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Transition-metal Template Synthesis of a Rotaxane Incorporating Two Different Coordinating Units in its Thread

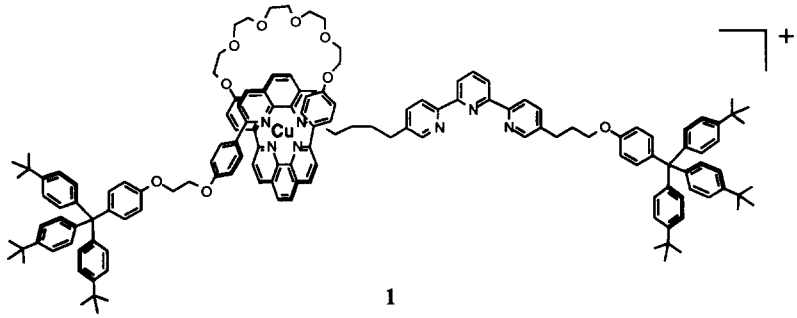
Pablo Gaviña and Jean-Pierre Sauvage*

Laboratoire de Chimie Organo-Minérale, associé au CNRS, Faculté de Chimie,
Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg, France

Abstract: A [2]rotaxane consisting of a molecular string threaded into a coordinating ring by means of the template effect of copper (I) has been synthesized. The acyclic fragment incorporates two different chelating sites (bidentate and terdentate ligands) whereas the macrocycle bears a bidentate chelate. Two bulky groups have been covalently attached at the ends of the thread. © 1997 Elsevier Science Ltd.

A [2]rotaxane is a molecular system consisting of a ring threaded by a string, two blocking groups being attached at both ends of the string in order to prevent dethreading.[1] Such compounds have been made long ago,[1,2] but they have been mostly considered as chemical curiosities. Recently, rotaxanes underwent a real revival thanks to the newly developed efficient synthetic procedures which make them relatively easy to make [3-5] and also because of their electro- and photochemical properties [6-8] or their aptitude to undergo controlled molecular motions.[9-10]

We would now like to report the synthesis of a copper (I)-assembled rotaxane (**1**) whose ring is a coordinating macrocycle containing a 1,10-phenanthroline (*phen*) moiety and whose threaded fragment incorporates both a *phen* unit and a 2,2',6',2"-terpyridine (*terpy*) coordination site. The particularity of the system relies on its potential dual complexing mode towards a metal involving binding of the *phen* or *terpy* motif.



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The synthesis strategy is indicated in *Figure 1*. A key step is the metal-directed threading process (i) often used in the past for making various catenanes and rotaxanes.[11]

E-mail: sauvage@chimie.u-strasbg.fr

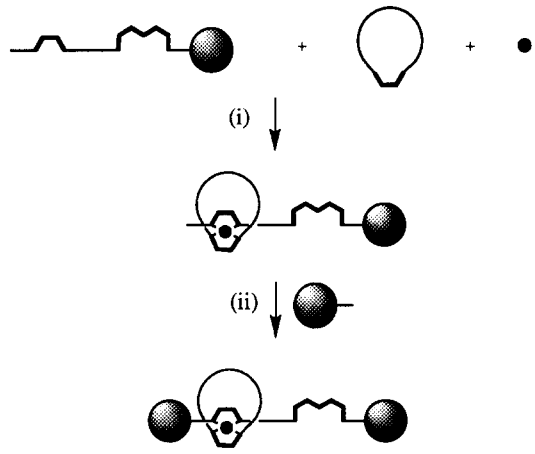

Figure 1 *Construction principle*: The bidentate chelate (*phen*, represented by an inverted U) and the terdentate unit (*terpy*, represented by an M) have been incorporated in an acyclic ligand already bearing a bulky stopper at one end. The ring contains a *phen* nucleus. (i) In the threading step, copper (I) (represented by a black circle) forces the string to pass through the ring. Since copper (I) has a strong tendency to be 4-coordinate, the threading reaction will selectively lead to the precursor represented. (ii) The blocking reaction will be done by attaching a voluminous group at the second end of the coordinating string.

The organic molecules used a precursors as well as the string, the ring and the threaded compounds are represented in *Figure 2*. 4-[tris(4-*tert*-butylphenyl)methyl]phenol [12] **6** was chosen as blocking group since it is large enough to prevent dethreading of the 30-membered macrocycle **12**. 5,5'-Dimethyl-2,2',6',2"-terpyridine **2** [13] was deprotonated with LDA in THF and then reacted with two equivalents of THP-protected bromoethanol (THP = tetrahydropyran-2-yl) to afford **3** in 45 % yield. Deprotection with conc. HCl in refluxing ethanol led to the corresponding diol **4** in high yield (96 %) as a white solid. This alcohol was converted into the dimesylate **5** in 90 % yield by reaction with mesyl chloride and NEt_3 in CH_2Cl_2 at -2 °C, and then reacted with one equivalent of **6** and K_2CO_3 in DMF to afford the monomesylate **7** (46 %). **7** was converted into the more reactive bromo derivative **8** by reaction with anhydrous LiBr in refluxing acetone in 92 % yield. 2-Methyl-9-(p-anisyl)-1,10-phenanthroline **9** [14] was deprotonated with LDA in THF, leading to a deep red compound which was further reacted with **8** in THF at room temperature to afford the string **10** (61 %), incorporating a *phen* and a *terpy* unit and a stopper at one end, as a yellow solid.

10 could be easily threaded into the coordinating ring **12** [15], containing a *phen* unit, through coordination to Cu(I), by taking advantage of the great stability of the pseudo-tetrahedral bis-chelate complex formed between Cu(I) and two *phen*. Thus, reaction between **12** and $[Cu(MeCN)_4]PF_6$ in CH_2Cl_2-MeCN under argon at room temperature led to an orange solution of $Cu(\mathbf{12})(MeCN)_2^+$ which was then reacted with a CH_2Cl_2 solution of **10** to give almost quantitatively a brown-red solution of *semi-rotaxane* $[\mathbf{13}^+][PF_6^-]$.

For the preparation of the fully blocked rotaxane **1**, ligand **10** was first demethylated by reaction with EtSNa in dry DMF at 110 °C to give **11** in 80 % yield as a yellow solid. **11** was threaded into macrocycle **12** by coordination to Cu (I) in the same way as for **13**. The threaded complex **14** was obtained in nearly quantitative yield as a brown-red solid. Separately, the phenolic blocking group **6** was converted into the appropriate bromo derivative **15** by alkylation with bromoethanol and K_2CO_3 in DMF followed by mesylation of the corresponding alcohol (mesyl chloride, NEt_3, CH_2Cl_2) and then reaction with LiBr in refluxing acetone (overall yield 51 %). Finally, the reaction of **14**, **15** and Cs_2CO_3 in DMF under argon at 55 °C, followed by counterion

exchange (KPF_6, H_2O, MeCN), led to rotaxane [1^+][PF_6^-] in 40 % yield.

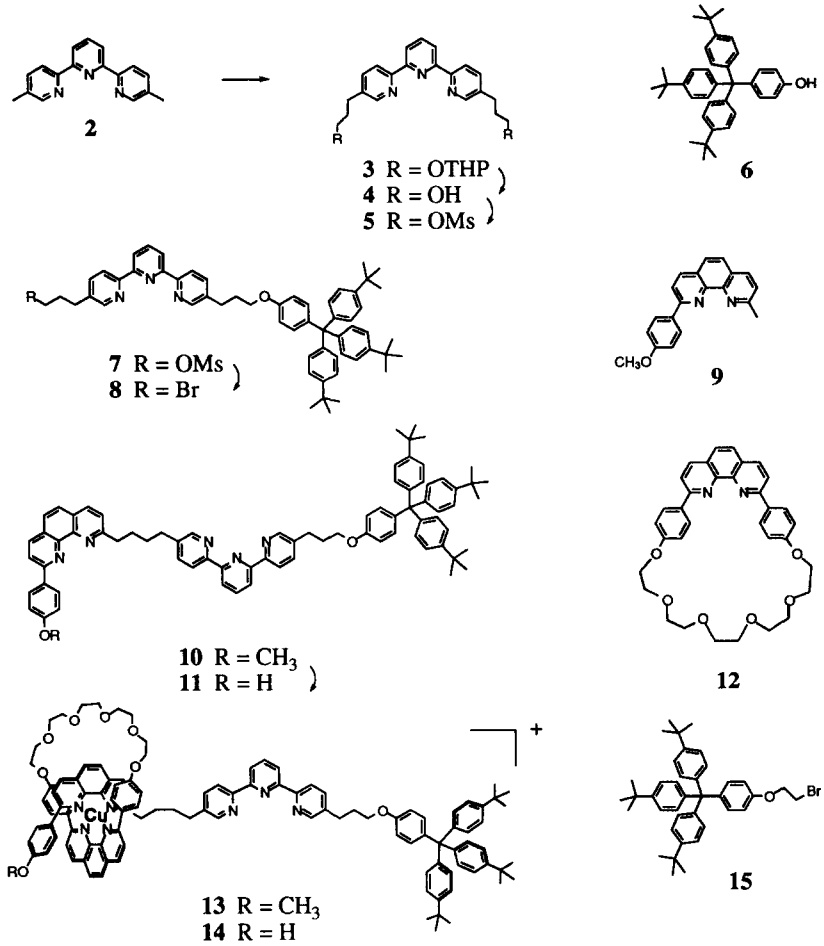

Figure 2

Both threaded structures, **1** and **13**, were unambiguously characterized by FABMS and ^1H NMR and UV-vis spectroscopies.[16] The ^1H NMR spectra show the typical upfield shifts of the aromatic protons of the phenoxy moieties attached to the phenanthrolines, due to the ring current effect of these phenanthrolines in their intertwined structure around the copper center. FABMS confirmed the structures showing intense peaks corresponding to the loss of the counterion.

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16. Semi-rotaxane **13**: UV-vis (CH_3CN): λ_{max} (nm) 442 (ε = 3100). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.68 (d, *J* = 8.3 Hz, 1H), 8.57 (br.s, 1H), 8.49-8.45 (m, 4H), 8.40 (d, *J* = 7.5 Hz, 1H), 8.29 (d, *J* = 8.8 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 8.10 (br.s, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 8.00 (s, 2H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.89 (t, *J* = 7.8 Hz, 1H), 7.76-7.73 (m, 2H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 4H), 7.29-7.14 (m, 17H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.97 (d, *J* = 8.7 Hz, 4H), 5.90 (d, *J* = 8.6 Hz, 2H), 4.02 (t, *J* = 6.2 Hz, 2H), 3.81 (s, 4H), 3.70-3.66 (m, 4H), 3.57-3.52 (m, 8H), 3.46 (s, 3H), 3.46-3.43 (m, 4H), 2.93-2.89 (m, 2H), 2.53-2.49 (m, 2H), 2.28 (t, *J* = 7.2 Hz, 2H), 2.19-2.12 (m, 2H), 1.56-1.50 (m, 2H), 1.30 (s, 27H), 1.32-1.26 (m, 2H). FABMS: *m/z* 1747.8 ($[M\text{-}PF_6]^+$, calcd 1747.8), 1180.5 ($[M\text{-}\mathbf{12}\text{-}PF_6]^+$), 629.2 ($[Cu(\mathbf{12})]^+$), 411.3 ($[(t\text{-}BuC_6H_4)_3C]^+$). Rotaxane **1**: UV-vis (CH_3CN): λ_{max} (nm) 442 (ε = 2700). ^1H NMR (400 MHz, CD_2Cl_2): δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.56 (br.s, 1H), 8.48-8.46 (m, 2H), 8.41-8.36 (m, 3H), 8.29 (d, *J* = 8.9 Hz, 1H), 8.24 (br.d, *J* ~ 7.8 Hz, 2H), 8.12 (br.s, 1H), 8.05 (d, *J* = 8.9 Hz, 1H), 7.89-7.85 (m, 5H), 7.76-7.71 (m, 2H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 4H), 7.32-7.15 (m, 29H), 7.11 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 5.97 (d, *J* = 8.7 Hz, 4H), 5.92 (d, *J* = 8.6 Hz, 2H), 4.26-4.24 (m, 2H), 4.00 (t, *J* = 6.0 Hz, 2H), 3.89-3.87 (m, 2H), 3.80 (br.s, 4H), 3.70-3.67 (m, 4H), 3.58-3.54 (m, 8H), 3.46-3.43 (m, 4H), 2.91-2.87 (m, 2H), 2.53-2.49 (m, 2H), 2.33-2.29 (m, 2H), 2.18-2.12 (m, 2H), 1.60-1.54 (m, 2H), 1.30 (s, 27H), 1.29 (s, 27H), 1.34-1.26 (m, 2H). FABMS: *m/z* 2265.2 ($[M\text{-}PF_6]^+$, calcd 2265.1), 1698.0 ($[M\text{-}\mathbf{12}\text{-}PF_6]^+$), 629.2 ($[Cu(\mathbf{12})]^+$).

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