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Iron(II)-Templated Synthesis of [3]Rotaxanes by Passing Two Threads through the Same Ring

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Catenanes and rotaxanes continue to attract much attention either as synthetic challenges¹ or in relation to functional compounds and materials.² The field of controlled dynamic systems, often referred to as “molecular machines”, seems to be particularly important since, potentially, practical applications may be discovered for these molecules or molecular assemblies, for example in the field of information storage and processing.³ The templated synthesis of 2-component catenanes and rotaxanes has revealed remarkably efficient, either based on transition metals⁴ or on organic templates.⁵ Several examples of topologically more complex molecules have also been reported, some of them being prepared in an efficient way from several precursor fragments.⁶ Among them, $[n]$ rotaxanes ($n > 2$) represent a subclass of interesting compounds.^{7a} $[n]$ -Rotaxanes generally consist of $n - 1$ rings threaded on the same thread,^{7b} as in the case of cyclodextrin-based rotaxanes.^{7c} As far as we know, most of the systems with more than one thread passing through the ring(s) are restricted to nonstoppered inclusion complexes,⁸ whereas only one example of real [3]rotaxane has been reported.^{8d} We would now like to report that the use of an octahedral transition metal as template allows high yield synthesis of two-string [3]rotaxanes.

The metal is used in a novel “gathering and threading” approach, 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.”⁹

The principle of the single threading reaction, based on copper(I)⁹ is represented in Figure 1 as well as that of the presently reported double threading process. It should be noted that the first reaction leads to a two-component entanglement, one of the components being cyclic (a), whereas the second reaction leads to an entanglement consisting of three components: a ring and two acyclic fragments (b).

The various ligands used in the “gathering and threading” process are represented in Figure 2. Some of them have already been recently described.^{10,11} The key feature of these 3,3'-biisoquinoline-based ligands is their endotopic or endocyclic nature combined with their nonsterically hindering nature.^{12a} The 3,3'-biisoquinoline (biiq) backbone is such that the two aromatic groups introduced at the 8 and 8' positions (8,8'-diphenyl-3,3'-biisoquinoline = dpbiiq) are sufficiently remote from the coordination site so as not to sterically interfere with it or do it in a very limited fashion only. Compound **1** has been shown to form octahedral complexes with Fe(II) or Ru(II) in high yield.¹² Ligand **2** is a modified version of **1** but the adjunction of two azide-functionalized chains will allow post-threading chemical modifications, toward the synthesis of rotaxanes.

The threading reaction of two equivalents of **1** through one equivalent of **3** was carried out in the following way: an CH₃CN solution of Fe(BF₄)₂·6H₂O (1 equiv) was added to a CH₂Cl₂ solution of ring **3** (1.1 equiv) at ambient temperature. Then 2 equiv of **1**

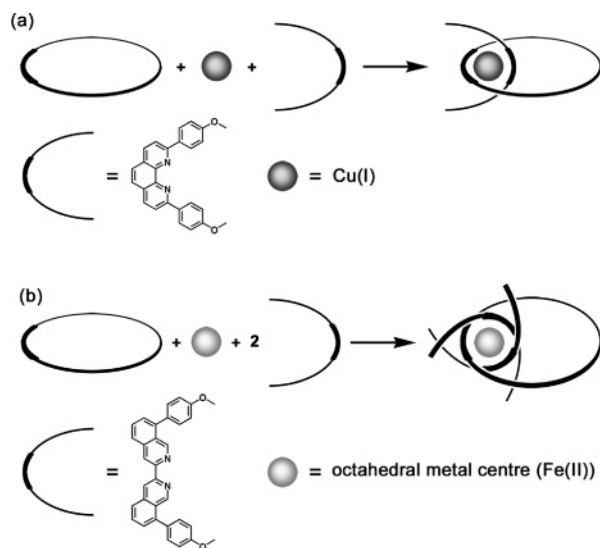


Figure 1. Principle of the threading reactions: (a) copper(I)-induced threading reactions leading to a [2]prerotaxane and (b) double-threading reaction driven by coordination of the ligands to an octahedral metal center such as Fe(II).

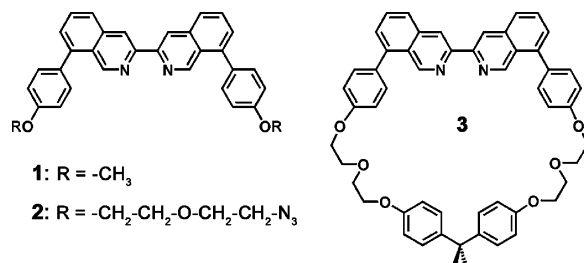


Figure 2. The ligands used for the threading reactions.

dissolved in CH₂Cl₂ was added drop by drop to the mixture. The workup led to an 82% yield of the three-ligand iron(II) complex **4**²⁺ (**4**²⁺ = [Fe(**3**)(**1**)₂]²⁺, Figure 3) as a red solid (PF₆⁻ salt). Following exactly the same procedure with **2** instead of **1**, the threaded compound [**5**²⁺][PF₆]₂ (**5**²⁺ = [Fe(**3**)(**2**)₂]²⁺) was prepared in 80% yield. To check whether Fe(II) complexes of the present family resist organic chemical reactions, we investigated the “click” chemistry¹³ applied to end-functionalization of the two threads of complex **5**²⁺. [**5**²⁺][PF₆]₂ was thus reacted with the propargyl derivative **6**,¹⁴ (Figure 3) in presence of copper(II) sulfate and sodium ascorbate, in a biphasic medium (CH₂Cl₂/CH₃CN/H₂O, 10:0.5:10). The tetratriazole derivative [**7**²⁺][PF₆]₂ was obtained in good yield (94%) after workup and chromatography, as a red solid. It has been fully characterized by the classical analytical techniques.

The kinetic stability of the complexes obtained is surprisingly high. Drastic demetalation conditions which lead to fast and

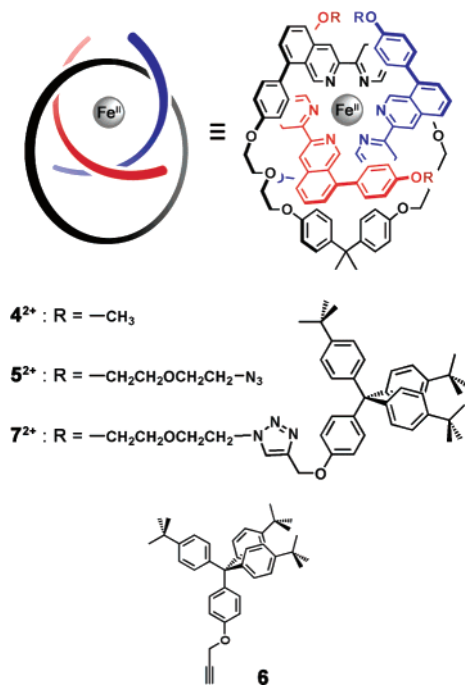


Figure 3. Two-string iron(II)-complexes: [3]pseudorotaxane 4^{2+} , [3]prerotaxane 5^{2+} , its stoppered analogue 7^{2+} , and the stoppering reagent **6**.

quantitative decooordination of the bipy ligands in $[\text{Fe}(\text{bipy})_3]^{2+}$ (bipy: 2,2'-bipyridine) are totally inefficient with 4^{2+} or 7^{2+} .¹⁵ This stabilization originates from metal center protection insured by the six aryl groups present in the three dpbiq-chelates. Although they do not prevent easy formation of octahedral complexes, these six aromatic nuclei form a remote organic layer^{12c} which strongly protects the metal center and shields it from potential aggressors.

In conclusion, a double threading principle has been presented and illustrated by two examples. The compatibility of the here reported Fe(II) complexes with copper(I)-catalyzed Huisgen 1,3-dipolar cycloaddition ("click" chemistry, developed by Sharpless, Medal and their co-workers¹³) is promising in relation to the synthesis of two-string [3]rotaxanes. The extremely high kinetic inertness of the complexes is an interesting property related to the structure of the dpbiq ligand.^{12d} The study of other transition metals¹⁶ and the use of the doubly threaded compounds presently described for generating new rotaxanes and catenanes is in progress.

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Supporting Information Available: Experimental details, spectral characterization data of all new iron(II) complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) For instance: the complex 4^{2+} was treated with a large excess of trisodium HEEDTA (0.1 M, $\text{CH}_3\text{OH}:\text{CH}_2\text{Cl}_2$, 1:1, room temp); decrease in intensity of color ($\lambda_{\text{max}} = 460$ nm) was negligible even after two weeks. Under the same conditions $[\text{Fe}(\text{bipy})_3]^{2+}$ was completely decomposed within 20 min.
- (16) A sample of the metal-free two-string [3]rotaxane has been obtained by decomplexation of the corresponding cobalt(II) complex with the same organic backbone as 7^{2+} . The free [3]rotaxane is stable in the solid state but it decomposes slowly in CD_2Cl_2 solution. Preliminary ^1H NMR data show that the half-dethreading time is ca. 90 h at 20°C (for comparison, see also: Saito, S.; Nakazono, K.; Takahashi, E. *J. Org. Chem.* **2006**, 71, 7477–7480). Detailed description of the synthesis of the cobalt(II) complex and its properties will be reported in a full paper.

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