Templated Synthesis of a Rotaxane with a $[Ru(diimine)_3]^{2+}$ Core

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Abstract: A rotaxane containing a ruthenium bisphenanthroline complex, acting as an axis, and a macrocycle incorporating a 2,2′-bipyridine (bpy) unit, threaded by the axis, has been synthesized. The bisphenanthroline ligand is such that its ruthenium(II) complexes possess a clearly identified axis, making such compounds ideal components of rotaxanes constructed around an octahedral ruthenium(II) center, which serves as a template. The ring is threaded by the axial ruthenium(II) precursor complex, to afford the corresponding pseudorotaxane in moderate yield. The X-ray structure analysis of this compound reveals the threaded nature of the complex. The length of the threaded ring (35 atoms in the periphery) is too short to allow easy threading of the axis through the macrocycle. As a consequence, an isomer is also obtained for which the axial ruthenium complex is attached in an *exo* fashion. ^{1}H NMR studies have been carried out, which reveal various conformational equilibria for the pseudorotaxane. Light-induced decoordination of the bpy-containing cyclic fragment was shown to be quantitative and to lead to the free ring and the axial ruthenium(II) complex, regardless of the starting compound (pseudorotaxane or *exo* isomer). Finally, the real rotaxane could be prepared, although it could not be separated from its *exo* isomer.

Keywords: macrocyclic ligands · N ligands · rotaxanes · ruthenium · template synthesis

Introduction

Catenanes and rotaxanes have experienced a spectacular development during the past two decades.[1–3] From the synthetic challenge which they used to represent, the interest in these compounds has recently moved towards their potential applications, in particular as molecular machines.[4–8]

Interlocking or threaded rings based on transition metals, either used as temporary templates[9] or incorporated in their backbone,[10, 11] represent a special class of such molecules. Conceptually, it is easy to design a synthetic strategy based on the entwining of two molecular threads around a transition-metal center. Many examples of such an approach have been reported; these are based on coordinating 1,10-phenanthroline-incorporating organic fragments perpendicularly to one another around a tetrahedral copper(I) center before cyclizing to afford the desired catenane.[12] An alternative but related approach is based on the copper(I)-directed threading of an acyclic coordinating fragment through a presynthesized ring containing a complexing unit pointing towards the inside of the ring. This strategy allows the preparation of rotaxanes and it has been extensively utilized to construct porphyrin-stoppered rotaxanes.[13]

An octahedral metal coordinated to three bidentate chelates is an attractive template for making rotaxanes, mainly because of the interesting electro- and photochemical properties that compounds of the $[Ru(bpy)_3]^{2+}$ family display. However, the use of a metal center of this type as the templating center is less straightforward.

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Results and Discussion

It was recently reported that a $[Ru(diimine)_2]^{2+}$ moiety can be inscribed in an axial compound by appropriate substitution of the diimine chelates or in a macrocyclic system, precursor of a catenand.[14] We have now incorporated the $[Ru(diimine)_2]^{2+}$-containing axial fragment in a rotaxane, the threaded ring being also coordinated to the ruthenium(II) center through a second diimine chelate unit. Preliminary experiments show

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that the cyclic component of the rotaxane can be photochemically decoordinated from the metal center, which will open the way to the construction of molecular machines set in motion by photonic signals only.[7, 15]

The synthetic strategy consists of a "threading" step (the axial component is threaded through the ring) followed by a "stoppering" reaction (a bulky substituent is attached at each end of the axis). The threading reaction was first tested on a model whose axis is end-functionalized by two unreactive chemical groups (ether functionalities; see Figure 1).

Complex **1**-$[PF_6]_2$ is a yellow solid that is formed quantitatively from its dichloro precursor[14] (purple complex) by replacing the Cl^- ligands by CH_3CN in H_2O/CH_3CN. The macrocyclic compound **2**, which incorporates a 2,2′-bipyridine ligand substituted at its 6- and 6′-positions by alkyl groups, and a dimethyldi(p-alkoxyphenyl)methane fragment derived from "bisphenol A", has been obtained by reaction of the suitable dibromo precursor (6,6′-di[2-(2-bromoethoxy)ethoxypropyl]-2,2′-bipyridine) with the "bis-phenol A" in 45% yield. Its X-ray structure[16] (Figure 2) shows that the bipyridine fragment displays a *trans* geometry in order to minimize the repulsion between the lone pairs on the nitrogen atoms. The torsion angle N1-C5-C6-N2 is 117°.

Compound **2** has a 35-membered ring, and CPK models indicate that its size should be sufficient to allow the threading reaction outlined in Figure 1, although the rotaxane-like molecule obtained should be tight, with contacts between the "bisphenol A" motif of the ring and the -CH_2-CH_2-C_6H_4-CH_2-CH_2- fragment of the axial component. This steric hindrance may in part explain the poor yield of the reaction: $\mathbf{1}^{2+}$ and **2** react in ethylene glycol (140 °C, 4 h; stoichiometric; concentration of the reactants: 0.01 mol L^{-1}) to afford a 20 to 25% yield of a mixture of complexes containing **3**-$[PF_6]_2$ and **3′**-$[PF_6]_2$ (orange solid) after chromatography (Figure 1). This mixture displays only one round-shaped spot on a thin layer chromatograph, making the separation of these two complexes extremely difficult. By comparison, $\mathbf{1}^{2+}$ reacts with the acyclic ligand 6,6′-dimethyl-2,2′-bipyridine (6,6′-dmbp) to

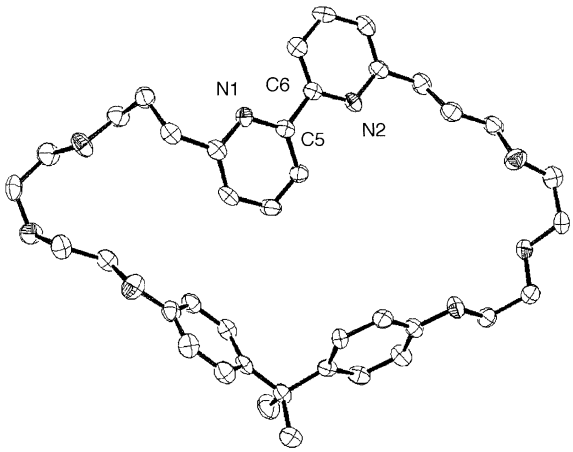


Figure 2. Molecular structure of **2**.

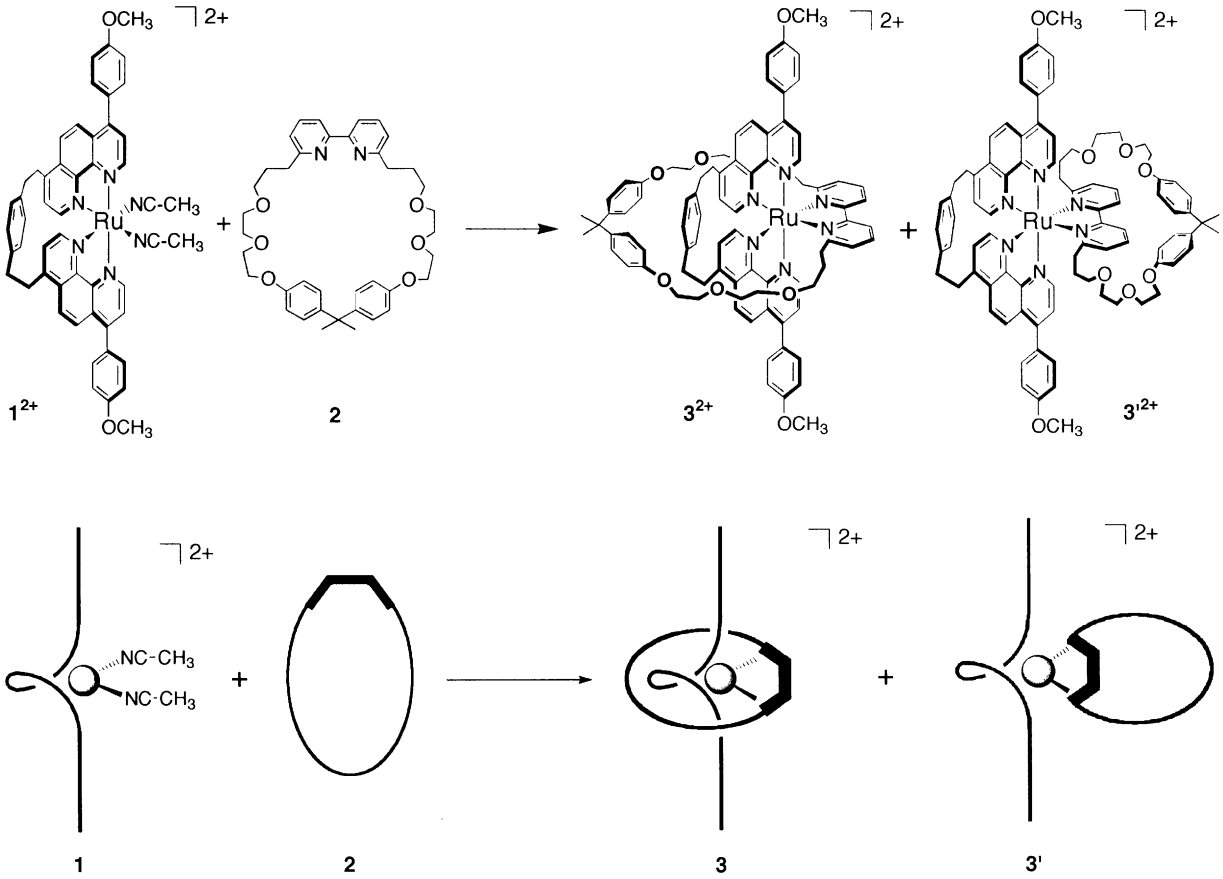


Figure 1. Synthesis of the pseudorotaxane $\mathbf{3}^{2+}$ and the *exo* isomer $\mathbf{3'}^{2+}$.

afford the corresponding complex in quantitative yield, under reaction conditions similar to those used for preparing $\mathbf{3}^{2+}$.

The formation of $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$ was supported by ES-MS and ^{1}H NMR studies. ES-MS of **3**-$[PF_6]_2$ and **3′**-$[PF_6]_2$ showed a peak at *m*/*z* 1589.6, which is attributed to the singly charged species (loss of one PF_6^-), and a very strong peak at *m*/*z* 722.4, corresponding to the doubly charged cation $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$, in agreement with the formula of the complexes. The room-temperature ^{1}H NMR spectrum of the mixture consists both of well-resolved, sharp peaks and broad signals that are more or less blurred in the baseline, suggesting that dynamic processes are taking place. The aromatic regions of the variable-temperature ^{1}H NMR spectra of $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$ from $-52\,^\circ$C to $+50\,^\circ$C (Figure 3) were interpreted with the help of 2D COSY and ROESY techniques (see Scheme 1 for the numbering of the protons concerned).

The lowest temperature ($-52\,^\circ$C) spectrum consists mostly of sharp signals that can be assigned to two families. The peaks colored in black belong to a C_2-symmetric species. Remarkably, they can be easily tracked as the temperature is increased, since both their shapes and chemical shifts do not show appreciable changes. ROE cross peaks are found in the following pairs of protons: (8, A), (8, B), (9, A), (9, B), (p3, A), (p3, B), (p4, A), (p4, B). These data strongly suggest that the corresponding species is the unthreaded conformer $\mathbf{3'}^{2+}$ (Figure 1). In this isomer, the macrocycle **2** is folded out in such a way that the "bisphenol-A" hinge can freely swing back and forth past the rear part of the bipyridyl fragment of the

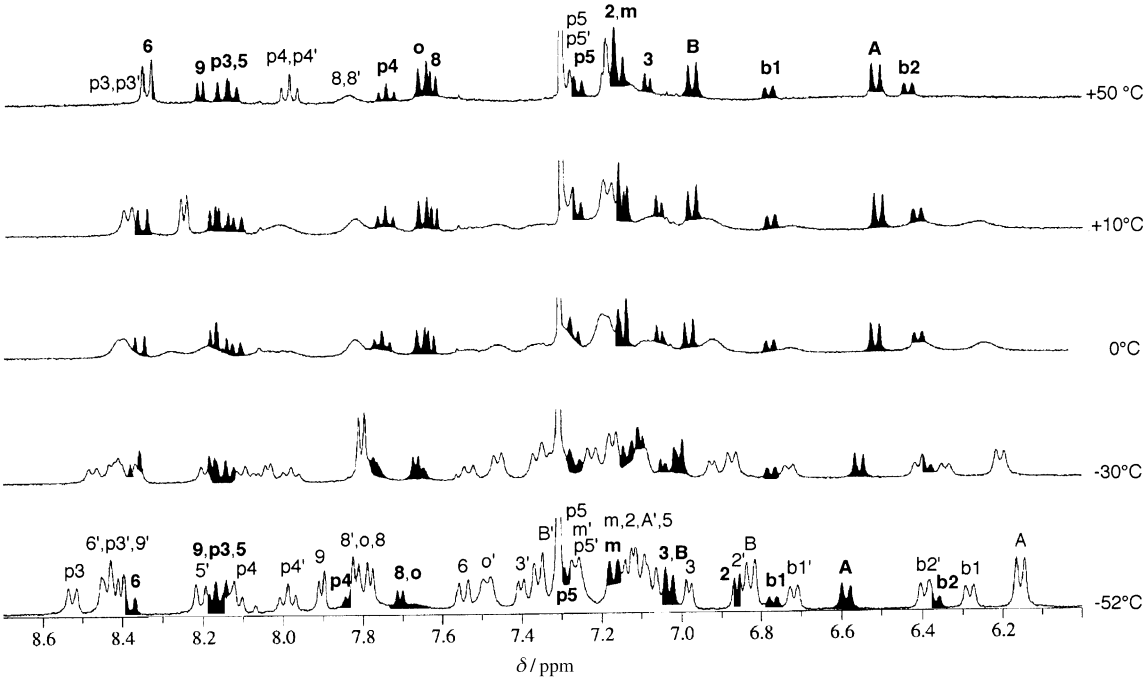
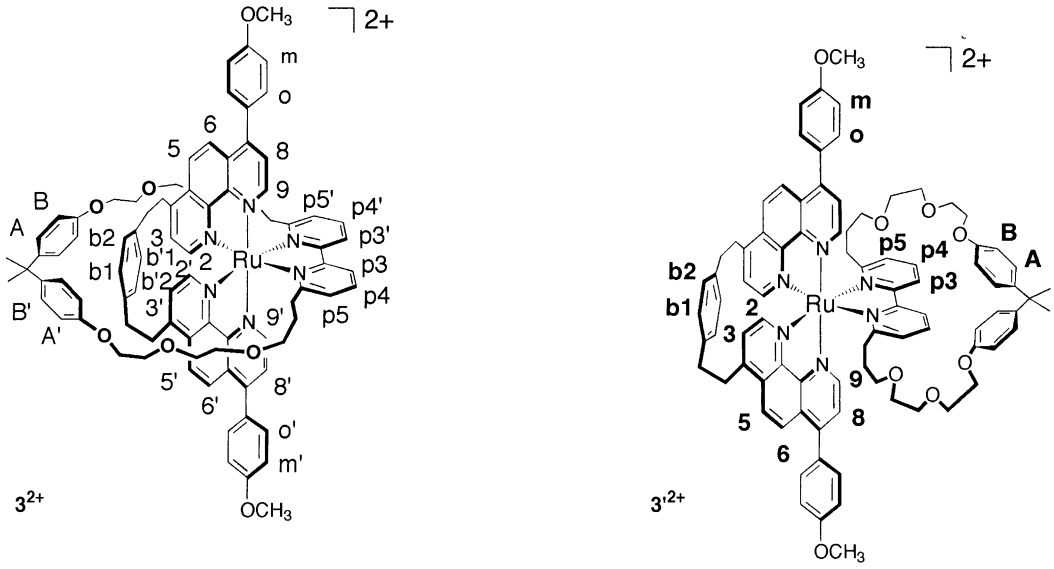


Figure 3. ^{1}H NMR spectra in $CDCl_3$ of the mixture of $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$ at different temperatures.



Scheme 1. Numbering scheme for $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$.

macrocycle. The uncolored peaks belong to a nonsymmetrical species, since most of the signals are clearly split in the $-52\,^{\circ}C$ spectrum, for example p4 and p4′, 3 and 3′, b1 and b1′. ROE cross peaks can be found between the following proton pairs: (6, B), (6, B′). We suggest that the corresponding isomer is the threaded conformer $\mathbf{3}^{2+}$, in which the "bisphenol-A" hinge is stuck between an anisyl substituent and the *p*-phenylene bridge of the axis fragment of $\mathbf{3}^{2+}$. This situation should be very similar to the one pictured in the view of the crystal structure shown in Figure 4, and discussed below. As the

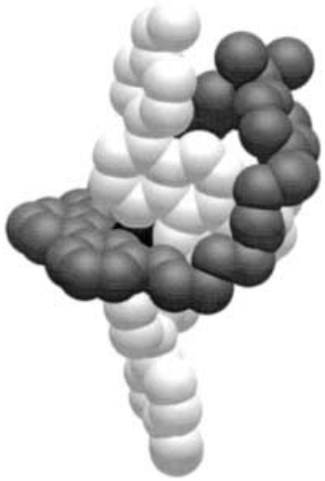


Figure 4. Molecular structure of the pseudorotaxane $\mathbf{3}^{2+}$; H atoms have been omitted for clarity. The ruthenium atom is black, the string is light gray and the ring is dark gray.

temperature is increased, most of the peaks broaden and finally merge in the baseline, with, in particular, the noticeable exception of the peaks belonging to the bipyridyl fragment of the macrocycle (p3, p4, p5). It can be clearly seen in Figure 3 that the two triplets corresponding to p4 and p4′ at $-52\,^{\circ}C$ merge together as the temperature increases (coalescence temperature: $0\,^{\circ}C$), giving rise to a sharp triplet as the temperature finally reaches $+50\,^{\circ}C$. Remarkably, the other peaks that do not merge in the baseline at $25\,^{\circ}C$ are those corresponding to protons m, o, 8, and 9 of the axis fragment of $\mathbf{3}^{2+}$. This can be clearly evidenced by changing the solvent ([D_6]acetone instead of $CHCl_3$, see Figure 6a, below). Therefore, increasing the temperature allows a swinging process of the "bisphenol-A" fragment of the macrocycle past the *p*-phenylene bridge of the axis. Up to $+50\,^{\circ}C$, there is no indication in the ^1H NMR spectra of chemical exchange between $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$. Indeed, the spectrum recorded at $+50\,^{\circ}C$ is a simple superposition of the spectra of $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$. Therefore, the expected "jump rope" motion past the anisyl groups is not taking place, at least at this temperature, and is apparently energetically less favorable than any of the swinging motions evidenced above for the two conformers. However, the baseline-level broadening of the peaks of the protons belonging to the "bisphenol-A" hinge and the rear part of the bisphenanthroline fragment of the axis (2, 3, 5, 6, A, B) cannot be overlooked, and must be due to another process, which takes place at low temperature, but is hampered as the temperature is increased. We suggest that this process corresponds to the rotation of the phenylene groups of the "bisphenol-A" moiety inside the threaded macrocycle. This motion can occur freely as long as the "bisphenol-A" fragment is located in the rear part of the phenanthroline chelates, but it is clearly hindered when this fragment has to pass the phenylene bridge of the axis. Therefore, the dynamic processes occurring within $\mathbf{3}^{2+}$ are far from being simple. However, as discussed below, photochemical dethreading experiments clearly support the formulation of the complex, consisting of one axial bisphen unit and one ring **2** fragment coordinated to the ruthenium center. To conclude the ^1H NMR experiments, in solution, and at least within the range $-52\,^{\circ}C$ to $+50\,^{\circ}C$, the mixture of isomeric complexes consists of two nonexchanging conformers: $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$, the former having the expected pseudorotaxane structure. Integration of the spectrum recorded at $-52\,^{\circ}C$ shows that the ratio between these conformers is 70:30.

Single crystals of **3**-[PF_6]$_2$ could be obtained by slow diffusion of hexane in a solution of the complex in acetone, and an X-ray structure was obtained.[17] As shown in Figure 4, $\mathbf{3}^{2+}$ is indeed a threaded species with a helical axis, the bisphen ligand being wrapped around the metal center in a way similar to that recently observed with non-rotaxane like species.[14] The metal center is octahedrally coordinated, with little distortion. The Ru–N distances and N-Ru-N angles have the expected values (Ru–N 2.055–2.068 Å for the phen ligands and Ru–N 2.12–2.13 Å for the bpy part). The most striking feature of the structure is the distortion of the ring from planarity. Clearly, the ring is too small to accommodate the relatively thick axle and it can not run around the -CH_2-CH_2-C_6H_4-CH_2-CH_2- part of the helical axis. The folded conformation of the macrocyclic component of $\mathbf{3}^{2+}$ results in a nonsymmetrical situation for which the "upper" and the "lower" parts of the rotaxane become nonequivalent in the solid state and in solution at low temperature, as evidenced by the ^1H NMR study discussed above.

The very congested situation in $\mathbf{3}^{2+}$, as evidenced by the X-ray structure tends to explain why the preparative yield is poor. The presence of a certain proportion of the nonthreaded species (Figure 1) is also understood: the "unnatural" conformation of the ring in this species may be unfavorable but this destabilization energy is compensated by that introduced by the steric repulsion between the ring and the thread in the pseudorotaxane $\mathbf{3}^{2+}$.

Light-driven molecular machines are of special interest.[15] We have recently taken advantage of the dissociative nature of the ligand-field excited state of [Ru(diimine)$_3$]$^{2+}$ complexes to photochemically induce motions, such as expulsion of a [Ru(phen)$_2$]$^{2+}$ unit from a macrocyclic receptor.[18] Compound $\mathbf{3}^{2+}$ contains a real axle and is thus closer to molecular machines of the rotaxane and catenane family. As expected, visible light irradiation of a solution of the $\mathbf{3}^{2+}$ + $\mathbf{3'}^{2+}$ mixture in acetonitrile leads quantitatively to the dethreading products, $\mathbf{1}^{2+}$ and **2** [Eq. (1)].

$$\mathbf{3}^{2+} + \mathbf{3'}^{2+} \xrightarrow[CH_3CN]{h\nu\ (\lambda>400\,nm)} \mathbf{1}^{2+} + \mathbf{2} \qquad (1)$$

The photochemical reaction can easily be monitored by UV/Vis spectroscopy. The mixture of isomeric complexes has

an absorption spectrum characteristic of $[Ru(diimine)_3]^{2+}$ complexes, with a metal-to-ligand charge-transfer (MLCT) absorption band centered at 461 nm. Under irradiation, this band is gradually replaced by the MLCT band of $\mathbf{1}^{2+}$ (λ_{max} = 404 nm). Isosbestic points are observed at 355 nm and 424 nm as shown in Figure 5.

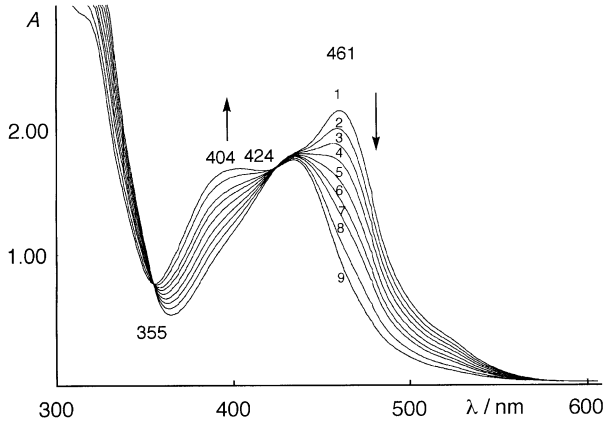


Figure 5. Electronic absorption spectra in CH_3CN of the mixture of $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$ before (1) and after different irradiation times (2: t = 20 s; 3: t = 40 s; 4: t = 60 s; 5: t = 90 s; 6: t = 120 s; 7: t = 150 s; 8: t = 210 s; 9: t = 300 s).

^{1}H NMR spectroscopy is also a useful method to monitor reaction (1). In particular H_9 (see Figure 6) is a convenient probe, and its chemical shift is very sensitive to the metal coordination sphere since it varies from δ = 8.61 ppm in $\mathbf{3}^{2+}$ to δ = 9.95 ppm in $\mathbf{1}^{2+}$ (in $[D_6]$acetone). Paradoxically, starting from a poorly resolved spectrum corresponding to a mixture of isomers ($\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$), a well-resolved spectrum is obtained after light irradiation, which corresponds to the superposition of the spectra of $\mathbf{1}^{2+}$ and **2**. This observation clearly shows that the photochemical decoordination of the ring is quantitative for both $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$.

Evidently, since the yield of the thermal backward reaction leading to $\mathbf{3}^{2+}$ is mediocre (~15%), the threading/dethreading process shows only poor reversibility. This lack of reversibility is probably due to the size of the ring whose cavity is too small to match the bulky ruthenium(II) complex part of the axle as already mentionned.

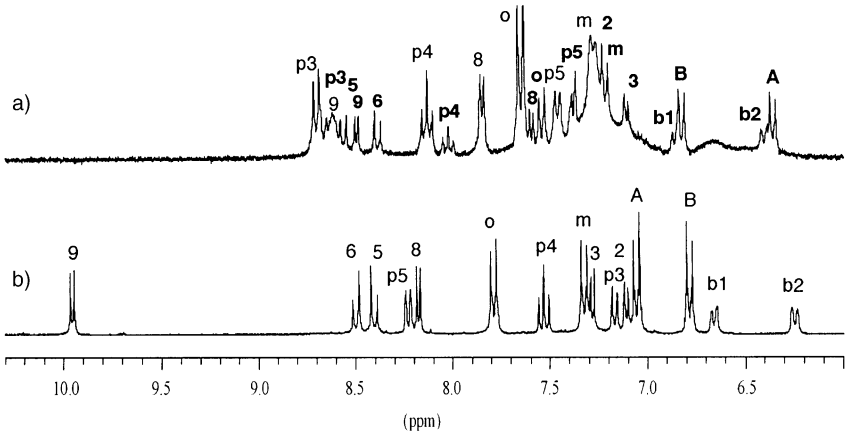


Figure 6. ^{1}H NMR spectra ($[D_6]$acetone) of the mixture of $\mathbf{3}^{2+}$ and $\mathbf{3'}^{2+}$ before (a) and after (b) light irradiation in acetonitrile.

Finally, the real rotaxane derived from $\mathbf{3}^{2+}$ was synthesized. Among the various routes tested in our group, only the one given in Figure 7 turned out to be successful.

Since the demethylation reaction of the anisyl groups of $\mathbf{1}^{2+}$ failed, probably because of the relative lability of the CH_3CN ligands, this same reaction was carried out on $\mathbf{4}^{2+}$, which can be regarded as a protected version of $\mathbf{1}^{2+}$. The 6,6′-dmbp chelate is indeed sufficiently strongly coordinated in the dark and chemically robust for the complex to resist the aggressive conditions required to cleave the methyl ethers (BBr_3). Cation $\mathbf{5}^{2+}$ was subsequently deprotected by photochemically expelling 6,6′-dmbp from the complex to afford $\mathbf{6}^{2+}$ (100% from $\mathbf{4}^{2+}$). The threading reaction of **2** by $\mathbf{6}^{2+}$ (ethylene glycol; 140 °C; 2 h) led to a mixture of isomers $\mathbf{7}^{2+}$ and $\mathbf{7'}^{2+}$ (overall yield: 27%). The stoppering step was performed on the mixture under classical conditions (DMF/K_2CO_3) using a stoichiometric amount of **8**.[19] Conformer **9**-$[PF_6]_2$ and the corresponding *exo* conformer **9′**-$[PF_6]_2$ were isolated as an inseparable mixture in 74% yield. After visible light irradiation it was possible to identify by ES-SM the real rotaxane **10**-$[PF_6]_2$ (m/z: 1293.9 for $\mathbf{10}^{2+}$/2 and 1253.3 for ($\mathbf{10}^{2+}$ – 2 CH_3CN)/2 since the *exo* conformer $\mathbf{9'}^{2+}$ leads to the mechanical separation of the string $\mathbf{11}^{2+}$ (m/z: 973.6) from the macrocycle **2**.

Conclusion

In conclusion, we could make the first rotaxane with a $[Ru(diimine)_3]^{2+}$ core and characterize the pseudorotaxane precursor $\mathbf{3}^{2+}$ by X-ray diffraction. The synthesis of related rotaxanes with larger rings and photochemical studies in relation to light-driven molecular machines are in progress.

Experimental Section

General: All commercial chemicals were used as received without further purification, *n*BuLi solution was titrated by the double titration method described by Gilman and al.[20] Some solvents were dried by distillation over the appropriate drying agent under argon. The melting points were measured on a Büchi SMP-20 apparatus. The NMR spectra were recorded on Bruker WP 200 SY (200 MHz), AM 300 (300 MHz), AV 300 (300 MHz), and AM 400 (400 MHz) spectrometers. The internal reference corresponds to the nondeuterated solvent peak. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer by using NaCl cells or KBr disks. Elemental analyses were performed by the Service de Microanalyse de l'Institut de Chimie de Strasbourg. Mass spectra were performed by using a ZAB-HF (FAB), (matrix: *m*-nitrobenzylic alcohol) and a VG-BIOQ triple quadripole, positive mode(ES-MS). UV/Vis absorption spectra were performed by using a Kontron UVIKON 860 in a 1 cm quartz cell.

2: A mixture of 6,6′-di[2-(2-bromoethoxy)ethoxypropyl]-2,2′-bipyridine (0.948 g, 1.65 mmol) and the commer-

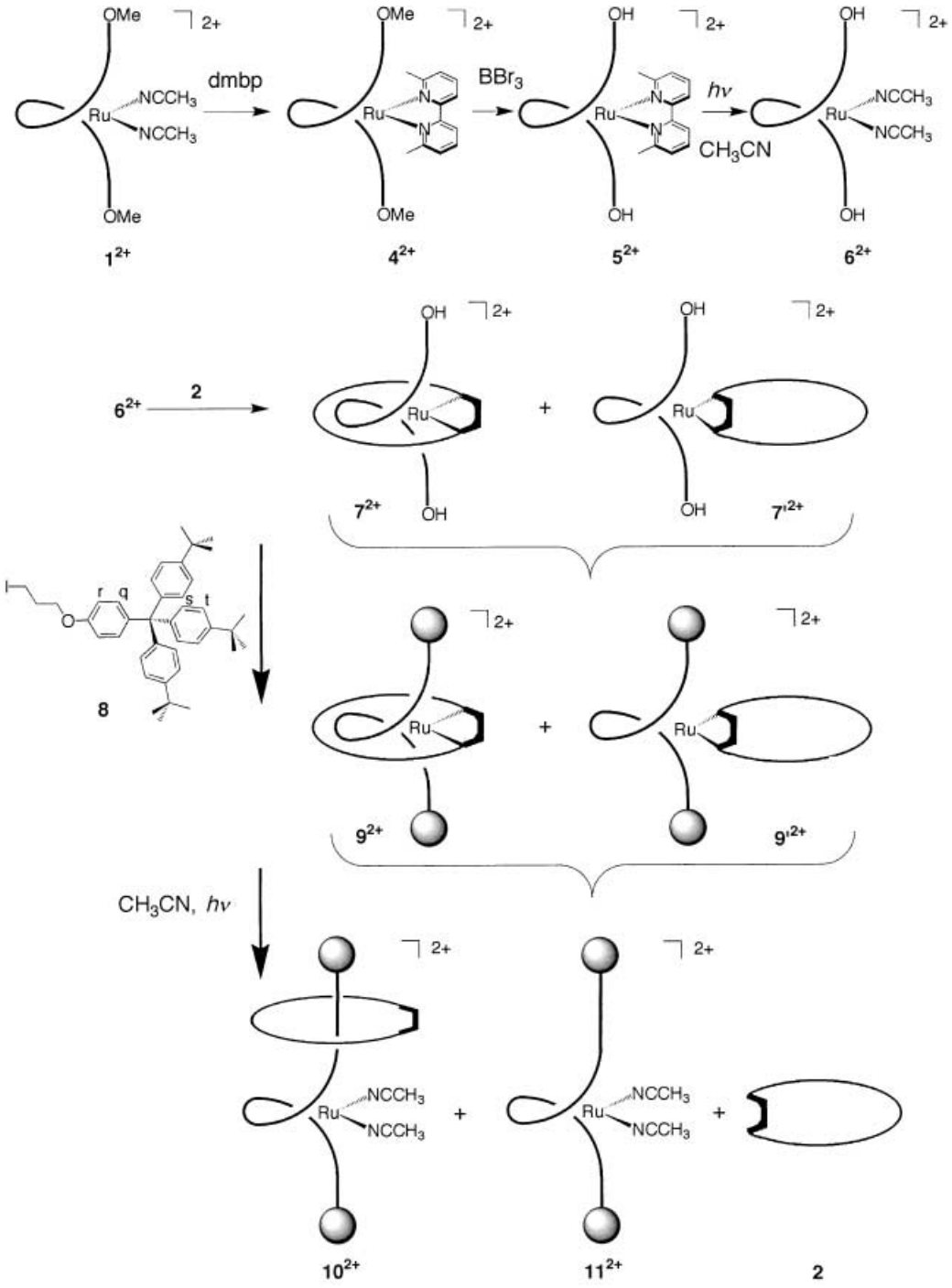


Figure 7. Synthesis of the rotaxane $\mathbf{10}^{2+}$.

cially available 4,4′-isopropylidenediphenol (0.38 g, 1.65 mmol) in degassed DMF (170 mL) was placed in a high dilution funnel fitted on a one liter three-necked flask containing Cs_2CO_3 in suspension in degassed DMF (320 mL). The vessel was heated to 60 °C and the mixture was added dropwise over 72 h. After stirring for a further 10 h, the solvent was removed and the residue was taken up in CH_2Cl_2/H_2O. The organic layers were combined, dried over $MgSO_4$, and after the solvent was removed, the resulting brown oil was chromatographed (Al_2O_3, eluent Et_2O) to give **2** (475 mg; 45 %) as a white solid. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.6$ (s, 6H; $2CH_3$), 2.09 (q, 4H; $^3J = 7.08$ Hz; H_β), 2.92 (t, 4H; $^3J = 7.56$ Hz; H_α), 3.55 (t, 4H; $^3J = 6.33$ Hz; H_γ), 3.6 – 4.2 (m, 16H; $H_{\delta,\varepsilon,\zeta,\eta}$), 6.78 (d, 4H; $^3J = 8.76$ Hz; H_B), 7.07 (d, 6H; $^3J = 8.79$ Hz; $H_{3,3'}$, and H_A), 7.48 (t, 2H; $^3J = 7.8$ Hz; $H_{4,4'}$), 8.19 ppm (d, 2H; $^3J = 7.08$ Hz; $H_{5,5'}$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.3$, 30.9, 34.5, 41.6, 67.5, 69.8, 70.2, 70.3, 71.0, 113.0, 118.2, 122.8, 127.6, 136.9, 143.3, 155.8, 156.6, 160.8 ppm.

1-[PF$_6$]$_2$: $RuLCl_2$[14] (L = 1,10-phenanthroline, 4,4′-(1,4-phenylenedi-2,1-ethanediyl)bis[7-(4-methoxyphenyl)]) was refluxed for 2 h under argon in acetonitrile/water (1/1; 20 mL). After the mixture was cooled, an aqueous solution of saturated potassium hexafluorophosphate (20 mL) was added and the acetonitrile was evaporated. The resulting precipitate was filtered under vacuum and chromatographed on silica. Elution with toluene/acetonitrile (1:1) afforded **1**-$[PF_6]_2$ (134 mg, 40 % overall including complexation) as a brown-yellow solid. Purification can alternatively involve chromatography on silica eluting with acetonitrile/water/saturated aqueous KNO_3 (100:3:1). ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 2.55$ (s, 6H;

CH_3CN), 2.8–4 (m, 8H; CH_2), 4.00 (s, 6H; OCH_3), 6.28 (d, $^3J = 7.9$ Hz, 2H; H_{b2},), 6.68 (d, $^3J = 8.1$ Hz, 2H; H_{b1}), 7.13 (d, $^3J = 5.3$ Hz, 2H; H_2), 7.28 (d, $^3J = 5.1$ Hz, 2H; H_3), 7.34 (d, $^3J = 8.3$ Hz, 4H; H_m), 7.82 (d, $^3J = 8.5$ Hz, 4H; H_o), 8.18 (d, $^3J = 5.3$ Hz, 2H; H_8), 8.42 (d, $^3J = 9.4$ Hz, 2H; H_5), 8.51 (d, $^3J = 9.4$ Hz, 2H; H_6), 9.96 ppm (d, $^3J = 5.5$ Hz, 2H; H_9); UV/Vis (CH_3CN, 5.0×10^{-5} M): λ_{max} (ε) = 394.0 (1.6×10^4), 436.0 nm (1.5×10^4); FAB MS *m/z*: 1031.3 ($[RuL(CH_3CN)_2](PF_6)^+$), 844.3 ($[RuL(CH_3CN) + e^-]^+$), 494.6 ($[RuL(CH_3CN)](PF_6)\text{-}e^-)^{2+}$).

3-$[PF_6]_2$ and 3′-$[PF_6]_2$ as a mixture of *endo*/*exo* conformers: **1**-$[PF_6]_2$ (0.050 g, 0.0425 mmol) and **2** (0.032 g, 0.050 mmol) were dissolved in ethylene glycol (5 mL) and refluxed under argon for 4 h at 140 °C. The brown solution turned dark red. After the mixture had cooled, an aqueous solution of saturated potassium hexafluorophosphate (20 mL) was added and the acetonitrile was evaporated. Filtration under vacuum of the resulting precipitate afforded a red solid which was chromatographed on silica. Elution with a gradient of acetonitrile/water/saturated aqueous KNO_3 from 100:1:1 to 100:9:1 then on alumina eluting with a dichloromethane gradient to dichloromethane/methanol 95:5 yielded **3**-$[PF_6]_2$ and **3′**-$[PF_6]_2$ (0.0224 g, 31 % as a mixture of conformers) as an orange solid. ^{1}H NMR (400 MHz, $CDCl_3$, −50 °C, low fields): $\delta = 6.11$ (d, $^3J = 8.4$ Hz, 2H; H_A), 6.23 (d, $^3J = 7.9$ Hz, 1H; H_{b1}), 6.32 (m, 3H; $H_{b2'}$, **H_{b2}**), 6.52 (d, $^3J = 8.5$ Hz, 4H; **H_A**), 6.67 (d, $^3J = 7.6$ Hz, 1H; $H_{b1'}$), 6.77 (m, 7H; **H_2**, H_B, $H_{2'}$, **H_{b1}**), 7.00 (m, 7H; **H_3**, **H_B**, H_3), 7.10 (m, 7H; **H_m**, H_m, H_2, $H_{A'}$, H_5), 7.22 (m, 5H; H_{p5}, **$H_{p5'}$**, $H_{m'}$, $H_{p5'}$), 7.30 (d, $^3J = 8.4$ Hz, 2H; $H_{B'}$), 7.35 (d, $^3J = 5.5$ Hz, 1H; $H_{3'}$), 7.44 (d, $^3J = 8.1$ Hz, 2H; $H_{o'}$), 7.50 (d, $^3J = 9.1$ Hz, 1H; H_6), 7.64 (m, 6H; **H_o**, **H_8**), 7.75 (m, 6H; **H_{p4}**, $H_{8'}$, H_8, H_o), 7.89 (d, $^3J = 5.4$ Hz, 1H; H_9), 7.92 (t, $^3J = 8.0$ Hz, 1H; $H_{p4'}$), 8.13 (m, 8H; $H_{5'}$, **H_{p3}**, **H_9**, **H_5**, H_{p4}), 8.35 (m, 5H; $H_{p3'}$, $H_{6'}$, $H_{9'}$, **H_6**), 8.47 (d, $^3J = 8.4$ Hz, 1H; H_{p3}); ES-MS *m/z*: 1589.6 (**3**-$[PF_6]$); 722.4 (**3^{2+}**).

Suitable crystals for X-ray analysis were obtained by diffusion of hexane in a solution of the complex in acetone.

4-$[PF_6]_2$: Cation $\mathbf{1}^{2+}$ (0.0375 g, 0.032 mmol) and 6,6′-dimethylbipyridine (0.0072 g, 0.038 mmol) were allowed to react for 3 h at 140 °C in ethylene glycol (10 mL). After cooling, an aqueous solution of saturated potassium hexafluorophosphate was added. This led to the formation of a red precipitate which was filtered under vacuum and then rinsed with diethyl ether to afford **4**-$[PF_6]_2$ (0.041 g, quant. yield) as a red solid.

^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta = 1.65$ (s, 6H; CH_3), 3.20 (m, 8H; CH_2), 3.97 (s, 6H; OCH_3), 6.43 (d, $^3J = 7.9$ Hz, 2H; H_{b2}), 6.88 (d, $^3J = 7.9$ Hz, 2H; H_{b1}), 7.14 (d, $^3J = 5.5$ Hz, 2H; H_3), 7.28 (d, $^3J = 8.7$ Hz, 4H; H_m), 7.41 (d, $^3J = 7.3$ Hz, 2H; H_{p5}), 7.46 (d, $^3J = 5.5$ Hz, 2H; H_2), 7.71 (d, $^3J = 8.7$ Hz, 4H; H_o), 7.90 (d, $^3J = 5.5$ Hz, 2H; H_8), 8.09 (t, $^3J = 7.9$ Hz, 2H; H_{p4}), 8.42 (d, $^3J = 9.4$ Hz, 2H; H_5), 8.57 (d, $^3J = 9.4$ Hz, 2H; H_6), 8.66 (d, $^3J = 5.3$ Hz, 2H; H_9), 8.72 (d, $^3J = 7.7$ Hz, 2H; H_{p3}).

5-$[PF_6]_2$: A commercial 1M dichloromethane solution of boron tribromide (0.3 mL) was further diluted with dry dichloromethane (1 mL) and added dropwise at −78 °C to a solution of $\mathbf{4}^{2+}$ (0.041 g, 0.320 mmol) in dichloromethane (5 mL). The mixture was stirred for 90 min at −78 °C and then 1 h at room temperature. Water, aqueous saturated potassium hexafluorophosphate, dichloromethane, and methanol were added. The organic solvents were evaporated and the crude product was filtered under vacuum to afford **5**-$[PF_6]_2$ (0.040 mg, quantitative yield) as a red solid. ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$): $\delta = 1.62$(s, 6H; CH_3), 3.20 (m, 8H; CH_2), 6.35 (d, $^3J = 9.4$ Hz, 2H; H_{b2}), 6.74 (d, $^3J = 9.4$ Hz, 2H; H_{b1}), 6.97 (d, $^3J = 5.5$ Hz, 2H; H_2), 7.06 (d, $^3J = 8.6$ Hz, 4H; H_m), 7.07 (d, $^3J = 5.5$ Hz, 2H; H_3), 7.25 (d, $^3J = 7.7$ Hz, 2H; H_{p5}), 7.57 (d, $^3J = 8.6$ Hz, 4H; H_o), 7.75 (d, $^3J = 5.5$ Hz, 2H; H_8), 7.95 (t, $^3J = 7.9$ Hz, 2H; H_{p4}), 8.25 (d, $^3J = 5.5$ Hz, 2H; H_9), 8.31 (d, $^3J = 9.4$ Hz, 2H; H_5), 8.41 (d, $^3J = 9.4$ Hz, 2H; H_6), 8.48 (d, $^3J = 8.1$ Hz, 2H; H_{p3}).

6-$[PF_6]_2$: Cation $\mathbf{5}^{2+}$ (0.086 mg, 0.068 mmol) was dissolved in acetonitrile and irradiated for one hour with visible light. An aqueous solution of saturated potassium hexafluorophosphate was added and acetonitrile evaporated. Filtration under vacuum of the resulting precipitate afforded **6**-$[PF_6]_2$ (0.075 g, quantitative yield) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3/CD_3OD$): δ 2.45(s, 6H; CH_3CN), 3.50 (m, 8H; CH_2), 6.21 (d, $^3J = 9.4$ Hz, 2H; H_{b2}), 6.55 (d, $^3J = 9.4$ Hz, 2H; H_{b1}), 6.95 (m, 4H; H_2, H_3), 7.12 (d, $^3J = 8.7$ Hz, 4H; H_m), 7.64 (d, $^3J = 8.5$ Hz, 4H; H_o), 8.08 (d, $^3J = 5.5$ Hz, 2H; H_8), 8.22 (d, $^3J = 9.4$ Hz, 2H; H_5), 8.39 (d, $^3J = 9.4$ Hz, 2H; H_6), 9.67 (d, $^3J = 5.3$ Hz, 2H; H_9).

7-$[PF_6]_2$ and 7′-$[PF_6]_2$ as a mixture of *exo*/*endo* conformers: Cation $\mathbf{6}^{2+}$ (0.075 g, 0.0653 mmol) and **2** (0.050 g, 0.081 mmol) were dissolved in ethylene glycol (8 mL) and refluxed under argon for 2 h at 140 °C. The brown solution turned dark red. After the mixture had cooled, an aqueous solution of saturated potassium hexafluorophosphate (20 mL) was added and the acetonitrile was evaporated. Filtration under vacuum and washing of the resulting precipitate with diethyl ether afforded a red solid which was chromatographed on silica (elution with a gradient of acetonitrile/water/saturated aqueous KNO_3 from 100:1:1 to 100:9:1) to yield the mixture of **7**-$[PF_6]_2$ and **7′**-$[PF_6]_2$ (0.030 g, 27 %) as an orange solid. ^{1}H NMR (400 MHz, [D$_6$]acetone) of the *exo* conformer (sharp signals): $\delta = 6.44$ (d, $^3J = 9.6$ Hz, 2H; **H_{b2}**), 6.89 (d, $^3J = 9.6$ Hz, 2H; **H_{b1}**) 7.17 (m, 10H; **H_m**, **H_2**, **H_A**), 7.43 (m, 4H; **H_{p5}**, **H_3**), 7.55 (d, $^3J = 8.3$ Hz, 4H; **H_o**) 7.61 (d, $^3J = 8.7$ Hz, 4H; **H_B**), 7.87 (d, $^3J = 5.5$ Hz, 2H; **H_8**), 8.10 (m, 2H; **H_{p4}**), 8.44 (d, $^3J = 9.4$ Hz, 2H; **H_5**), 8.56 (d, $^3J = 9.4$ Hz, 2H; **H_6**), 9.63 (d, $^3J = 5.5$ Hz, 2H; **H_9**), 8.70 (d, $^3J = 5.5$ Hz, 2H; **H_{p3}**); ES-MS: *m/z*: 708.4 **7^{2+}**.

9-$[PF_6]_2$ and 9′-$[PF_6]_2$ as a mixture of *exo*/*endo* conformers: The mixture of **7**-$[PF_6]_2$ and **7′**-$[PF_6]_2$ (0.020 g, 0.0113 mmol) and K_2CO_3 (0.010 g, 0.072 mmol) were dissolved in dry DMF at 60 °C under argon. Compound **8** (0.0307 g, 0.0456 mmol) was dissolved in dry DMF and added dropwise to the reaction mixture, which was stirred at 60 °C for 24 h. After the mixture cooled, an aqueous solution of saturated potassium hexafluorophosphate (20 mL) was added, and the resulting precipitate was filtered under vacuum and washed with diethyl ether. The orange solid was chromatographed on silica (elution with CH_2Cl_2/MeOH (99:1)) to yield **9**-$[PF_6]_2$ and **9′**-$[PF_6]_2$ (0.024 g, 74 % as a mixture of *endo*/*exo* isomers) as an orange solid. ^{1}H NMR (400 MHz, [D$_6$]acetone): $\delta = 6.38$ (d, $^3J = 8.9$ Hz, 4H; **H_A**), 6.42 (d, $^3J = 8.0$ Hz, 2H; **H_{b2}**), 6.90 (m, 10H; **H_B**, **H_{b1}**, H_r), 7.13 (m, 18H; H_q, H_s), 7.30 (m, 18H; **H_m**, H_t), 7.50 (br., 2H; H_{p5}), 7.54 (d, $^3J = 8.7$ Hz, 4H; **H_o**), 7.61 (d, $^3J = 5.5$ Hz, 2H; **H_8**), 7.67 (d, $^3J = 8.7$ Hz, 4H; H_o), 7.88 (br., 2H; **H_8**), 8.10 (m, 4H; H_{p4}, **H_{p4}**), 8.40 (d, $^3J = 9.3$ Hz, 2H; **H_6**), 8.55 (m, 4H; **H_5**, **H_9**), 8.68 (m, 6H; H_{p3}, **H_{p3}**, H_9); ES-MS: *m/z*: 1252.8 (**9^{2+}** and **$9'^{2+}$**).

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[16] Crystal data for $2(C_{39}H_{48}N_2O_6)$: colorless crystal, $M_w = 1281.65$, triclinic, $a = 15.6356(2)$, $b = 21.2472(3)$, $c = 23.4524(4)$ Å, $\alpha = 95.775(5)$, $\beta = 107.462(5)$, $\gamma = 108.025(5)^\circ$, $U = 6904.7(2)$ Å^3, $T = 173$ K, space group $P\bar{1}$, $Z = 4$, $\rho_{calcd} = 1.23$ g cm^{-3}, $\mu = 0.083$ mm^{-1}, crystal dimensions: $0.20 \times 0.16 \times 0.14$ mm, $F_{000} = 2752$, $\lambda = 0.71073$ Å, radiation: $Mo_{K\alpha}$ graphite monochromated, diffractometer: KappaCCD, Φ scans, *hkl* limits: $-15,15/-21,21/-23,20$, θ limits: 2.5/20.82°, number of data meas.: 26322, number of data with $I > 3\sigma(I)$: 8754, weighting scheme: $4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4)$, number of variables: 1671, R(F): 0.058, wR(F): 0.070, GOF: 1.190, largest peak in final difference: 1.185 e Å^{-3}. Package use: OpenMolen, Interactive Structure Solution, B. V. Nonius, Delft, The Nederlands, **1997**.

[17] Crystal data for $C_{201}H_{230}F_{24}N_{12}O_{27}P_4Ru_2$: $2(C_{87}H_{86}N_6O_8Ru) \cdot 4PF_6 \cdot 9C_3H_6O \cdot 2H_2O$, orange crystal, $M_w = 4028.14$, triclinic, $a = 16.3590(2)$, $b = 17.8897(3)$, $c = 19.8402(4)$ Å, $\alpha = 107.831(5)$, $\beta = 109.742(5)$, $\gamma = 99.059(5)^\circ$, $U = 4977.2(1)$ Å^3, $T = 173$ K, space group $P\bar{1}$, $Z = 2$, $\rho_{calcd} = 1.34$ g cm^{-3}, $\mu = 0.276$ mm^{-1}. Crystal dimensions: $0.20 \times 0.16 \times 0.14$ mm, $F_{000} = 2100$, $\lambda = 0.71073$ Å, radiation: $Mo_{K\alpha}$ graphite-monochromated, diffractometer: KappaCCD, Φ scans, *hkl* limits: $0,21/-23,22/-25,23$, θ limits: 2.5/27.50°, number of data meas.: 22355, number of data with $I > 3\sigma(I)$: 10419, weighting scheme: $4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4)$, number of variables: 1214, R(F): 0.061, wR(F): 0.086, GOF: 1.514, largest peak in final difference: 1.085 e Å^{-3}. All the non-hydrogen atoms have been refined anisotropically with the exception of the atoms C91, C92, C93 and O10. Package use: OpenMolen, Interactive Structure Solution, B. V. Nonius, Delft, The Netherlands **1997**. CCDC-200198 (**2**) and CCDC-189634 (**3**-$[PF_6]_2$) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html.

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