A Ru(terpy)(phen)-incorporating ring and its light-induced geometrical changes†

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A Ru(terpy)(phen) motif has been inscribed in a 39-membered ring by functionalizing the ligands and subsequently performing a cyclization reaction on the complex; by visible light irradiation, a dramatic geometrical changeover of the cyclic complex takes place which can be reversed thermally.

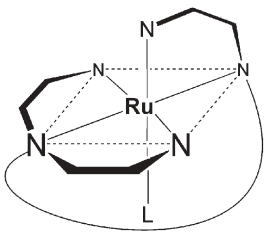
Including and controlling molecular motions *via* various types of signals is a key feature for the development of mechanical devices at the nanoscopic level.[1] Photonic signals are particularly promising and several molecular machines have recently been reported which are set in motion by light irradiation.[2] Our group in particular has described various ruthenium(II)-complexed rotaxanes and catenanes whose movements are induced by populating a dissociative excited state from a metal-to-ligand charge transfer (MLCT) state, this latter state being simply formed by visible light irradiation.[3]

Rings are essential components of molecular machine prototypes, especially within the catenane family.[4] A limited number of ruthenium(II)-incorporating macrorings have been made.[5] Since Ru(II) is substitutionallly inert, the so-called self-assembly approach cannot be utilized.[6] In the present report, we would like to describe the synthesis of a novel Ru(II)-containing cycle, the ligand set consisting of a terpy derivative (terpy = 2,2′,6′,2″-terpyridine) and a phen chelate (phen = 1,10-phenanthroline). The sixth ligand can thermally or photochemically be substituted by another monodentate ligand.[7] It consists of pyridine (py), acetonitrile or S-linked DMSO. In addition, a new photoisomerisation reaction of the ruthenium(II) complex leads to a dramatic change of the ring shape under the action of visible light, the reverse process regenerating the initial state by a thermal reaction.

The embedding of a Ru(terpy)(phen)$^{2+}$ moiety in a ring is certainly not trivial since the terpy fragment occupies three meridional sites of the metal octahedron and the phen chelate is almost opposite to the terpy in the metal coordination sphere.

We thought that a convenient way to connect the phen and the terpy fragments was to interlink a lateral position of the phen (3 position) and the para position (4′) of the central pyridinic nitrogen atom of the terpy. This strategy should allow formation of a large ruthenium(II)-containing ring (Scheme 1).

The starting terpy and phen ligands used are represented in Fig. 1.[8] Since the phen chelate L_2 is asymmetrically substituted, the formation of two isomeric complexes containing L_1, L_2 and the ancillary sixth ligand L seemed to be possible.



Scheme 1

The only complex formed by reacting RuL_1Cl_3 and L_2 was the one for which the sterically hindering mesityl group was in close contact with the terpy nucleus, the sixth ligand Cl^- being located inside the ring cavity.[9] For the moment, the reason for this selectivity is unclear, as well as the reaction mechanism leading to this isomer. $[RuL_1L_2(Cl)]_{th}^+$ (thermal isomer) was subjected to ligand exchange under light irradiation, in CH_3CN–H_2O (5 : 1). Clean substitution of the chloride ligand for CH_3CN was observed, *as well as quantitative isomerisation to the other isomer*, considered as the photoisomer. The substitution–isomerisation reaction $\mathbf{1}^+ \rightarrow \mathbf{2}^+$ is represented in Fig. 1. The isomerisation reaction is remarkably clean, although its mechanism is still unclear. Ligand

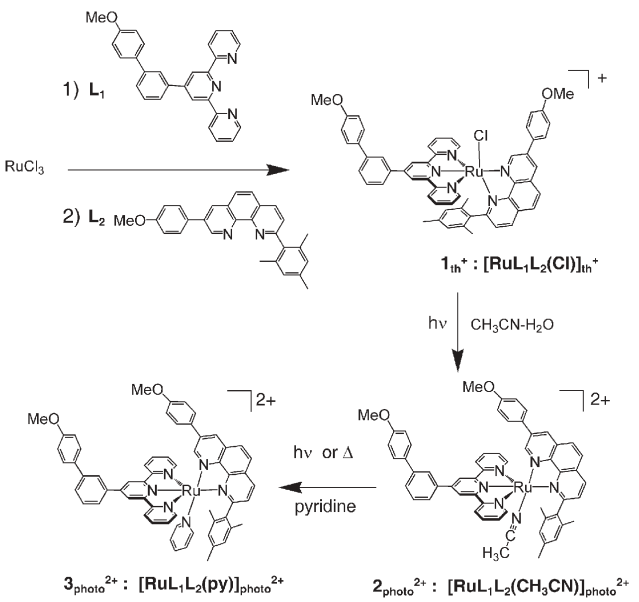


Fig. 1 Synthesis of the photoisomer $Ru(L_1)(L_2)(py)]_{photo}^{2+}$ ($\mathbf{3}_{photo}^{2+}$).

† Electronic supplementary information (ESI) available: ^{1}H NMR spectra of the complexes $\mathbf{1}_{th}^+$ to $\mathbf{5}_{th}^{2+}$. See http://www.rsc.org/suppdata/cc/b5/b503411f/

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exchange was again carried out but, this time, thermally. $[RuL_1L_2(CH_3CN)]_{photo}^{2+}$ was heated in refluxing pyridine and, after work-up, a quantitative yield of the pyridine complex $[RuL_1L_2(py)]_{photo}^{2+}$ was obtained. It is noteworthy that the py complex obtained belongs to the photoisomer family and, thus, no isomerisation takes place during ligand exchange under the relatively harsh conditions used. $[RuL_1L_2(py)]_{photo}^{2+}$ was the starting complex to prepare the ruthenium(II)-containing ring. All the organic chemistry transformations involving the ligands were carried out on the complex. Due to its chemical stability, no decomplexation problems were encountered.

The sequence of reactions leading to the 39-membered ring $\mathbf{5}_{photo}^{2+}$ (still belonging to the photoisomer family) is depicted in Fig. 2. The synthetic procedure is particularly efficient since the overall yield is ~70% from $[Ru\ L_1L_2(py)]_{photo}^{2+}$. The yield of the ring closing metathesis (RCM) reaction leading to the cyclic compound is similar to those corresponding to the preparation of other macrocyclic transition metal complexes of the catenane or knot families.[10] It is very likely that the geometry of the photoisomer $\mathbf{4}_{photo}^{2+}$, precursor of the ring, is favourable to the formation of a cycle. Indeed, the two $-(CH_2)_8-CH=CH_2$ fragments can easily be oriented parallel to one another, with close proximity of the terminal olefins.

Although the photoisomers are very inert towards isomerisation for all members of the family, a procedure was discovered which allowed conversion of the photoisomer $\mathbf{5}_{photo}^{2+}$ to the thermal isomer $\mathbf{5}_{th}^{2+}$. This procedure is quite general and can also be applied to acyclic complexes. The reaction is represented in a very schematic fashion in Fig. 3. It has been carried out with either pyridine or CH_3CN as the entering ligand from the intermediate DMSO complex.

The conversion of $\mathbf{5}_{photo}^{2+}$ to $\mathbf{5}_{th}^{2+}$ is performed in two steps: (1) substitution of py by DMSO and isomerisation, (2) substitution of DMSO by py. Its overall yield is above 80%. In order to perform a complete cycle, the photochemical reaction leading back to $\mathbf{5}_{photo}^{2+}$ was carried out in the usual way (irradiation performed at room temperature with a 1000 W xenon arc-lamp filtered by a water filter) in pyridine. It turned out to be virtually quantitative. The

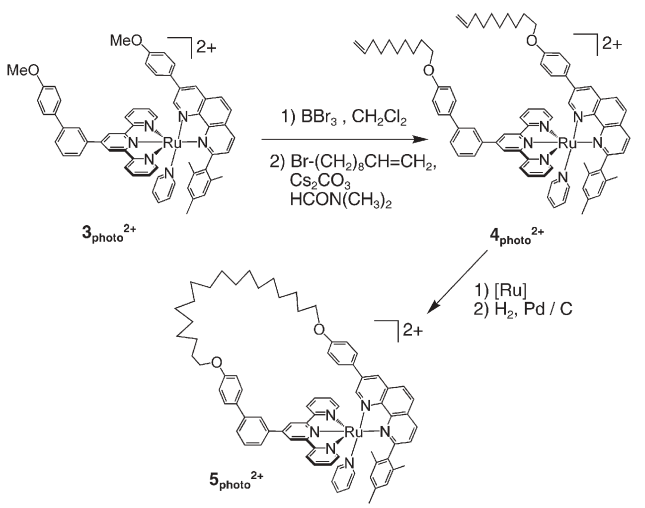

Fig. 2 Preparation of the ruthenium(II)-incorporating 39-membered ring $\mathbf{5}_{photo}^{2+}$; [Ru] = $RuCl_2[P(C_6H_{11})_3]_2(=CHPh)$.

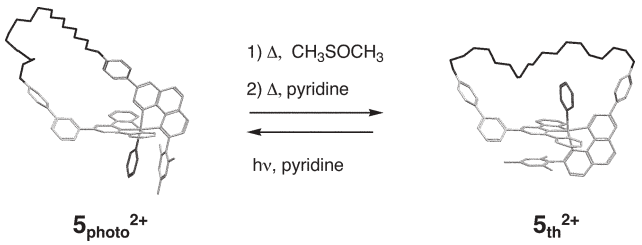

Fig. 3 Thermal isomerisation of the photoisomer $\mathbf{5}_{photo}^{2+}$ and the photochemical back reaction. The pyridine ligand moves from an external position to an intra-ring location while the $-(CH_2)_{18}-$ fragment undergoes a folding–unfolding process.

whole isomerisation process can thus be summarized by the following equation:

$$\mathbf{5}_{photo}^{2+} \underset{h\upsilon}{\overset{\text{1) DMSO, }\Delta\text{ 2) Pyridine, }\Delta}{\rightleftharpoons}} \mathbf{5}_{th}^{2+}$$

This photochemical–thermal isomerisation of the ruthenium-containing ring is accompanied by a dramatic geometrical change of the compound. Molecular modelling studies[11] suggest that the distance between the two oxygen atoms borne by the phenyl rings of the terpy and phen ligands varies from 9.7 Å for the photochemical isomer $\mathbf{5}_{photo}^{2+}$ to 17.7 Å for $\mathbf{5}_{th}^{2+}$. The $-(CH_2)-_{18}$ linker which connects these two oxygen atoms undergoes a folding–stretching process, as depicted in Fig. 3. In the past, the photochemical *cis–trans* isomerisation of an azo (–N=N–) bond has been used to modify the shape of cyclic compounds.[12] Related geometrical changes have also been triggered by a chemical means in dinuclear copper(II) complexes.[13]

In conclusion, a Ru(terpy)(phen) subunit could be inscribed in a ring by connecting the terpy unit and the phen motif by a $-(CH_2)-_{18}$ linker *via* two appropriate positions. A novel photochemical–thermal isomerisation interconverts two very distinct situations: by heating the macrocyclic complex (photoisomer) in DMSO and, subsequently, in pyridine, the folded $-(CH_2-)_{18}$ fragment is stretched. In parallel, the sixth ligand (pyridine), originally located outside the ring, moves to an intracavity position. The process is reversible, since the starting form is regenerated by visible light irradiation.

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8 The detailed synthesis of L_1 and L_2 will be reported elsewhere. L_1 : 3-bromobenzaldehyde and 2-acetylpyridine were coupled with sodium hydroxide in methanol to yield quantitatively the corresponding chalcone, which was reacted with acetylpyridinium iodide and an excess of ammonium acetate in methanol to give 4′-(3-bromophenyl)-2,2′;6′,2″-terpyridine (yield = 63%). To this bromoterpyridine was coupled *p*-anisylboronic acid in the presence of sodium carbonate and $Pd(PPh_3)_4$ in a toluene–water mixture to give L_1 (yield = 70%). L_2: 1,10-phenanthroline hydrochloride was brominated with Br_2 in nitrobenzene to yield 3-bromo-1,10-phenanthroline (26%). The *p*-anisylboronic acid was coupled to this bromophenanthroline using the standard Suzuki cross-coupling conditions (yield = 90%). To the resulting 3-anisyl-1,10-phenanthroline in dried toluene or ether was added an ether solution of mesityllithium monoanion, to afford the two corresponding regioisomers 3-anisyl-2-mesityl-1,10-phenanthroline (yield = 20%) and 8-anisyl-2-mesityl-1,10-phenanthroline (L_2, yield = 26%).
9 Complex $\mathbf{1}^{+}\cdot PF_6^{-}$ was prepared in the following way: 1.0 equiv. of L_2 and 1.5 equiv. of $Ru(L_1)Cl_3$ were mixed together with an excess of LiCl and NEt_3 in a 1 : 4 water–ethanol mixture and heated to reflux for 4 h. A saturated aqueous solution of KPF_6 was added to precipitate the crude mixture, which was filtered, washed with water and recovered with acetone. The ruthenium complex was purified by (1) precipitation of an acetone solution into toluene and filtration and (2) silica gel chromatography of the solid filtrate, to yield $\mathbf{1}^{+}\cdot PF_6^{-}$ as a violet solid (yield = 30%). All the ruthenium(II) complexes , $\mathbf{1}^{+}$ to $\mathbf{6}^{2+}$, were characterized by ^{1}H 1D, 2D COSY and ROESY, ^{1}H–^{13}C HSQC and HMBC NMR spectroscopy, UV-vis spectroscopy and high resolution electrospray mass spectrometry.
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