Molecular Devices

Light-Driven Machine Prototypes Based on Dissociative Excited States: Photoinduced Decoordination and Thermal Recoordination of a Ring in a Ruthenium(II)-Containing [2]Catenane**

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In memory of Jean-Marc Kern

Inducing molecular motions in a controlled fashion under the action of an external signal, either to mimic some of the functions of biological motors[1] or in relation to artificial molecular switches, machines, and devices,[2] is particularly challenging. As far as synthetic systems are concerned, catenanes and rotaxanes occupy a special position,[3] although non-interlocking systems have also been investigated.[4] In the majority of the systems the movements have been triggered by an electrochemical[5] or a chemical signal.[6] Photonic stimuli are particularly promising, but only a few examples have been reported.[7]

We have recently described multicomponent ruthenium(II) complexes in which one part of the molecule can be set in motion photochemically.[8] In these systems the light-driven motions are based on the formation of dissociative excited states. Complexes of the $[Ru(diimine)_3]^{2+}$ family are particularly well adapted to this approach: They display intense absorption in the visible region and the magnitude of the ligand field can be controlled by the steric and electronic properties of the chelates. If distortion of the coordination octahedron is sufficient to change the ligand field, which can be realized by using one or several sterically hindering ligands, the strongly dissociative ligand-field state (LF or d-d state) can be efficiently populated from the metal-to-ligand charge transfer (^{3}MLCT) state to result in expulsion of a given ligand. The principle of the whole process is represented in Figure 1. It is based on well-established ruthenium(II) photochemistry,[9] but, in the past, the d-d state has mostly been considered as a detrimental state, which leads to decomposition of catalytic species in various photochemical reactions.

The [2]catenane **1** of Scheme 1 has recently been synthesized[10] by using an octahedral ruthenium(II) center as template. Compound **1** consists of a 50-membered ring (M50) which incorporates two 1,10-phenanthroline (phen) units and a 42-membered ring (M42) which contains the 2,2′-bipyridine (bipy) chelate. The related compound **2** has also been prepared by using a slightly different procedure.[11] Compound **2** contains the same bipy-incorporating ring as **1**, but the other ring is much larger than in **1**: it is now a 63-membered ring.[11] The light-induced motion and the thermal back reaction carried out with **1** or **2** are represented in a very schematic way in Scheme 1 together with the chemical structures of the two forms for each catenane. The ancillary ligand (L) is either the solvent (CH_3CN) or Cl^-.

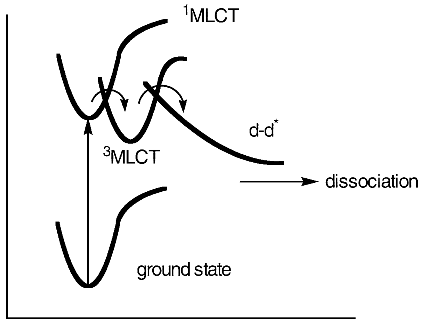

Figure 1. Relative relationship of the states involved in the dissociation process. The dissociative d-d* state must be accessible from the ^{3}MLCT state to set a $[Ru(diimine)_3]^{2+}$-based molecular machine in motion.

Catenanes **1′** and **2′** contain two disconnected rings as the photochemical reaction leads to decomplexation of the bipy chelate from the ruthenium(II) center. It must be stressed that the drawings of the decoordinated forms **1′** and **2′** are only indicative and do not imply that the geometries of the molecules are those shown. The photochemical reactions **1**→**1′** and **2**→**2′a** (in the presence of chloride ions) as well as the thermal backward reactions were monitored by UV/Vis measurements (**1**/**1′** and **2**/**2′a**) and by ^{1}H NMR spectroscopy (**1**/**1′**). In a typical reaction, a degassed 10^{-4} M solution of **2** in CH_2Cl_2 containing a tenfold excess of $NEt_4^+Cl^-$ was irradiated at room temperature using a 250 W halogen lamp ($\lambda >$ 300 nm). The color of the solution rapidly changed from red (**2**: $\lambda_{max} = 458$ nm) to purple (**2′a**: $\lambda_{max} = 561$ nm) and after a few minutes the reaction was complete. A clean isosbestic point at 484 nm was observed (Figure 2), which indicates that the conversion **2**→**2′a** is quantitative.

The recoordination reaction **2′a**→**2** was carried out by heating a solution of **2′a** in ethylene glycol either at 140 °C for 15 minutes or at 80 °C for 2 h. The photochemical decoordination of the ring and its thermal recomplexation to form **1**/**1′** are quantitative (> 95 %), as evidenced by ^{1}H NMR spectroscopic studies. A particularly useful probe, which allows the rearrangement processes of the ruthenium(II)-complexed catenanes to be readily monitored, is the ^{1}H NMR signal of the H_9 proton (Scheme 1 b). Decoordinating the bipy fragment from the metal resulted in a strong downfield shift, which illustrates the pronounced ring-current effect of the bipy nucleus on H_9 in **1** and its absence in **1′**: $\delta(H_9) = 8.13$ ppm for H_9 in **1** and $\delta(H_9) = 10.53$ ppm in **1′**, $\Delta(\delta(H_9)) = 2.4$ ppm (CD_3CN/CD_2Cl_2). The photoproducts have also been characterized by electrospray mass spectrometry (ES-MS).[12]

The same effects were also observed for the analogous reaction of **2** in CH_3CN, the ancillary ligand now being the

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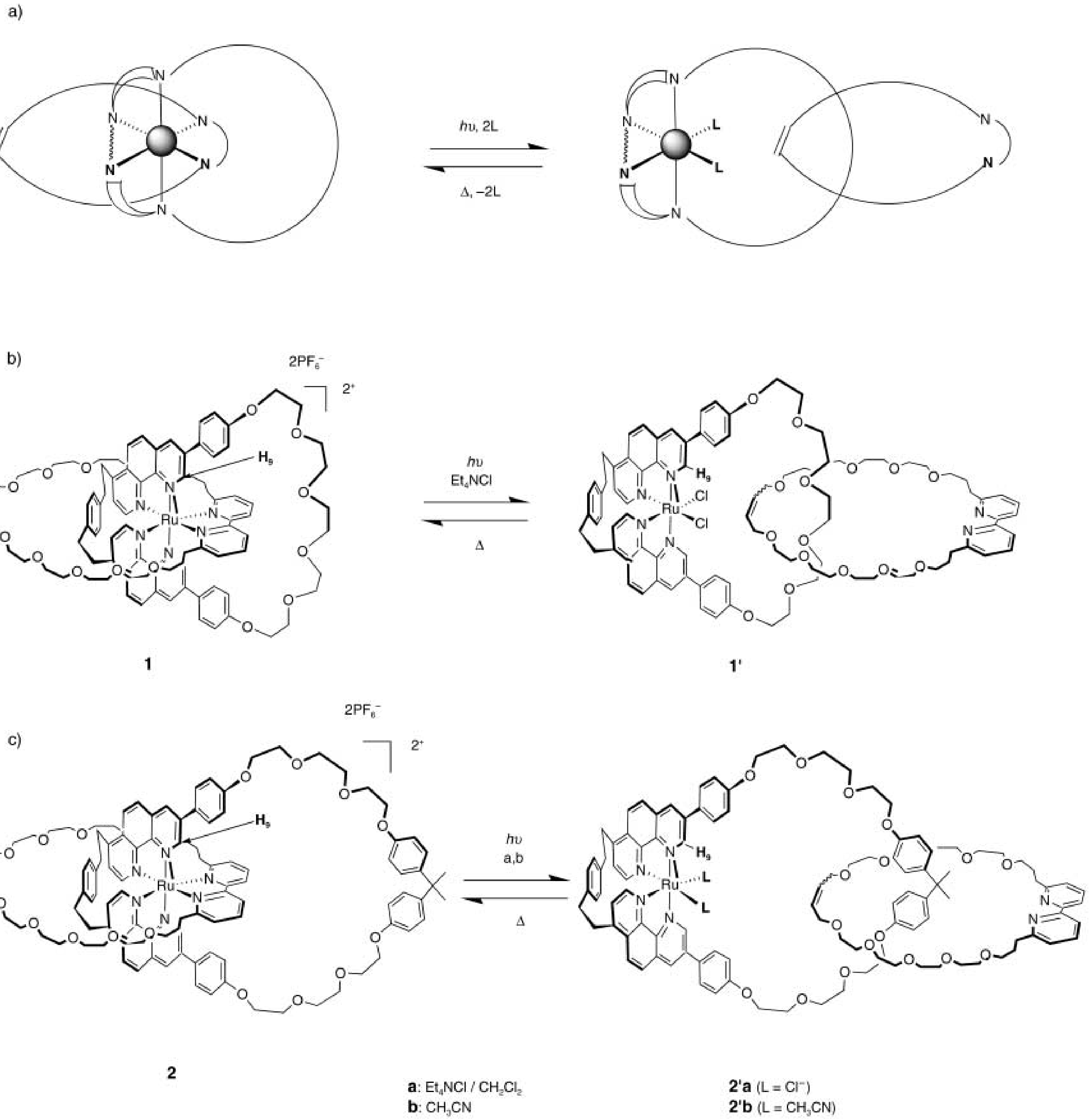

Scheme 1. a) Schematic representation of the photoinduiced and thermal motions taking place in the present catenanes, b) and c) chemical structure of catenanes **1** and **2** and their photoproducts **1**′, **2**′**a**, and **2**′**b**. M42 is one of the constitutive rings containing the bipy fragment.

solvent instead of Cl^-. The photochemical decoordination of the ring and its thermal recomplexation in **2**/**2**′**b** are also quantitative (> 95 %) as evidenced by ^{1}H NMR spectroscopy. The quantum yield for the photochemical reaction **2**→**2b**′ at 25 °C and $\lambda \approx 470$ nm (± 50 nm) can be very roughly estimated as 0.014 ± 0.005.

Interestingly, a marked ring-size effect was noticed. The smaller catenane **1** was less photoreactive than the larger one (**2**), but slightly easier to reform from its decomplexed form **1**′ than was its higher homologue. Catenane **1** could not be converted into its decoordination product with CH_3CN as the entering ligand (no photochemical reaction after a few hours of irradiation) whereas **2** was converted into the bisacetonitrile analogue **2**′**b** very efficiently (quantitative reaction in two or three minutes of irradiation). Similarly, the reaction **1**→**1**′ is about 40 times slower than the similar reaction for the larger catenane (**2**→**2**′**a**). The thermal back reaction is less affected by the ring size of the ring containing two phen units: the rates

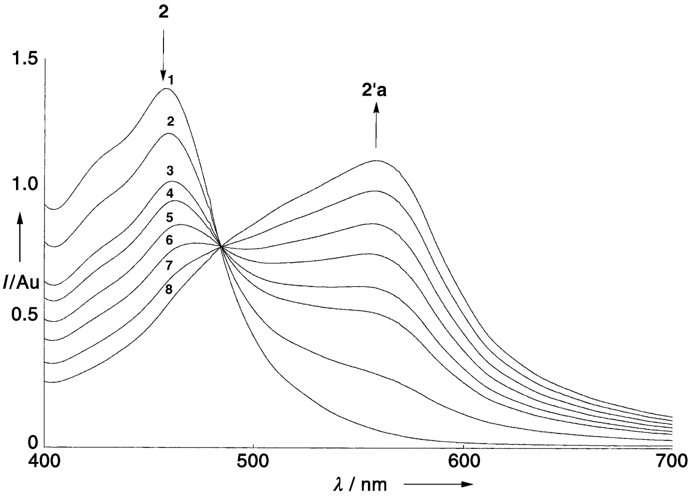

Figure 2. Absorption spectra (visible region) of a solution containing **2** and $NEt_4^+Cl^-$ in CH_2Cl_2 before, during, and after irradiation. Spectra were recorded at *t* = 0 s (**1**), 20 s (**2**), 40 s (**3**), 60 s (**4**), 80 s (**5**), 110 s (**6**), 150 s (**7**), 310 s (**8**). The conversion **1**→**1'** is also quantitative.

of the two reactions **1'**→**1** and **2'a**→**2** differ by a factor of approximately two to three, with **1'** being faster to recoordinate the bipy unit than **2'a**. The ring-size effect observed for the decoordination and the recoordination reactions can be rationalized in terms of the effective concentrations of the respective reacting components $[Ru(phen)_2]^{2+}$ and bipy. The apparent concentration is higher for the smaller catenane than for the larger one, which leads to the expected difference of reactivity, at least for the recomplexation reaction of the 42-membered ring. The cramped nature of **1** with a strained 50-membered ring[13] may explain why mutual motions of both rings are inhibited (with L = CH_3CN) or substantially slown down (with L = Cl^-).

In conclusion, the present ruthenium(II) catenanes represent new prototypes of light-driven machines, with a photonic signal being used to set one of the rings in motion by disconnecting it from the ring incorporating the metal center. Simple heating regenerates the starting complex, with both reactions (decoordination/recoordination) being quantitative. The pronounced difference in reactivity between the two catenanes studied gives some clues as to the potential importance of subtle structural factors in controlling the rate of a given motion in catenane-based molecular machines.

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[11] **2** was prepared by using the same strategy as the synthesis of **1**.[10] Instead of using a 50-membered ring, a new 63-membered-ring macrocycle was prepared. The 63-membered ring was synthesized by treating a bisphenanthroline ligand[10] bearing two phenol-terminated functionalities with a long dibromide fragment under high dilution conditions. Its synthesis will be reported elsewhere: P. Mobian, J.-M. Kern, J.-P. Sauvage, *Helv. Chim. Acta*, **2003**, *86*, 4195–4213.

[12] **1**′ and **2b**′ were characterized by using mass spectrometry and ^{1}H NMR techniques. A solution of catenane **1** (2 mg, 1.029×10^{-6} mol) in CH_2Cl_2 (20 mL) was stirred under argon in the presence of a large excess of Et_4NCl (3 mg, 1.8×10^{-5} mol) and irradiated for 90 mins. The color changed progressively from yellow-orange to violet. The reaction was controlled by TLC (CH_2Cl_2/MeOH 90/10). After evaporation of the solvent, the crude product was dissolved in CD_2Cl_2. ^{1}H NMR (400 MHz, CD_2Cl_2): $\delta = 10.53$ (d, 2H, H_9), 8.45 (d, 2H), 8.2 (d, $^3J = 7.8$ Hz, 2H), 8.14–8.08 (2 × d, $^3J = 9.1$ Hz, 4H), 7.78 (d, $^3J = 8.8$ Hz, 4H), 7.65 (d, $^3J = 7.8$ Hz, 2H), 7.2–7.0 (m, 6H), 6.74 (d, $^3J = 7.8$ Hz, 4H), 6.58 (d, $^3J = 5.3$ Hz, 2H), 6.42 (d, $^3J = 7.8$ Hz, 2H), 5.69 (m, 2H), 4.4 (m, 2H), 4.2 (m, 2H), 3.96 (m, 4H), 3.80–3.00 (m, 60H), 2.88 ppm (t, $^3J = 7.7$ Hz, 4H), 2.00 (m, 4H); FAB-MS: $m/z =$ 1726.7 [**1**′ + H^+] (calcd: 1726), 1690.1 [**1**′-Cl] (calcd: 1689.5), 1654.1 [**1**′−2 Cl] (calcd: 1654), 1049 [**1**′−M42] (calcd: 1049), 1013 [**1**′−M42−Cl] (calcd: 1013), 979.7 [**1**′−M42−2 Cl] (calcd: 979). Complex **2b**′ (2 mg) was dissolved in CD_3CN and the NMR tube was irradiated. NMR spectra were recorded every 30 s. The photolysis reaction was complete after 9 mins. ^{1}H NMR (500 MHz, CD_3CN): $\delta = 9.61$ (s, 2H, H_9), 8.95 (s, 2H), 8.24 (br d, 4H), 7.94 (d, $^3J = 8.6$ Hz, 4H), 7.91 (d, $^3J = 7.7$ Hz, 2H), 7.48 (t, $^3J = 7.7$ Hz, 2H), 7.23 (d, $^3J = 8.6$ Hz, 4H), 7.02 (d, $^3J = 8.8$ Hz, 4H), 6.92 (d, $^3J = 7.7$ Hz, 2H), 6.82 (d, $^3J = 5.5$ Hz, 2H), 6.78 (d, $^3J = 5.5$ Hz, 2H), 6.71 (d, $^3J = 8.8$ Hz, 4H), 6.57 (d, $^3J = 7.9$ Hz, 2H), 6.20 (d, $^3J = 7.9$ Hz, 2H), 5.31 (m, 2H), 4.32 (m, 4H), 3.97 (m, 4H), 3.84 (m, 4H) 3.72 (m, 4H), 3.70–2.90 (m, 52H), 2.59 (m, 4H), 1.65 ppm (m, 4H); ES-MS: $m/z = 2135$ [**2b**′−PF_6^-] (calcd: 2135.9), 2055 [**2b**′−2 CH_3CN−PF_6^-] (calcd: 2053.9), 995 [**2b**′−2 PF_6^-] (calcd: 995.45), 954 [**2b**′−2 CH_3CN−2 PF_6^-] (calcd: 954.4), 1459 [**2b**′−PF_6^+−M42] (calcd: 1459.5), 657 [**2b**′−2 PF_6^-−M42] (calcd: 657.25), 636 [**2b**′−2 PF_6^-−CH_3CN](calcd: 636.75), 616 [**2b**′−2 PF_6^-−M42−2 CH_3CN] (calcd: 616.25), 677.4 [M42 + H^+] (calcd: 677.4), 684 [M42 + Li^+] (calcd: 687.4), 664 [**2b**′−2 PF_6^- + H^+](calcd: 664), 650 [**2b**′−2 PF_6^-−CH_3CN + H^+] (calcd: 650), 636 [**2b**′−2 PF_6^-−2 CH_3CN + H^+] (calcd: 636).

[13] As evident from CPK models and the X-ray structure of the precursor to **1** containing the ruthenium center complexed to the 50-membered ring and 2 CH_3CN molecules (P. Mobian, J.-M. Kern, J.-P. Sauvage, *Helv. Chim. Acta*, **2003**, *86*, 4195–4213).