Letter

Photochemical expulsion of a Ru(phen)$_2$ unit from a macrocyclic receptor and its thermal reco-ordination

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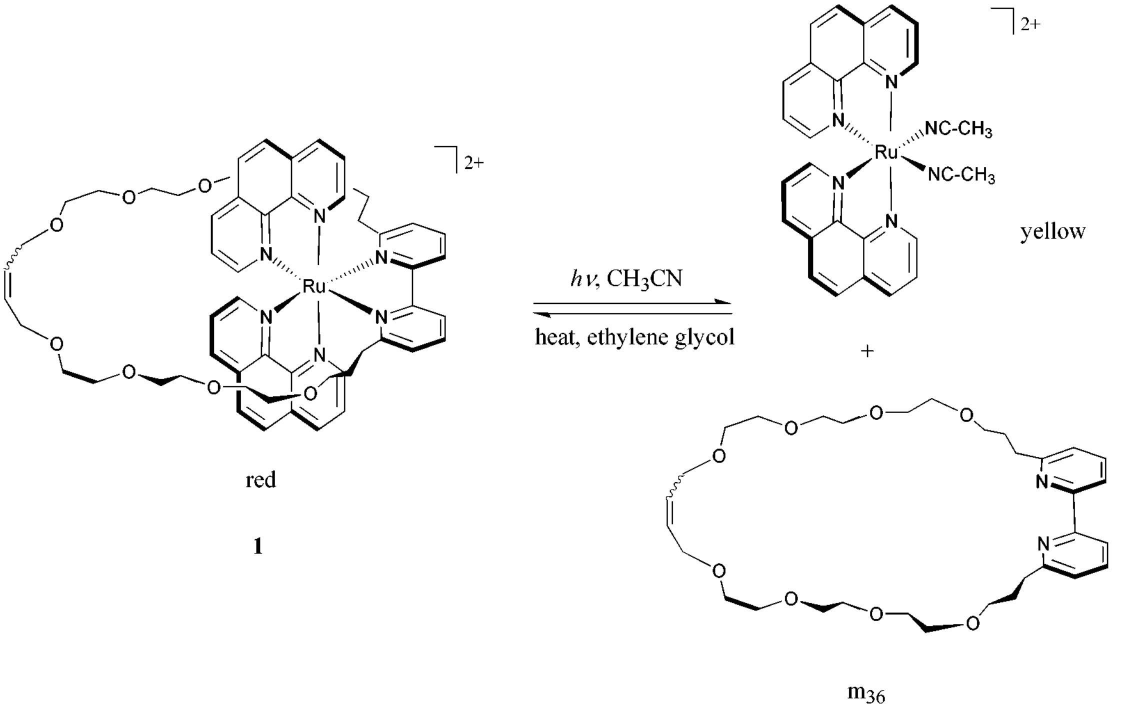
A ruthenium complex containing two 1,10-phenanthroline ligands as well as a bipyridine fragment incorporated in a macrocycle (36 atoms) has been synthesized; photoexpulsion of the Ru(phen)$_2$ unit from the macrocycle and its thermal reco-ordination take place efficiently and quantitatively.

Until now, most molecules or molecular assemblies considered as "machines" or "motors"[1] have been set into motion using chemical or electrochemical signals. Electrochemically driven movements are all based on the same principle: by reducing or oxidizing a given component of the compound, a new, thermodynamically unstable situation is generated which spontaneously will evolve to the thermodynamic well of the system while geometrical changes occur.[2] An interesting photochemical variant of this principle has been proposed by Balzani and co-workers.[3] By exciting a certain fragment of the molecule under light irradiation an excited state having a pronounced electron donor or acceptor character is formed. In the presence of a "sacrificial" agent, electron transfer from or to the excited state takes place, affording the oxidized or reduced form of the compound while the sacrificial agent is consumed.

We would now like to report another type of photochemically induced movement based on *dissociative photo-excited states.* Ru(bipy)$_3{}^{2+}$ (bipy = 2,2′-bipyridine) and its numerous homologues have mostly been used as photochemical electron or energy transfer agents, in relation to light energy conversion into chemical energy.[4] In this respect, the photochemical stability of these compounds represents a real advantage, but a few examples of photochemical dissociation of such complexes have been reported.[5] In some cases the "photoexpulsion" process of a given ligand can be relatively efficient[6] and it opens the gate to a new way of setting molecular systems into motion. The use of a sterically hindered chelate, such as 6,6′-dimethyl-2,2′-bipyridine (dmbp), turned out to be especially promising since selective and efficient dissociation of this particular chelate was observed under light irradiation.[7] In the present system a hindered bipyridine fragment has been incorporated into a macrocycle and the ruthenium(II)-containing unit includes two 1,10-phenanthroline (phen) fragments. Ru(phen)$_2{}^{2+}$ is a stable unit which will not be affected by light irradiation. The principle of the photochemically driven motion and the thermal backward reaction is shown in Scheme 1.

The macrocyclic complex **1** was synthesized from the ruthenium(II) precursor **3** incorporating a 2,2′-bipy ligand substituted at its 6 and 6′ positions by two long chains bearing terminal olefins (see Scheme 2). Compound **2** was prepared in



Scheme 1 Principle of the photochemically driven motion and the thermal backward reaction.

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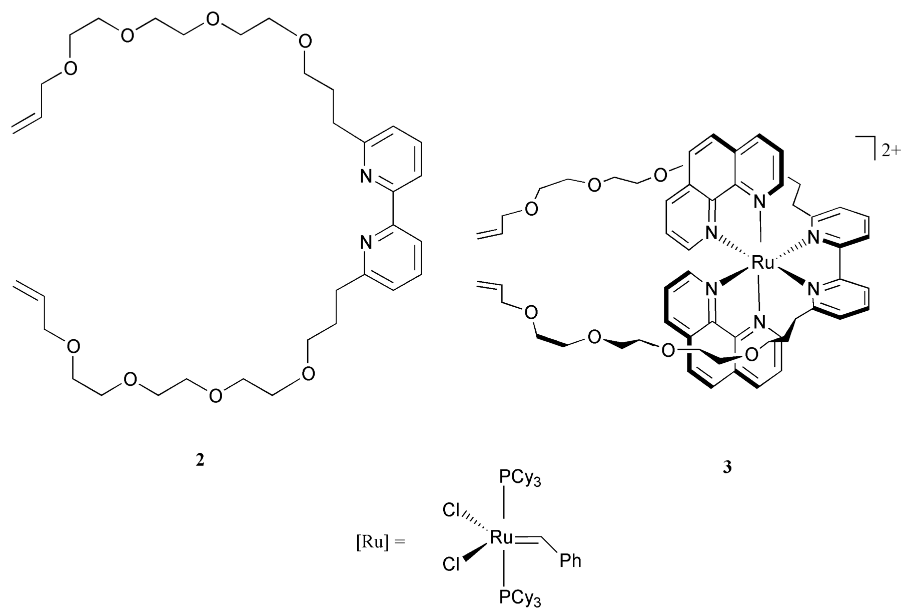


Scheme 2 The precursors **2** and **3** of the ruthenium complex **1**.

5 steps from dmbp[8] and its synthesis will be reported elsewhere. The precursor complex **3** was obtained in good yield (75%) from **2** and Ru(phen)$_2$(CH$_3$CN)$_2{}^{2+}$ by heating a stoichiometric mixture of them in ethylene glycol at 140 °C for 2 hours. **3** was isolated as its PF$_6{}^-$ salt. It is obtained pure as a red powder after column chromatography. The ^{1}H NMR spectrum is in accordance with its structure. The next step consists of cyclizing the two terminal functions of the coordinated bipy. Ring-closing metathesis of olefins (RCM), recently proposed by Grubbs and his group,[9] has been used in numerous cases, most of the time with remarkable success.[10] This catalytic reaction is compatible with a large variety of functions and, in particular, with transition metal complexes such as copper(I) or iron(II) polyimine compounds.[11,12] In the present case the RCM reaction turned out to be equally efficient since a 67% yield of the desired complex **1** was obtained, without utilizing high dilution conditions (0.01 M dichloromethane solution of **3**, room temperature, 5 days, 7% of ruthenium catalyst [Ru]). The reaction can easily be monitored by ^{1}H NMR since the characteristic signals of the terminal olefins constitute a convenient probe. Gradually, these two sets of signals (δ 5.18 and 5.04 in acetone-d$_6$) are replaced by those corresponding to the cyclic olefin of **1** (5.31 and 5.39), obtained as a mixture of *cis* and *trans* isomers. The mass spectrum (FAB-MS) of **1** confirms the expected structure (M − PF$_6$, *m*/*z* 1195.3).

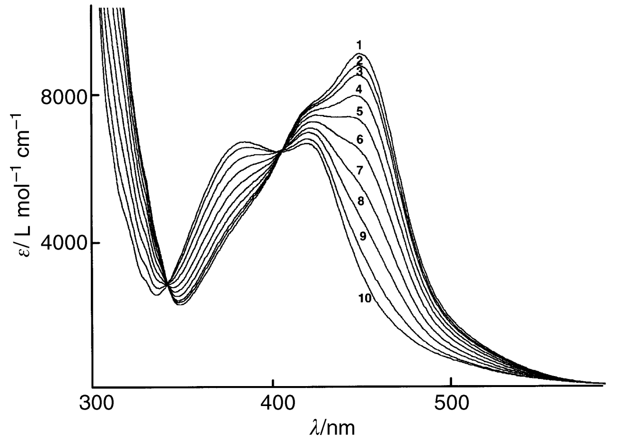


Fig. 1 Electronic spectra of acetonitrile solution of complex **1** after visible light irradiation: 1(0); 2(6); 3(12); 4(30); 5(40); 6(60); 7(90); 8(130); 9(192); 10(370 s).

The photochemical behaviour of complex **1** has been examined by both UV-Visible and ^{1}H NMR spectroscopy in acetonitrile. Under light irradiation ($\lambda > 300$ nm), it undergoes an efficient and quantitative photolabilization of the macrocycle m$_{36}$ as demonstrated in Fig. 1 by the different visible spectra recorded during the progress of the reaction. After 6 min of irradiation there is no change in the electronic spectrum and curve 10 is characteristic of the Ru(phen)$_2$(CH$_3$CN)$_2{}^{2+}$ species.[13] Also, two well resolved isosbestic points at 342 and 406 nm demonstrate the selectivity of the process. By analysing the absorbance variations *vs.* time, an apparent rate constant can be deduced ($t_{1/2} = 75$ s). The efficiency of this photochemical reaction is less than that of a previously studied system[7] in which a Ru(phen)$_2$ core is associated to dmbp itself ($t_{1/2} = 28$ s under the same conditions). Since the steric hindrance is more prononced in **1** than in Ru(phen)$_2$dmbp^{2+}, it seems that some deco-ordination steps of the chelate unit are probably slower due to the presence of the macrocyclic chain. The cyclic nature of the complex is also expected to favour a *cis* conformation for the bipy unit, making its stepwise decomplexation slightly more difficult than with its unconstrained analogue, dmbp.

Similar results could be obtained using ^{1}H NMR spectroscopy with direct light irradiation of the NMR tube. The characteristic spectrum of complex **1** is gradually replaced by the sum of the spectra of Ru(phen)$_2$(CD$_3$CN)$_2{}^{2+}$ and free macrocyclic m$_{36}$.

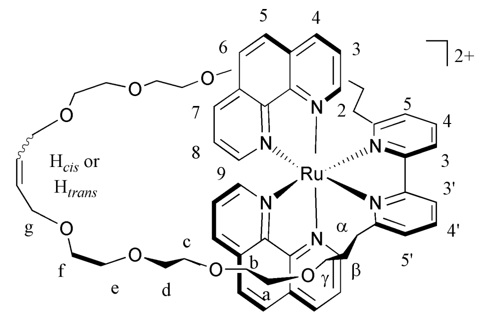
The thermal back reaction was also proved to be quantitative. An equimolecular mixture of Ru(phen)$_2$(CH$_3$CN)$_2{}^{2+}$ and m$_{36}$ leads back to the starting complex **1** in quantitative yield (refluxing ethylene glycol; two hours).

These first results are promising for the construction of photomechanical devices in which the macrocycle m$_{36}$ and the Ru(phen)$_2$ unit will be respectively the ring and the core of the string of a rotaxane.

Experimental

Characterization of **1**, **2** and **3**

1: ^{1}H NMR (acetone-d$_6$, 200 MHz) δ 8.94 (dd, 2 H, H^4, $J = 8.36$ and 1.24) 8.76 (dd, 2 H^2, $J = 5.41$ and 1.23), 8.68 (dd, 2 H, H^7, $J = 8.37$ and 1.23), 8.62 (d, 2 H, H$^{3,3'}$, $J = 7.38$), 8.47 (d, 2 H, H^5, $J = 8.86$), 8.38 (d, 2 H, H^6, $J = 8.86$), 8.09 (dd, 2 H, H$^{4,4'}$, $J = 8.12$ and 7.14), 8.09 (dd, 2 H, H$_3$), 7.92 (dd, 2 H, H^9, $J = 5.29$ and 1.11), 7.67 (dd, 2 H, H^8, $J = 5.42$ and 8.12), 7.43 (d, 2 H, H$^{5,5'}$, $J = 7.88$ Hz), 5.39 (m, 2 H, H$_{cis}$, 75%), 5.31



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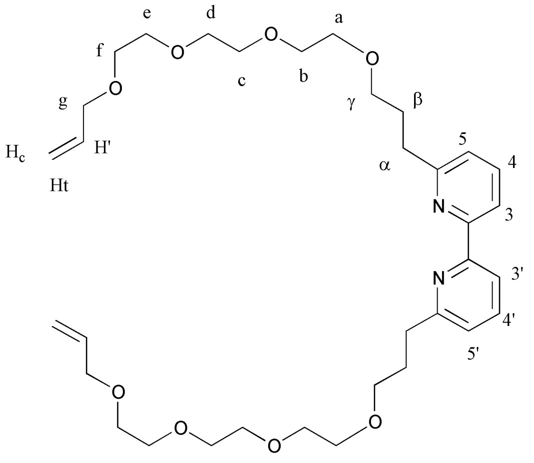

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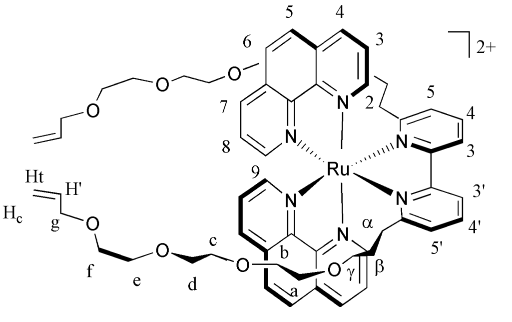

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(m, 2 H, H_{trans}, 25%), 3.90–1.50 (m, 40 H, H_g, $H_{a, b, c, d, e, f}$, $H_{\alpha, \beta, \gamma}$); FAB-MS: $m/z = 1195.3$, $[M - PF_6]^+$, calc. 1195.35, 8%; 1049.3, $[M - 2\ PF_6 + e^-]^+$, calc. 1050.38, 11%; 462.0 $[M - 2\ PF_6\text{-}m_{36} + e^-]^+$, calc. 462.04, 32%. UV-Vis (CH_3CN) λ 450 nm (ε 9200 L mol^{-1} cm^{-1}).

2: ^1H NMR ($CDCl_3$, 200 MHz) δ 8.24 (d, 2 H, $H^{3,3'}$, $J = 7.86$), 7.68 (t, 2 H, $H^{4,4'}$, $J = 7.75$), 7.14 (dd, 2 H, $H^{5,5'}$, $J = 7.62$ and 0.98), 5.91 (ddt, 2 H, H′, $J = 17.22$, 10.32 and 5.66), 5.26 (dtd, 2 H, H_t, $J = 17.10$, 3.44 and 1.60), 5.16 (m, 2 H_c, $J = 10.32$, 1.72 and 1), 4.01 (dt, 4 H, H_g, $J = 5.66$ and 1.36), 3.67–3.50 (m, 28 H, $H_{a, b, c, d, e, f}$, 4 H_γ), 2.92 (t, 4 H, H_α, $J = 7.50$), 2.11 (tt, 4 H_β, $J = 6.52$ and 6.88 Hz); FAB-MS: $m/z = 617.5$, $[M + H]^+$, calc. 617.38, 100%.

3: ^1H NMR (acetone-d_6, 200 MHz) δ 8.94 (dd, 2 H, H^4, $J = 8.15$ and 1.10), 8.74 (dd, 2 H, H^2, $J = 5.17$ and 1.22), 8.67 (dd, 2 H, H^7, $J = 8.35$ and 1.22), 8.63 (d, 2 H, $H^{3,3}$, $J = 8.86$), 8.47 (d, 2 H, H^5, $J = 8.86$), 8.38 (d, 2 H, H^6, $J = 8.86$), 8.10 (dd, 2 H, $H^{4,4'}$, $J = 7.86$ and 7.88), 8.10 (dd, 2 H, H^3, $J = 5.23$ and 8.24), 7.97 (dd, 2 H, H^9, $J = 5.40$ and 1.23), 7.62 (dd, 2 H, H^8, $J = 5.28$ and 8.24), 7.44 (dd, 2 H, $H^{5,5'}$, $J = 7.87$ and 0.99), 5.82 (ddt, 2 H, H′, $J = 17.34$, 10.44 and 5.23), 5.18 (m, 2 H, H_t), 5.04 (m, 2 H, H_c), 3.88 (dt, 4 H, H_g, $J = 5.42$ and 1.54 Hz), 3.60–3.20 (m, 24 H, $H_{a, b, c, d, e, f}$), 3.20–1.00 (12 H, $H_{\alpha, \beta, \gamma}$).

Photoirradiation was performed in a quartz UV cell ($P = 1.0$ cm) or in a NMR tube (diameter = 5.0 mm) by the use of a Hanimex slide projector (150 W halogen lamp).

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