Copper(I)-induced threading of two bis-macrocycles on two rods: a cyclic [4]rotaxane

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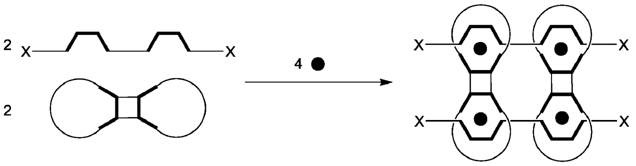
A cyclic pseudo-rotaxane tetramer has been synthesised quantitatively at room temperature by threading two two-coordination site rods through two bis-macrocycles in the presence of copper(I) as a template.

Introduction

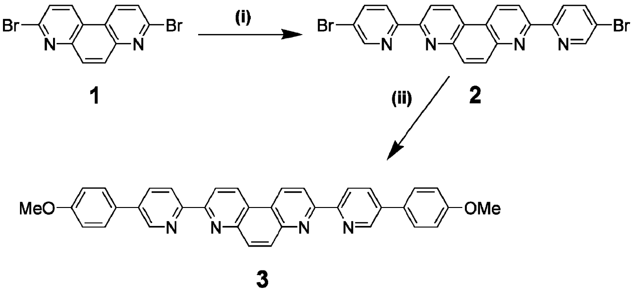
Within the last two decades, the field of catenanes and rotaxanes has experienced a spectacular development.[1] Whereas the synthesis of such relatively simple compounds is well documented, the elaboration of multirotaxanes incorporating several rings and several thread-like fragments is still challenging, especially if precisely defined species are to be obtained.[2] The copper(I) templated strategy proposed long ago has been extended to more and more complex molecules, incorporating several metal centres.[3] As far as Cu(I)-complexed rotaxanes are concerned, two compounds are worth noting which contain 4 metal centres: a [5]rotaxane with porphyrinic stoppers[4] and a cyclic rotaxane tetramer whose organic components consist of a coordinating "filament" appended to a ring.[5]

Recently, our group has reported an unusual topology consisting of a large ring threading the two halves of a bis-macrocycle[6] ("handcuff"). Such a topology had already been reported by Becher *et al.*,[7] containing totally different components. The bis-macrocycle used for this synthesis can be utilised for constructing more complex systems such as, in particular, a rotaxane tetramer or its non-stoppered analogue, as depicted in Scheme 1.



Scheme 1 Transition metal-directed formation of a cyclic pseudo-rotaxane tetramer; the black dot represents a metal centre and the U-shaped symbol corresponds to a bidentate chelate.

By taking advantage of the template effect of Cu(I) we could assemble two bis-macrocycles and two linear threads to form a 2D interlocking network, as shown in Scheme 1. Purely organic systems displaying the same topological properties have recently been reported by Aricó *et al.*[8] One of the key factors to the success of the present threading reaction, leading to the [4]pseudo-rotaxane, is the rigidity of the organic fragments used. In fact, these ligands cannot easily lead to other discrete complexes than the desired 4-metal system. Two phenanthrolines attached back to back and included in a bis-macrocycle were previously published by our group,[6] whereas the bis-bidentate thread built around a 4,7-phenanthroline nucleus is a new compound, synthesised as described in Scheme 2.



Scheme 2 Synthesis of the 3,8-bis(4′-(4-methoxyphenyl)-2′-pyridyl)-4,7-phenanthroline fragment. Reagents and conditions: (i) 5-bromo-2-trimethylstannyl pyridine,[9] Pd(PPh$_3$)$_4$, toluene, 140 °C, 18 h; (ii) 4-methoxyphenylboronic acid, K$_2$CO$_3$, Pd(PPh$_3$)$_4$, DMF, 120 °C, 18 h.

The backbone of the central 4,7-phenanthroline unit forces the two bipyridine chelates in the same direction and provides the system with the required rigidity.

1 was obtained in 80% overall yield from commercially available 4,7-phenanthroline, following the procedure described in the literature.[10] The bis-bidentate ligand **2** was prepared by Stille coupling of **1** with 2-trimethylstannyl-5-bromopyridine[9] in 87% yield. The crude product was filtered over celite, washed with MeOH and Et$_2$O and, subsequently, extracted from the celite with hot chloroform in which it is slightly soluble. The ligand was then elongated by a Suzuki coupling with 4-methoxyphenylboronic acid. After following the same work-up procedure as for compound **2**, the final ligand was obtained in 64% yield. All compounds were characterised by ^{1}H-NMR and ES-mass spectroscopy (ES-MS).

The final threading reaction of two bis-bidentate linear axles with two bis-macrocycles **4**, using the template effect of Cu(I) is described in Scheme 3.

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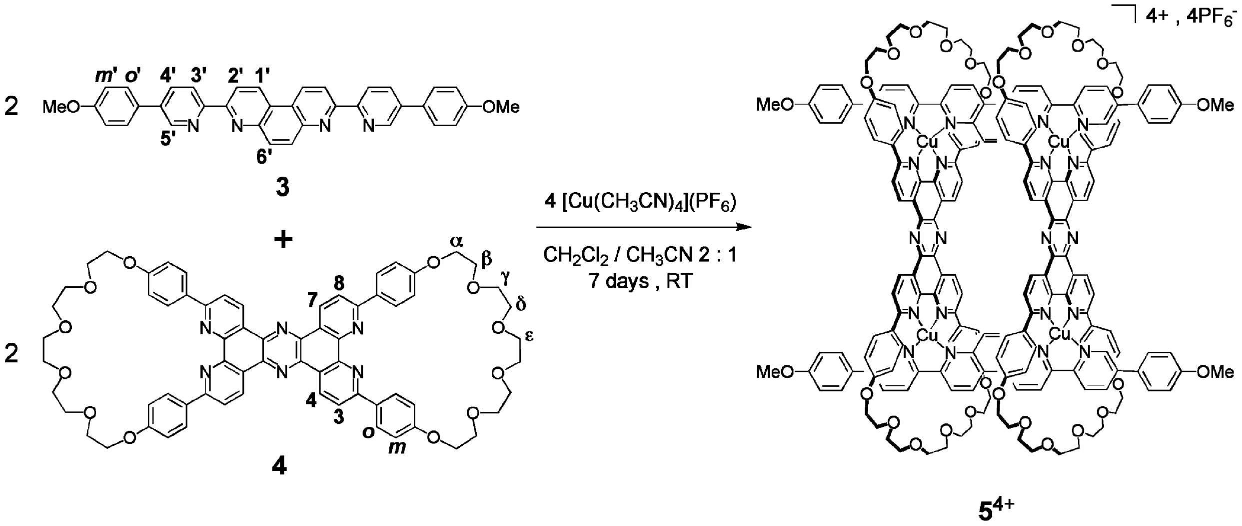

Scheme 3 Transition metal directed threading step leading to the 4-copper(I) centre threaded network species $\mathbf{5}^{4+}$.

A degassed solution of $[Cu(CH_3CN)_4](PF_6)$ in acetonitrile was added to a suspension of the bis-macrocycle **4** in freshly distilled dichloromethane. After 15 h, the bis-bipyridine thread **3** was added as a solid to the orange solution. Both the bis-macrocycle **4** as well as the thread are barely soluble in the solvents used. Interestingly, coordination of the various ligands to the Cu(I) centres makes them perfectly soluble, just as well as the target molecule $\mathbf{5}^{4+}$. After one week at room temperature and in the absence of light, the solvents were evaporated and the final compound was extracted from water with dichloromethane and then precipitated in a saturated KPF_6 solution. The thermodynamically most stable four-Cu(I) containing threaded species $\mathbf{5}^{4+}$ was obtained in 95% yield as a greenish brown solid and was characterised by ^{1}H-NMR (500 MHz) as well as COSY and ROESY NMR and ES-MS.

The ^{1}H-NMR spectrum of the final copper(I) complex $\mathbf{5}^{4+}$ is shown in Fig. 1; the chemical shifts of the complex and the building blocks **3** and **4** are listed in Table 1. Important changes, ranging from −0.9 to −1.3 ppm, can be seen for $H_{5',6'}$ of the thread and $H_{o,m}$ of the bis-macrocycles compared to the free ligands (see Scheme 3 for numbering). Clear evidence for the threading of the linear bis-bipyridine ligands through the 30-membered rings is provided by 2D-ROESY NMR. Dipolar coupling between the hydrogen atoms of the pentaethyleneglycol chains with $H_{2'}$ and $H_{3'}$ of the thread is observed. The ES-MS spectrum shows one peak at m/z 915.2614 corresponding to $[\mathbf{5}]^{4+}$ (calcd. 915.2621).

Compound $\mathbf{5}^{4+}$ contains four identical Cu(I) centres, each one being coordinated to 1,10-phenanthroline and 2,2′-bipyridine type ligands. Each metal centre is roughly in a tetrahedral environment and hence the Cu(I) is strongly stabilised. The electronic properties of the compound are in perfect agreement with its structure. Three different absorption bands are observed in the UV region ($\lambda_{max} \sim 240$ nm, $\varepsilon \sim 1.03 \times 10^6$ L mol^{-1} cm^{-1}, $\lambda_{max} \sim 263$ nm, $\varepsilon \sim 9.36 \times 10^5$ L mol^{-1} cm^{-1} and $\lambda_{max} \sim 355$ nm, $\varepsilon \sim 1.35 \times 10^6$ L mol^{-1} cm^{-1}), which correspond to ligand-localised transitions. A much less intense band, which is very likely to correspond to a Metal-to-Ligand Charge Transfer (MLCT) transition, is observed in the visible region ($\lambda_{max} \sim 585$ nm, $\varepsilon \sim 5900$ L mol^{-1} cm^{-1}). The MLCT band appears at unusually low energy for bis-diimine copper(I) complexes,[11] which is in agreement with the strong π-accepting nature of the organic ligands used, in agreement with previous observations made on copper(I) complexes with related ligands.[12] Cyclic voltammetry shows that the Cu^{II}/Cu^{I} couple has a redox potential around 0.6 V *vs.* SCE in acetonitrile, in accordance with previously reported values for similar systems.[13]

In conclusion, the gathering and threading effect of copper(I) turned out to be, once again, particularly efficient. It allowed assembly of a pseudo-rotaxane tetramer quantitatively from 4 organic fragments. In the future, such complex structures will be incorporated in new and more sophisticated molecular machines involving the motion of two-dimensional molecular networks.

Experimental

Instrumentation

^{1}H-NMR spectra were acquired on a Bruker AM 300 (300 MHz) spectrometer, operating at 300.17 MHz, using the deuterated

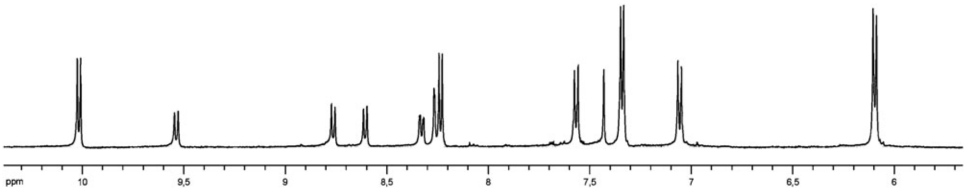

Fig. 1 ^{1}H-NMR (500 MHz) spectrum of compound $\mathbf{5}^{4+}$ (aromatic region), (also see Table 1).

Table 1 ^{1}H-NMR (500 MHz) chemical shifts for **3**, **4** and [$\mathbf{5}^{4+}$]($4PF_6^-$).[a,b]

	$H_{4,7}$	$H_{1'}$	$H_{2'}$	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{3,8}$	$H_{o'}$	$H_{6'}$	H_o	$H_{m'}$	H_m
$\mathbf{5}^{4+}$	10.02	9.54	8.76	8.61	8.33	8.27	8.24	7.57	7.43	7.34	7.06	6.10
3		9.44	8.56	8.56	8.56	9.13		7.71	8.75		7.15	
4	10.19						8.72			8.28		7.36
$\Delta\delta^c$	−0.17	0.10	0.20	0.05	−0.13	−0.86	−0.48	−0.14	−1.32	−0.94	−0.06	−1.26

[a] The very poor solubility of **3** and **4** in normal organic solvents did not allow NMR studies without protonating these ligands so as to dissolve them. [b] Solvent: CD_2Cl_2 + 3% TFA for **3** and **4**, CD_2Cl_2 for $\mathbf{5}^{4+}$. [c] $\Delta\delta = \delta(\mathbf{5}^{4+}) - \delta(\mathbf{3}\text{ or }\mathbf{4})$.

solvent as the lock and residual solvent as the internal reference. Mass spectra were obtained by using a VG-BIOQ triple quadrupole, positive mode (ES-MS). UV/Vis spectrometry was done on a BIO-TEC UVIKON XL spectrometer.

Syntheses

3,8-Bis(4-bromo-2′-pyridyl)-4,7-phenanthroline (2). 5-Bromo-2-trimethylstannyl pyridine (1.96 g, 6.05 mmol) and 3,8-dibromo-4,7-phenanthroline (**1**) (1.00 g, 2.96 mmol) were dissolved in dry toluene (130 mL) and the mixture was degassed. To this solution, $Pd(PPh_3)_4$ (230 mg, 0.2 mmol) was added and the resulting reaction mixture further degassed for 5 min. It was then refluxed (140 °C) under argon for 18 h. Another 160 mg of catalyst were added and the reaction stirred for a further 44 h under reflux. Evaporation of toluene afforded the crude product as a grey solid that was washed with MeOH (2 × 150 mL) and Et_2O (2 × 150 mL). Compound (**2**) was extracted from the remaining solid by washing it 5 times with 150 mL of chloroform. After evaporating the chloroform and washing the grey solid again with MeOH and Et_2O, 1.26 g of a greyish yellow solid were obtained (87% yield). **2**: ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 9.05 (d, ^3J = 8.7 Hz, 2H; $H_{1'}$), 8.80 (d, ^4J = 2.4 Hz, 2H; $H_{5'}$), 8.74 (d, ^3J = 8.7 Hz, 2H; $H_{2'}$), 8.64 (d, ^3J = 8.6 Hz, 2H; $H_{3'}$), 8.31 (s, 2H; $H_{6'}$), 8.03 (dd, ^3J = 8.4 Hz and ^4J = 2.4 Hz, 2H; $H_{4'}$). FAB-MS: *m*/*z* (%) = 493 (100) [M + H^+].

3,8-Bis(4′-(4-methoxyphenyl)-2′-pyridyl)-4,7-phenanthroline (3). A suspension of 3,8-bis(4-bromo-2′-pyridyl)-4,7-phenanthroline (**2**) (200 mg, 0.4 mmol), 4-methoxyphenylboronic acid (134 mg, 0.88 mmol, 2.2 eq.) and potassium carbonate (425 mg, 2 mmol, 2.5 eq.) in 25 mL DMF was degassed (3 times vacuum/argon) and $Pd(PPh_3)_4$ (46 mg, 0.04 mmol, 10% mol) was added. The solution was then heated up to reflux (120 °C) under argon and stirred for 3 h, then 15 mg of catalyst were added. After another 18 h of heating, the reaction mixture was cooled down to room temperature and poured into 250 mL of water. The product thus precipitated with impurities and was then filtered over celite and washed with EtOH. The celite–product mixture was then washed with dichloromethane (4 × 200 mL) and hot chloroform (6 × 200 mL). The left-overs were extracted in boiling chloroform over night. The chloroform and dichloromethane phases were collected and the solvents evaporated. The 200 mg of recovered product were recrystallized in chloroform. 140 mg of pure product were obtained (64% yield). **3**: ^{1}H-NMR (300 MHz, CD_2Cl_2, TFA 3%): δ = 9.44 (d, ^3J = 8.4 Hz, 2H; $H_{1'}$), 9.12 (d, ^4J = 1.3 Hz, 2H; $H_{5'}$), 8.78 (dd, ^3J = 8.6 Hz, ^4J = 1.3 Hz 2H; $H_{4'}$), 8.73 (d, ^3J = 8.2 Hz, 2H; $H_{2'}$), 8.58 (d, ^3J = 8.8 Hz, 2H; $H_{3'}$), 8.50 (s, 2H; $H_{6'}$), 7.72 (d, ^3J = 8.9 Hz, 4H; $H_{o'}$), 7.6 (d, ^3J = 8.8 Hz, 4H; $H_{m'}$), 3.99 (s, 6H; H_{OMe}). ES-MS: *m*/*z* (%) = 547.225 (100) [M + H^+].

4-Copper(I) centre threaded species network ($\mathbf{5}^{4+}$). To the bis-macrocycle (**4**) (50 mg, 4.32 × 10^{-5} mol) in argon atmosphere, 40 mL of freshly distilled dichloromethane and then 20 mL of a freshly degassed solution of MeCN containing [Cu $(MeCN)_4$](PF_6) (33.3 mg, 8.94 × 10^{-5} mol) were added. After 15 h of stirring, the thread (**3**) (23.6 mg, 4.32 × 10^{-5} mol) was added as a solid and the solution was left at room temperature for 7 days in the absence of light. The solvents were then evaporated and the product extracted from water with dichloromethane. After precipitation from a saturated KPF_6 solution 78 mg of the green-brownish product was obtained with 95% yield. $\mathbf{5}^{4+}$: ^{1}H-NMR (500 MHz, CD_2Cl_2): δ = 10.02 (d, ^3J = 8.2 Hz, 8H; $H_{4,7}$), 9.54 (d, ^3J = 8.9 Hz, 4H; $H_{1'}$), 8.76 (d, ^3J = 9.0 Hz, 4H; $H_{2'}$), 8.61 (d, ^3J = 8.6 Hz, 4H; $H_{3'}$), 8.33 (dd, ^3J = 8.6 Hz and ^4J = 2.2 Hz, 4H; $H_{4'}$), 8.27 (d, ^4J = 1.8 Hz, 4H; $H_{5'}$), 8.24 (d, ^3J = 8.2 Hz, 8H; $H_{3,8}$), 7.57 (d, ^3J = 9.1 Hz, 8H; $H_{o'}$), 7.43 (s, 4H; $H_{6'}$), 7.34 (d, ^3J = 8.4 Hz, 8H; H_o), 7.06 (d, ^3J = 9.1 Hz, 8H; $H_{m'}$), 6.10 (d, ^3J = 8.5 Hz, 8H; H_m), 3.95–3.78 (m, 92H; $H_{\text{–O–}CH_2\text{–}CH_2\text{–O–}}$ + H_{OMe}). ES-MS: *m*/*z* (%) = 915.261 (100) [M^{4+}].

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