{18}\text{N}_6\text{O}_6\text{P}_3 \cdot 3\text{H}_2\text{O}$ (1953.51) calc.: C 59.02, H 4.02, N 4.30; found: C 58.84, H 4.01, N 4.23. ^1H NMR (CD_3CN , 300 MHz): δ = 9.20 (s, 6H, H^f), 8.22 (d, 6H, J = 8.2 Hz, H^7), 8.10 (dd, 6H, J_1 = 8.2 Hz, J_2 = 7.1 Hz, H^9), 7.64 (d, 6H, J_1 = 7.1 Hz, H^7), 7.46 (s, 6H, H^f), 6.69 (d, 12H, J = 8.6 Hz, H^a), 6.53 (d, 12H, J = 8.6 Hz, H^b), 3.68 (s, 18H, OMe). ES-MS: m/z : 1754.427 (calculated 1754.416 for $\text{C}_{96}\text{H}_{72}\text{CoF}_{12}\text{N}_6\text{O}_6\text{P}_2^+$). UV–vis, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$): 194 (1.91), 242 (1.42), 259 (1.43), 318 (0.46), 371 (0.47), 390 (0.50). Cyclic voltammetry, $E_{1/2}$ (V vs SCE): + 0.16 ($\text{Co}^{3+/2+}$), −0.99.

X-ray quality crystals of $\mathbf{12}(\text{PF}_6)_3 \cdot 2\text{CO}(\text{CH}_3)_2$ were grown by slow diffusion of di-isopropyl ether in acetone. Crystal data: M = 2131.75, orange prism, $0.40 \times 0.30 \times 0.20 \text{ mm}^3$, monoclinic, space group $C2/c$, a = 31.0363(5) Å, b = 13.1163(2) Å, c = 27.6377(6) Å, β = 117.889(1)°, V = 9944.1(3) Å³, Z = 4, ρ_{calcd} = 1.424 g·cm^{−3}, F_{000} = 4400, Mo $K\alpha$ radiation, λ = 0.71073 Å, μ = 0.318 mm^{−1}, T = 173(2) K, θ_{max} = 27.49°, 27572 reflections collected, 11272 unique (R_{int} = 0.0653), 6081 with $I_0 > 2\sigma(I_0)$, structure solved by SHELXS-97³⁷ and refined with SHELXL-97³⁸ full-matrix least-squares on F^2 , 634 parameters, 0 restraints, GoF = 1.073, R_1 = 0.0880, wR_2 = 0.2969 (all reflections), $-1.219 < \Delta\rho < 1.016 \text{ e} \cdot \text{Å}^{-3}$.

4.13. $\mathbf{13}(\text{PF}_6)_3$. A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0091 g, 0.0312 mmol) in 20 mL of acetonitrile was added to a solution

of **2** (0.0280 g, 0.0346 mmol) in 20 mL of dichloromethane and stirred for 30 min at ambient temperature. A solution of **5** (0.0292 g, 0.0623 mmol) in 200 mL of dichloromethane was added drop by drop during 3 h to the yellow reaction mixture, and stirring was continued overnight. A solution of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (0.0171 g, 0.0312 mmol) in 20 mL of acetonitrile was added drop by drop, solvents were evaporated under reduced pressure, and the solid residue was redissolved in acetonitrile: water mixture (5: 2, 35 mL). A saturated aqueous solution of KPF_6 (4 mL) was added, the organic solvent was evaporated, and the precipitate of the product was collected and copiously washed with water. Chromatography on silica (acetone/water/ KNO_3 sat. − 70:5:0.3), ion-exchange with KPF_6 , and precipitation by ether from the solution in acetone afforded yielded a pure complex as an orange crystalline solid. Yield: 0.062 g (89%). $\text{C}_{117}\text{H}_{96}\text{F}_{18}\text{CoN}_6\text{O}_{10}\text{P}_3 \cdot 3\text{H}_2\text{O}$ (2293.92) calc.: C 61.26, H 4.48, N 3.66; found: C 61.29, H 4.90, N 3.45. ^1H NMR (CD_3CN , 500 MHz at 298 K): δ = 9.15 (s, 2H, H^f), 9.10 (s, 2H, H^f), 9.09 (s, 2H, $H^{f'}$), 8.51 (d, 2H, J = 8.3 Hz, $H^{5''}$), 8.22 (d, 2H, J = 8.3 Hz, $H^{5'}$), 8.20 (d, 2H, J = 8.3 Hz, H^5), 8.19 (dd, 2H, J_1 = 7.3 Hz, J_2 = 8.3 Hz, $H^{6''}$), 8.11 (dd, 2H, J_1 = 7.3 Hz, J_2 = 8.3 Hz, $H^{6'}$), 8.10 (dd, 2H, J_1 = 7.3 Hz, J_2 = 8.3 Hz, H^6), 7.88 (d, 2H, J_1 = 7.3 Hz, $H^{7''}$), 7.67 (d, 2H, J_1 = 7.3 Hz, H^7), 7.67 (d, 2H, J_1 = 7.3 Hz, $H^{7'}$), 7.58 (s, 2H, $H^{f'}$), 7.48 (s, 2H, $H^{f''}$), 7.40 (s, 2H, H^f), 6.86 (d, 4H, J = 8.8 Hz, H^a), 6.72 (d, 4H, J = 8.7 Hz, H^a), 6.59 (d, 4H, J = 8.8 Hz, H^a), 6.58 (d, 4H, J = 8.7 Hz, $H^{a'}$), 6.55 (d, 4H, J = 8.0 Hz, H^a), 6.47 (d, 4H, J = 8.7 Hz, H^b), 6.41 (d, 4H, J = 8.0 Hz, H^b), 6.35 (d, 4H, J = 8.7 Hz, $H^{b'}$), 4.33 (m, 2H, $H^{\delta 1+\delta 2}$), 4.26 (m, 2H, $H^{\delta 3+\delta 4}$), 4.18 (m, 2H, $H^{\gamma 1+\gamma 2}$), 4.09 (m, 2H, $H^{\alpha 1+\alpha 2}$), 4.01–3.91 (m, 8H, $H^{\alpha,\beta,\gamma}$), 3.65 (s, 6H, H^f), 3.62 (s, 6H, $H^{f'}$), 1.42 (s, 6H, H^e). ES-MS: m/z : 2094.648 (calculated 2094.583 for $\text{C}_{117}\text{H}_{96}\text{F}_{12}\text{CoN}_6\text{O}_{10}\text{P}_3^+$). UV–vis, $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/10^5 \text{ mol}^{-1} \cdot \text{L} \cdot \text{cm}^{-1}$): 195 (2.48), 235 (1.46), 241 (1.45), 260 (1.44), 318 (0.46), 371 (0.48), 390 (0.51). Cyclic voltammetry, $E_{1/2}$ (V vs. SCE): + 0.14 ($\text{Co}^{3+/2+}$), −1.01.

X-ray quality crystals of $\mathbf{13}(\text{PF}_6)_3 \cdot 2\text{CO}(\text{CH}_3)_2$ were grown by slow diffusion of di-isopropyl ether in acetone. Crystal data: M = 2355.99, orange needle, $0.40 \times 0.15 \times 0.10 \text{ mm}^3$, triclinic, space group $P\bar{1}$, a = 13.4954(3) Å, b = 19.0943(6) Å, c = 25.8961(8) Å, α = 89.2340(10)°, β = 78.448(2)°, γ = 84.786(2)°, V = 6510.7(3) Å³, Z = 2, ρ_{calcd} = 1.202 g·cm^{−3}, F_{000} = 2436, Mo $K\alpha$ radiation, λ = 0.71073 Å, μ = 0.251 mm^{−1}, T = 173(2) K, θ_{max} = 27.45°, 80608 reflections collected, 29651 unique (R_{int} = 0.1692), 9949 with $I_0 > 2\sigma(I_0)$, structure solved by SHELXS-97³⁷ and refined with SHELXL-97³⁸ full-matrix least-squares on F^2 , 1452 parameters, 0 restraints, GoF = 1.117, R_1 = 0.1465, wR_2 = 0.4388 (all reflections), $-0.869 < \Delta\rho < 2.173 \text{ e} \cdot \text{Å}^{-3}$.

4.15. $\mathbf{14}(\text{PF}_6)_3$. A solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0094 g, 0.032 mmol) in 20 mL of acetonitrile was added to a solution of **2** (0.0291 g, 0.036 mmol) in 20 mL of dichloromethane and stirred for about 30 min at ambient temperature. A solution of **6** (0.0432 g, 0.065 mmol) in 200 mL of dichloromethane was added in droplets during 3 h to the orange-red reaction mixture and stirring was continued overnight. A solution of $(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (0.0213 g, 0.039 mmol) in 20 mL of acetonitrile was added drop by drop, the solvents were evaporated under reduced pressure, and the solid residue was redissolved in acetonitrile: water mixture (5: 2, 35 mL). A saturated aqueous solution of KPF_6 (4 mL) was added, the organic solvent was evaporated, and the precipitate of the product was collected and copiously washed with water. The crude product was dissolved in 4 mL of acetone and added drop by drop to 200 mL of *n*-pentane under stirring. The precipitate was collected by filtration, washed with *n*-pentane, and dried on air. Yield of $\mathbf{13}(\text{PF}_6)_3$ (orange crystalline solid): 0.0704 g (0.027 mmol - 82% calculated for Co^{2+}). $\text{C}_{129}\text{H}_{116}\text{F}_{18}\text{CoN}_8\text{O}_{14}\text{P}_3$ (2636.24). The compound was used for the next reaction without purification; elemental analysis was not performed. ^1H NMR (CD_3CN , 300 MHz at 298 K): δ = 9.16 (s, 2H, H^f), 9.12 (s, 2H, $H^{f'}$), 9.09 (s, 2H, H^f), 8.50 (d, 2H, J = 8.2 Hz, $H^{5''}$), 8.25–8.11 (m, 10H, $H^{5'}$, H^5 , $H^{6''}$, $H^{6'}$, H^6), 7.88 (d, 2H,

$J_1 = 7.1$ Hz, H''), 7.66 (d, 4H, $J_1 = 7.1$ Hz, H' , H''), 7.59 (s, 2H, H'), 7.45 (s, 2H, H''), 7.39 (s, 2H, H'), 6.84 (d, 4H, $J = 8.8$ Hz, H^d), 6.72 (d, 4H, $J = 8.8$ Hz, H^a), 6.59–6.51 (m, 12H, H^c , $H^{a'}$, H^a), 6.47 (d, 4H, $J = 8.8$ Hz, H^b), 6.40 (d, 4H, $J = 8.8$ Hz, H^b), 6.35 (d, 4H, $J = 8.8$ Hz, $H^{b'}$), 4.35–4.16 (m, 8H, $H^{\alpha,\beta,\gamma}$), 4.05–3.96 (m, 8H, $H^{\alpha,\beta,\gamma}$), 3.91–3.75 (m, 24H, $H^{\alpha,\beta,\gamma,\alpha',\beta',\gamma'}$), 3.52 (t, 4H, $J = 4.7$ Hz, H^{δ} or $H^{\delta'}$), 3.48 (t, 4H, $J = 4.7$ Hz, H^{δ} or $H^{\delta'}$), 1.40 (s, 6H, H^e). ES-MS: m/z : 1172.9617 (calculated 1173.3982 for $C_{129}H_{116}F_6FeN_{18}O_{14}P_2^{2+}$).

4.15. $15(PF_6)_3$. The starting reagents, a sample of crude **14**(PF_6)₃ (0.070 g, 0.027 mmol) and **7** (0.2153 g, 0.397 mmol, ~ 14.8 equiv), were dissolved in 10 mL of dichloromethane and 0.5 mL of acetonitrile, and added to a solution of sodium ascorbate (0.060 g, 0.303 mmol, ~ 10 equiv) in 10 mL of water under stirring. Then, an aqueous saturated solution of KPF₆ (0.5 mL) was added, and the mixture was degassed and put under argon. An aqueous solution of CuSO₄ (0.1 mL (0.3 mol·L⁻¹), 0.030 mmol, ~ 1 equiv) was added, and stirring was continued overnight (argon, ambient temperature). The organic solvent was evaporated under reduced pressure. The oily precipitate was collected and copiously washed with water. Then it was dissolved in 50 mL of dichloromethane and mixed with 50 mL of an aqueous solution containing Na₃HEEDTA (3.5 g, 10.2 mmol, ~ 330 equiv) and sodium ascorbate (0.060 g, 0.303 mmol, ~ 10 equiv). The reaction mixture was stirred vigorously for 5 h at ambient temperature, dichloromethane was evaporated without heating, and the oily precipitate was collected. For ion-exchange, the precipitate was redissolved in CH₂Cl₂: CH₃CN (1: 1, 20 mL), and precipitated again using an aqueous saturated solution of KPF₆ (4 mL). After removing of the organic solvents and filtration, the precipitate was copiously washed with water and dried. It was dissolved in dichloromethane and absorbed on silica column. The column was washed with dichloromethane to remove unreacted **7**. Then the eluent was changed to mixture CH₂Cl₂/CH₃OH (99:1), and a single strongly fluorescent band was eluted. Evaporation of this eluate resulted in 0.023 g (0.0132 mmol) of pure **11** indicating that at least 25% of the starting **6** were bound into the homoleptic complex. Finally, the polarity of the eluent was increased (CH₂Cl₂: CH₃OH (9: 1)), and a single yellow band containing **15**²⁺ was collected. The solvents were evaporated, the solid was dissolved in dichloromethane in a 20 mL measuring flask, and the solution was separated into two 10 mL portions which were treated separately.

The first portion of **15**²⁺ solution (10 mL) was treated with (NH₄)₂[Ce(NO₃)₆] (0.0204 g, 0.0372 mmol) in 20 mL of acetonitrile. Then a saturated aqueous solution of KPF₆ (4 mL) was added, the organic solvent was evaporated, and the precipitate of the product was collected and copiously washed with water. The product was dissolved in 4 mL of dichloromethane and added dropwise to 200 mL of *n*-pentane under stirring. The precipitate was collected by filtration, washed with *n*-pentane, and dried in vacuum. Yield of **15**(PF_6)₃ (yellow crystalline solid): 0.0434 g (0.0093 mmol - 70% calculated for the starting **2**). C₂₈₉H₃₀₀F₁₈CoN₁₈O₁₈P₃·5H₂O (4897.49) calc.: C 70.87, H 6.38, N 5.15; found: C 70.57, H 6.20, N 4.83. ¹H NMR (CD₃CN, 500 MHz at 298 K): $\delta = 9.25$ (s, 2H, H^d), 9.14 (s, 2H, H^d), 9.12 (s, 2H, $H^{d'}$), 8.48 (d, 2H, $J = 8.3$ Hz, $H^{d'}$), 8.16 (d, 2H, $J = 8.3$ Hz, H^d or $H^{d'}$), 8.12 (dd, 2H, $J_1 = 7.2$ Hz, $J_2 = 8.3$ Hz, $H^{d'}$), 8.11 (d, 2H, $J = 8.3$ Hz, H^d or $H^{d'}$), 7.94 (s, 2H, $H^{d'}$ or $H^{d'}$), 7.94 (dd, 2H, $J_1 = 7.2$ Hz, $J_2 = 8.3$ Hz, H^d or $H^{d'}$), 7.92 (dd, 2H, $J_1 = 7.2$ Hz, $J_2 = 8.3$ Hz, H^d or $H^{d'}$), 7.91 (s, 2H, $H^{d'}$ or $H^{d'}$), 7.81 (d, 2H, $J = 7.2$ Hz, $H^{d'}$), 7.53 (s, 2H, H^d), 7.53 (d, 2 × 2H, $J = 7.2$ Hz, H^d or $H^{d'}$), 7.39 (s, 2 × 2H, H^d or $H^{d'}$), 7.24 (d, 12H, $J_1 = 8.6$ Hz, H^d or $H^{d'}$), 7.21 (d, 12H, $J_1 = 8.6$ Hz, H^d or $H^{d'}$), 7.10 (d, 12H, $J_1 = 8.6$ Hz, $H^{d'}$ or $H^{d'}$), 7.07 (d, 12H, $J_1 = 8.6$ Hz, H^d or $H^{d'}$), 7.07 (d, 4H, $J_1 = 8.6$ Hz, H^d or $H^{d'}$), 7.03 (d, 4H, $J_1 = 8.6$ Hz, H^d or $H^{d'}$), 6.83 (d, 4H, $J = 8.6$ Hz, H^d), 6.77 (d, 4H, $J_1 = 8.6$ Hz, H^d or $H^{d'}$), 6.73 (d, 4H, $J_1 = 8.6$ Hz, H^d or $H^{d'}$), 6.67 (d, 4H, $J = 8.6$ Hz, H^d), 6.55 (d, 4H, $J = 8.6$ Hz, H^c), 6.52 (d, 4H, $J = 8.6$ Hz, H^a), 6.50 (d, 4H, $J = 8.6$ Hz, $H^{a'}$), 6.42 (d, 4H, $J = 8.7$ Hz, H^b), 6.36 (d, 4H, $J = 6.0$ Hz, H^b), 6.29 (d, 4H, $J = 8.4$ Hz,

$H^{b'}$), 5.04 (m, 8H, H^e , and $H^{e'}$), 4.65–4.58 (m, 8H, H^{δ} and $H^{\delta'}$), 4.28–4.10 (m, 8H, $H^{\alpha,\beta,\gamma}$), 4.05–3.70 (m, 32H, $H^{\alpha,\beta,\gamma,\alpha',\beta',\gamma'}$), 1.38 (s, 6H, H^e), 1.24 (s, 54H, $H^{m'}$ or $H^{m''}$), 1.22 (s, 54H, $H^{m'}$ or $H^{m''}$). ES-MS: m/z : 1457.3502 (calculated 1457.4175 for C₂₈₉H₃₀₀CoN₁₈O₁₈³⁺). UV-vis, λ_{max}/nm ($\epsilon/10^5$ mol⁻¹·L·cm⁻¹): 196 (5.73), 241 (1.93), 260 (1.57), 318 (0.46), 371 (0.47), 390 (0.43). Cyclic voltammetry, $E_{1/2}$ (V vs SCE): + 0.15 (Co^{3+/2+}), -1.00.

4.16. **16.** The second portion of **15**²⁺ solution (10 mL) (*vide supra*) was evaporated to dryness and redissolved in 60 mL of DMSO. At ambient temperature, the **15**²⁺ solution was added slowly added for 2 h to a solution of Na₃HEEDTA (6 g, 17.4 mmol, ~ 1120 equiv) in a mixture of solvents: water (20 mL), methanol (20 mL), and DMSO (40 mL) under vigorous stirring. The mixture was cooled in an ice bath and slowly diluted with 200 mL of cold water while stirring. The **16** was extracted with dichloromethane (4 × 50 mL), the organic phase was washed with water, dried over MgSO₄, evaporated under reduced pressure without heating, and dried in vacuum. Yield: 0.0380 g. (0.0088 mmol, 66% calculated for the starting **2**). ¹H NMR (CD₃CN, 500 MHz at 298 K): $\delta = 9.31$ (s, 4H, H^d), 9.23 (s, 2H, H^d), 8.85 (s, 4H, $H^{d'}$), 8.22 (s, 2H, H^d), 7.92 (s, 4H, $H^{d'}$), 7.82 (d, 4H, $J = 8.1$ Hz, $H^{d'}$), 7.81 (d, 2H, $J = 8.1$ Hz, $H^{d'}$), 7.65 (dd, 2H, $J_1 = 7.2$ Hz, $J_2 = 8.1$ Hz, $H^{d'}$), 7.57 (dd, 4H, $J_1 = 7.2$ Hz, $J_2 = 8.1$ Hz, $H^{d'}$), 7.49 (d, 2H, $J = 7.2$ Hz, $H^{d'}$), 7.34 (d, 4H, $J = 7.2$ Hz, $H^{d'}$), 7.32 (d, 4H, $J = 8.6$ Hz, H^c), 7.23 (d, 8H, $J = 8.6$ Hz, H^a), 7.21 (d, 24H, $J = 8.7$ Hz, H^b), 7.13 (d, 4H, $J = 8.6$ Hz, H^d), 7.12 (d, 8H, $J = 9.0$ Hz, $H^{b'}$), 7.11 (d, 24H, $J = 8.7$ Hz, $H^{b'}$), 7.10 (d, 4H, $J = 8.6$ Hz, $H^{b'}$), 7.06 (d, 8H, $J = 9.0$ Hz, $H^{b'}$), 6.91 (d, 4H, $J = 8.6$ Hz, H^c), 6.70 (d, 8H, $J = 9.0$ Hz, H^e), 4.97 (s, 8H, $H^{e'}$), 4.44 (t, 8H, $J = 5.0$ Hz, $H^{e'}$), 4.13 (t, 4H, $J = 4.8$ Hz, H^a), 4.00 (t, 8H, $J = 4.8$ Hz, $H^{a'}$), 3.96 (t, 4H, $J = 4.5$ Hz, H^b), 3.85 (t, 4H, $J = 4.5$ Hz, $H^{b'}$), 3.81 (t, 8H, $J = 5.0$ Hz, $H^{b'}$), 3.81 (t, 4H, $J = 4.8$ Hz, H^b), 3.66 (t, 8H, $J = 4.8$ Hz, $H^{b'}$), 1.55 (s, 6H, H^e), 1.26 (s, 108H, $H^{m'}$). MALDI-TOF: m/z : 4313.6797 ([M]⁺, C₂₈₉H₃₀₀N₁₈O₁₈⁺; calc. 4313.3112).

In a kinetic ¹H NMR experiment, a sample of **16** (10 mg) was dissolved in 0.7 mL of CD₂Cl₂ and treated as described in the Discussion section (*vide supra*). As no internal standard was added, the ¹H NMR kinetic data were analyzed according to the following considerations: (i) Ratio of the actual concentration of [3]rotaxane (C) to the initial concentration of this species (C₀) is equal to the ratio between the relative integral intensities of the signals at 4.97 ppm in the corresponding ¹H NMR spectrum (I^A) and those in the spectrum of the starting solution (I_0^A), i.e. $(C)/(C_0) = (I^A)/(I_0^A)$; (ii) the sum of the absolute integral intensities of the signals at 4.97 ppm (I^A) and at 5.13 ppm (I^B) defines a relative intensity as $I^* = (I^A)/(I^A + I^B)$; (iii) for each set of data, the ratio of the concentrations was calculated according to the formula: $(C)/(C_0) = (I^A(I_0^A + I_0^B))/(I_0^A(I^A + I^B))$. The integral I^A was always taken in intervals from 4.940 to 4.986 ppm. Analogously, I^B was taken in intervals from 5.104 to 5.160 ppm. For simplicity, the values of I^B were set as the references (e.g., $I^B = 1.00$) for each spectrum.

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Supporting Information Available: Crystallographic information files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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