Macrocyclic Complexes of $[Ru(N\text{-}N)_2]^{2+}$ Units [N-N = 1,10 Phenanthroline or 4-(*p*-Anisyl)-1,10-Phenanthroline]: Synthesis and Photochemical Expulsion Studies

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Two ruthenium complexes $[Ru(phen)_2(m\text{-}36)]^{2+}$ and $[Ru(aphen)_2(m\text{-}36)]^{2+}$, indicated as **1** and **2** respectively, which contain a 36-membered macrocycle incorporating a sterically hindered bipyridine (m-36), and two 1,10-phenanthroline (phen) or 4-(*p*-anisyl)-1,10-phenanthroline (aphen) ligands, have been synthesised. Under light irradiation, as seen from the metal-to-ligand-charge-transfer (MLCT) bands of the visible spectral region, the $[Ru(phen)]_2^{2+}$ core of **1** and **2** is selectively expelled from the macrocycle to give the corresponding bis-acetonitrile derivative. This photochemical process was found to be notably less efficient than that observed in a simpler related complex $[Ru(phen)_2dmbp]^{2+}$ (dmbp = 6,6′dimethyl-2,2′-bipyridine), that lacks the macrocyclic motif. In the case of **1** thermal back reaction takes place quantitatively affording a completely reversible system. The isolation, by chromatographic techniques, of the axial-axial *cis*-$[(a,a)Ru(aphen)_2Cl_2]$ isomer, where the two aphen ligands bear two *p*-anisyl groups disposed trans to one another enabled the preparation of **2**. This type of complex undergoes a more complicated photochemical process, in fact, following the expected photolabilisation of the $[Ru(aphen)_2]^{2+}$ unit, photoisomerisation of the primary photo-product occurs and gives a statistical mixture of the three geometrical isomers: *cis*-$[(a,a)Ru(aphen)_2(CH_3CN)_2](PF_6)_2$, *cis*-$[(a,e)Ru(aphen)_2(CH_3CN)_2](PF_6)_2$ and *cis*-$[(e,e)Ru(aphen)_2(CH_3CN)_2](PF_6)_2$. This side-reaction precludes its use as rotaxane precursor suggesting that, for this purpose, a bis-phenanthroline ligand stabilising the ruthenium core is needed.

Introduction

The accessibility to rotaxanes and catenanes by strategies based on various template effects allowed their involvement in different research fields such as photo-induced energy and electron transfer or molecular machines.[1] The presence of mechanical bonds, an intrinsic property of such species, should confer good reversibility to systems designed for specific tasks related to large amplitude movements. The control of molecular motion for example is an essential function in artificial[2] as well as in biological systems[3] (ATPsynthase, myosin-actin, etc.).Very often, motions in the molecules or molecular assemblies have been triggered by chemical[4] or electrochemical signals.[5] Relatively few systems rely on *purely photonic* input.[6] We now report on a transition metal light-driven system based on dissociative photoexcited states. Ru^{II} complexes of the $[Ru(diimine)_3]^{2+}$ family (diimine = bidentate ligand) seem to be promising in building light-driven machines, since the use of a sterically hindered chelate (e.g. a 6,6′ substituted bipy) associated with a $[Ru(phen)_2]^{2+}$ core (phen = 1,10-phenanthroline) leads to the specific and quantitative photolabilisation of the chelate.[7] Indeed, excitation into the absorption bands of Ru^{II}-polyimine complexes corresponding to the singlet metal-to-ligand-charge-transfer transitions (^{1}MLCT) is followed by intersystem crossing to the lowest-lying triplet level (^{3}MLCT) which, by thermal redistribution, may populate upper-lying dissociative d-d metal centred (MC) states.[8] The MC/MLCT energy gap is small and the thermal deactivation of the ^{3}MLCT state is particularly effective when the ligand field is weakened by distortions due to the sterically hindering ligands. A recent communication described a system constituted by a $[Ru(phen)_2]^{2+}$-type fragment hosted in a macrocyclic receptor.[9] The present article extends this previous example to a possible rotaxane precursor and evidences the limitations brought by a competitive photoisomerisation reaction. Figure 1 displays the basis of the photochemical expulsion of the ruthenium unit from a macrocycle and its thermal back re-coordination.

Results and Discussion

The ruthenium complexes $[Ru(phen)_2(m\text{-}36)]^{2+}$ (**1**) and $[Ru(aphen)_2(m\text{-}36)]^{2+}$ (**2**) [see a) in Figure 2] in which a bipyridine unit is incorporated in a macrocycle have been synthesised as possible rotaxane precursors. Indeed, the re-

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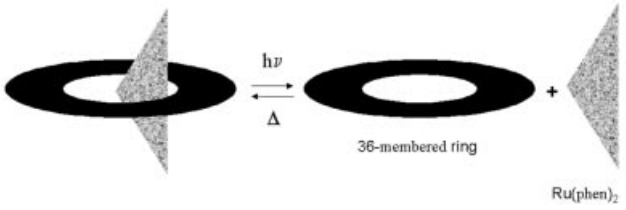


Figure 1. Principle of the photochemically driven motion and the thermal backward reaction

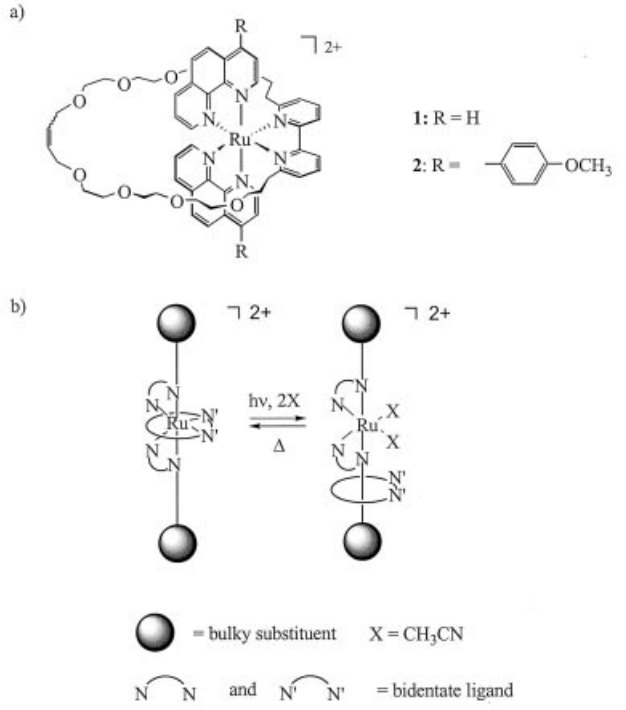
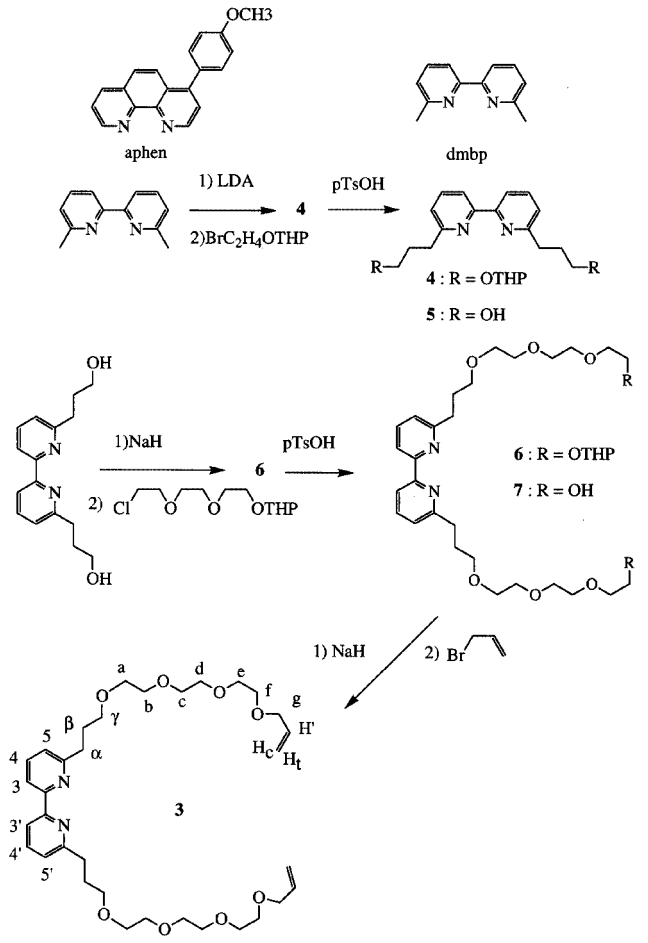


Figure 2. (a) Chemical structures of complexes **1** and **2**. (b) Possible photochemical reaction leading to a rotaxane if bulky stoppers are attached in the 4 positions

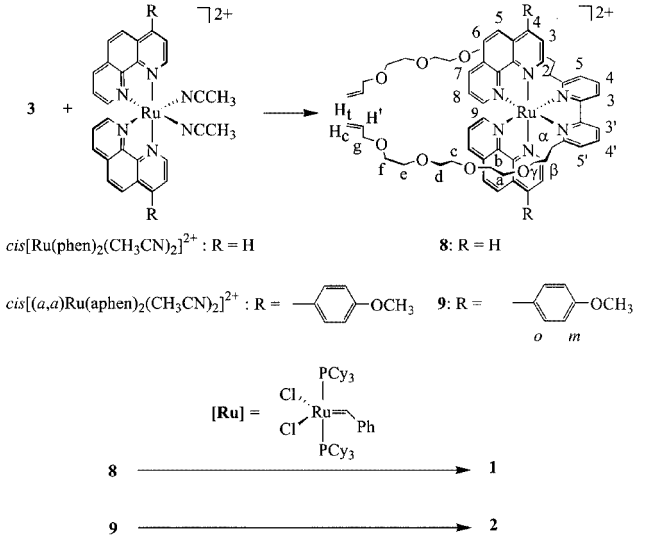
placement of the R group by bulky substituents and the photosubstitution of the bipyridine-based macrocycle by two molecules of solvent (CH_3CN) could lead to a real rotaxane as depicted in Figure 2, b). The synthesis of **1** and **2** is accomplished by applying the strategy of threading or clipping.

In this latter strategy the complexation of an appropriate bipyridine derivative bearing terminal olefins (**3**) precedes the closure of the macrocycle (Scheme 1 and 2).

The 2,2′-bipyridine ligand **3** substituted at its 6 and 6′ positions by two long chains terminated by olefinic groups was prepared in five steps from the 6,6′-dimethyl-2,2′-bipyridine (dmbp).[10] By deprotonation of dmbp with LDA in THF and reaction with two equivalents of THP-protected bromoethanol (THP = tetrahydropyran-2-yl) **4** was obtained in 63% yield. Deprotection of **4** afforded **5** in 70% yield. This alcohol was converted into **6** following the Williamson methodology (NaH/DME) by reaction with 2-{2-[2-(2-chloroethoxy)ethoxy)]ethoxy}tetrahydro-2*H*-pyran (53% yield). Deprotection with catalytic amounts of *para*-



Scheme 1



Scheme 2

toluenesulfonic acid (*p*TsOH) in ethanol led to the corresponding diol **7** in good yield (84%). The conversion of **7** to ligand **3** bearing terminal olefins was achieved with a large excess of allyl bromide in the presence of NaH in DME (75% yield).

It was recently shown that *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$ is a more efficient starting material than the classical bis-chloro derivative *cis*-$[Ru(phen)_2Cl_2]$ for introducing a third chelate onto the ruthenium centre.[11] Good yields of **8** were obtained by heating a stoichiometric mixture of *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$ [12] and **3** in ethylene glycol at 140 °C for 2 h. After column chromatography and anion exchange with PF_6^-, **8** was recovered as a red powder. The preparation of the analogous precursor **9** requires the isomeric form *cis*-$[(a,a)Ru(aphen)_2(CH_3CN)_2](PF_6)_2$ as the axle of the rotaxane (see b in Figure 2). It is itself obtained by solvolysis of the dichloride derivative *cis*-$[(a,a)Ru(aphen)_2Cl_2]$ (Figure 3).

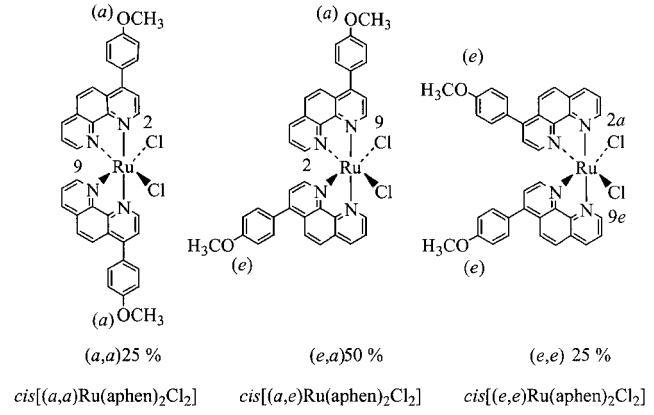


Figure 3. Schematic view of the isomeric complexes for the general species *cis*-$[Ru(aphen)_2Cl_2]^{2+}$ (*a* for axial, *e* for equatorial)

The use of an unsymmetrical ligand such as 4-(*p*-anisyl)-1,10-phenanthroline (aphen) is a challenging task since stereo- and geometric isomers are expected. The sequential addition of different bidentate polypyridyl ligands onto the ruthenium centre is actually described in the literature but several attempts following these methodologies failed.[13,14] Recently, $[Ru(CH_3CN)_4Cl_2]$ was used by von Zelewsky et al.[15] to prepare ruthenium bis-chloro complexes with a bis-bidentate ligand (chiragen). With this starting material and two equivalents of aphen a statistical mixture of three isomers as represented in Figure 3 was recovered in 46% yield. The separation of the geometric isomer *cis*-$[(a,a)Ru(aphen)_2Cl_2]$ from the mixture turned out to be possible on silica columns and on numerous acidic alumina columns with a yield of 87% being obtained. The identification of each isomer was made possible by analysing their ^1H NMR spectra (COSY and ROESY experiments). On heating the *cis*-$[(a,a)Ru(aphen)_2Cl_2]$ isomer in a CH_3CN/H_2O (50:50) mixture the bis-acetonitrile derivative *cis*-$[(a,a)Ru(aphen)_2(CH_3CN)_2]$ was isolated as a single isomer proving that no isomerisation occurs under these conditions. The reaction of ligand **7** with the complex *cis*-$[(a,a)Ru(aphen)_2(CH_3CN)_2](PF_6)_2$ gave the precursor complex **9** in 90% yield.

The cyclisation of the two terminal olefinic functions following the method developed by Grubbs et al.[16] (ring closing metathesis or RCM) turned out to be efficient. This method is compatible with a large variety of functions and has also been proved to be well suited to the synthesis of catenanes and molecular knots.[17] By using a relatively high concentration of the precursor complexes **8** and **9** (0.01 M, CH_2Cl_2 solution) and 7% of the ruthenium complex [Ru] (Scheme 2) as a catalyst the targeted complexes **1** and **2** were obtained in 67 and 45% yield, respectively. The progress of the cyclisation reactions can be monitored by the disappearance of the characteristic ^1H NMR signals of the terminal olefins and the concomitant appearance of signals corresponding to the cyclic olefin in its *cis* and *trans* isomeric forms. The electronic and mass spectra (FAB-MS) as well as the assignment of their ^1H NMR spectra (ROESY experiments) confirm the expected structures of **1** and **2**.

Upon irradiation at 404 nm (isosbestic point, see below) of an acetonitrile solution of **1**, a photochemical reaction is triggered that can be monitored by absorption and ^1H NMR spectroscopy. The starting 2.5×10^{-5} M red solution of **1** gradually changes its colour into yellow, as a consequence of the changes in position and intensity of the MLCT absorption bands. In particular, the band that peaked at 450 nm decreases with irradiation time and a new absorption band with a maximum at 380 nm grows (Figure 4).

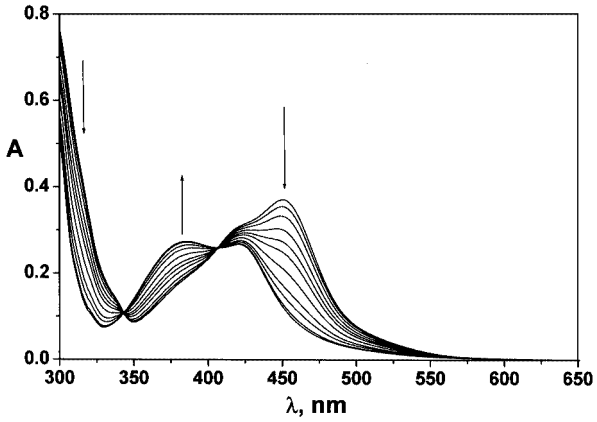


Figure 4. Changes in the electronic absorption spectra of a 2.5×10^{-5} M acetonitrile solution of **1** under irradiation with a 150 W xenon lamp at 404 nm. Spectra are recorded at t = 0, 2, 5, 10, 15, 20, 30, 45, 60, 90, 120 min of irradiation

Neat isosbestic points appear at 342 and 404 nm, emphasising the selectivity of the photochemical process and the final spectrum (Figure 4) is identical to that of the *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$ species. Importantly, **1** is stable when kept in the dark for indefinite periods. The experimental data led us to conclude that an efficient photolabilisation of the $[Ru(phen)_2]^{2+}$ unit takes place, analogous with the results obtained for the simpler $[Ru(phen)_2(dmbp)]^{2+}$ complex.[7] Notably, in the case of **1**, under the same experimental conditions (150 W xenon lamp, λ_{exc} = 404 nm) the time required to complete the reaction (120 min) is longer than that for $[Ru(phen)_2(dmbp)]^{2+}$ (50 min), suggesting that the expulsion of the dmbp-containing macrocycle is kinetically less favoured than the loss of a plain dmbp ligand in $[Ru(phen)_2(dmbp)]^{2+}$, due to steric hindrance.

Experiments performed by ^{1}H NMR spectroscopy confirmed the above results. The spectrum obtained after irradiating an NMR tube containing **1** in CD_3CN corresponds to a mixture of *cis*-$[Ru(phen)_2(CD_3CN)_2]^{2+}$ and the free macrocycle m-36. Once again, the efficiency of this photochemical reaction is found to decrease in comparison with the previously studied system in which a $[Ru(phen)_2]^{2+}$ core is associated with dmbp.[7]

Complexes **1** and $[Ru(phen)_2dmbp]^{2+}$ are not luminescent at room temperature due to thermally induced deactivation of the potentially luminescent MLCT state via the upper lying MC level (possibly leading to photodissociation, see above). Lowering the temperature prevents this thermal deactivation process. Very intense, long-lived luminescence is observed at 77 K for both compounds (Table 1, Figure 5). *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$ also exhibits intense MLCT luminescence at 77 K, and its maximum peak is substantially blue-shifted relative to **1** and $[Ru(phen)_2dmbp]^{2+}$.[18] Notably, after irradiation the emission spectra of **1** and $[Ru(phen)_2dmbp]^{2+}$ strongly resemble that of *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$, revealing the presence of only a small residual amount (< 10%) of starting material (see spectral shoulder at 625 nm, Table 1). The excited state lifetime (3.0 μs) also strongly supports the view that photochemical induced expulsion of the bipy-type fragment has occurred, leading to the formation of a *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$ coordination centre for both complexes.

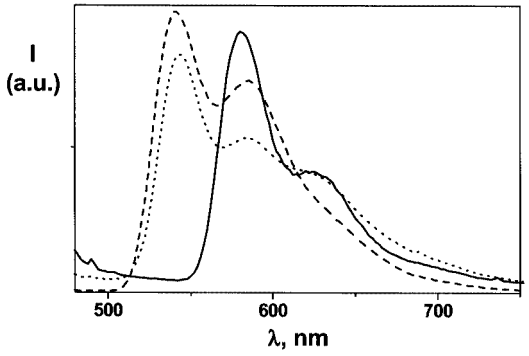
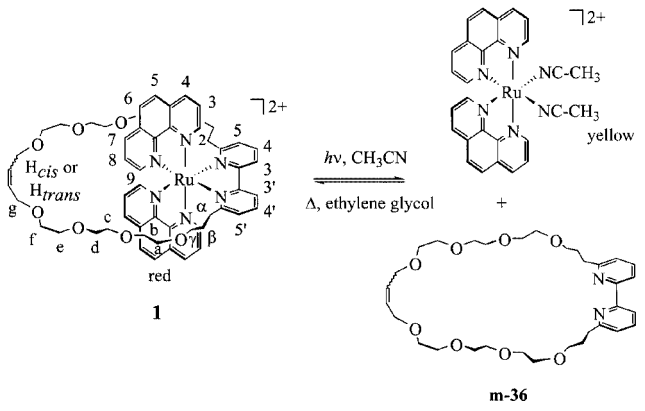


Figure 5. Emission spectra at 77 K of a CH_3CN rigid matrix of **1** before (full line, λ_{exc} = 449 nm) and after (dotted line, λ_{exc} = 420 nm) irradiation and of *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$ (dashed line, λ_{exc} = 420 nm). O. D. = 0.5 for all samples at the excitation wavelength

At 25 °C, quantum yields for photolabilisation are 0.020 ± 0.002 and 0.008 ± 0.001 in the case of $[Ru(phen)_2dmbp]^{2+}$ and **1,** respectively. Since the steric hindrance is more pronounced in **1** than in $[Ru(phen)_2dmbp]^{2+}$, it seems that some decoordination steps of the chelate unit are slower due to the presence of the macrocyclic chain. The cyclic nature of the complex is also expected to favour a *cis* conformation of the alkene group of the bipy-based macrocycle, making the stepwise decomplexation slightly more difficult than it is with its unconstrained analogue, dmbp.

After irradiation, it was possible to quantitatively recover complex **1** by refluxing the equimolar mixture of *cis*-$[Ru(phen)_2(CH_3CN)_2]^{2+}$ and macrocycle m-36 in ethylene glycol for two hours. The principle of the photochemically driven motion and the thermal backward reaction is indicated in Scheme 3.



Scheme 3

The photochemical behaviour of complex **2** has also been studied under similar conditions as for complex **1**, i.e. with an efficiency similar to that observed for the same process in **1**. However, a careful examination of the area around the isosbestic point (417 nm) shows that some by-products were formed during the photoirradiation. By monitoring the photochemical reaction using ^{1}H NMR spectroscopy (CD_3CN, 500 MHz) the appearance of the free macrocycle is concomitant with the formation of the three isomeric forms of the complex *cis*-$[Ru(aphen)_2(CD_3CN)_2]^{2+}$ in the ratio 1(*a*,*a*)/2(*a*,*e*)/1(*e*,*e*). This experiment suggests that a photochemical isomerisation of the primary photo-product *cis*-[(*a*,*a*)$Ru(aphen)_2(CD_3CN)_2]^{2+}$ takes place at a similar or higher rate than that of the photosubstitution of the macrocycle m-36. A bis-phenanthroline ligand[19], that is able to stabilise the ruthenium core in a single isomeric form, is

Table 1. Luminescence Properties of the CH_3CN rigid matrix at 77 K

	$[Ru(phen)_2dmbp]^{2+}$ before irradiation	$[Ru(phen)_2dmbp]^{2+}$ after irradiation	**1** before irradiation	**1** after irradiation	$[Ru(phen)_2(CH_3CN)_2]^{2+}$
λ_{max}[a] (nm)	592, 644	545, 584, 625(sh)	584, 634	545, 584, 625(sh)	545, 584
τ[b] (μs)	2.7	3.0	5.7	3.0	3.0

[a] Band maxima from uncorrected emission spectra, excitation wavelengths are the maxima of the room temperature MLCT absorption spectra, namely 450 nm for $[Ru(phen)_2dmbp]^{2+}$ and **1** before irradiation and 420 nm for these compounds after irradiation and $[Ru(phen)_2(CH_3CN)_2]^{2+}$. [b] Excited state lifetimes, λ_{exc} = 337 nm.

needed to circumvent this undesirable process. Preliminary experiments show that no photoisomerisation occurs when the phenanthroline ligands are linked by a *p*-xylyl bridge. We are currently working on a ruthenium complex that incorporates both this bis-phenanthroline ligand and a bipy-based macrocycle.

Experimental Section

Physical Measurements: ^{1}H NMR spectra were obtained with Bruker WP200 SY (200 MHz), Bruker AM 400 and ARX 500(400 and 500 MHz, respectively) spectrometers. Chemical shifts reported are referenced to Me_4Si as an internal standard. All the photochemical and photophysical experiments were carried out in acetonitrile (Carlo−Erba for spectroscopy). The absorption spectra were recorded with a Perkin−Elmer λ5 spectrophotometer. Emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter (continuous 150-W Xe lamp), equipped with a Hamamatsu R-928 photomultiplier tube. Excited state lifetimes were determined with an IBH single photon counting spectrometer equipped with a thyratron gated nitrogen lamp working in the 4−30 kHz range (λ_{exc} = 337 nm, 0.5 ns time resolution); the detector was a red-sensitive (185−850 nm) Hamamatsu R-3237−01 photomultiplier tube.

Photochemical reactions were performed as follows: dilute solutions of the complexes (about 2.5×10^{-5} M), were put into 1 cm path spectrophotometric cuvettes and irradiated under continuous stirring with a 150 W xenon lamp (Osram XBOW/1) at 404 nm using slits of 2.5 mm (9.4 nm) at the entrance and exit of a Spex 1681 0.22M monochromator. At the end of the photoreaction, after removing CH_3CN under vacuum, the orange residue was dried under vacuum to give, quantitatively, the complex $[Ru(phen)_2(CH_3CN)_2]^{2+}$ and the macrocycle.

Quantum yields of the photoreaction at 436 nm were obtained by measuring the intensity of the light source with the "micro-version" of the ferric oxalate actinometer.[20]

Synthesis of Ligands and Complexes

Some ligands and complexes were prepared following literature procedures: 3-chloro-1-(*p*-methoxyphenyl)propanone,[21] 6,6′-dimethyl-2,2′-bipyridine (6,6′-dmbp),[10] *cis*-$[Ru(phen)_2(CH_3CN)_2](PF_6)_2$,[12] $[Ru(phen)_2(6,6'\text{-dmbp})](PF_6)_2$.[7] All charged species were isolated as PF_6^- salts. The solvents were distilled over the appropriate drying agents.

4-(*p*-Anisyl)-1,10-phenanthroline (aphen): In a three-neck round-bottomed flask equipped with a reflux condenser and a thermometer, a mixture of 8-aminoquinoline (20.0 g, 0.139 mol), arsenic pentoxide As_2O_5 (18.7 g, 0.081 mol), concentrated H_2SO_4 (30 mL) and H_2O (10 mL) was heated to 100 °C under strong magnetic stirring. 3-chloro-1-(*p*-methoxyphenyl)propanone (39.0 g, 0.197 mol) was then added rapidly. The reaction mixture was heated at reflux for 2.5 h, and then poured onto ice and made alkaline with concentrated aqueous 7 M KOH. After addition of CH_2Cl_2, the organic phase was separated, the aqueous layer was extracted 5 times with CH_2Cl_2 (500 mL) and the combined organic layers were washed with water (3 times), then dried over $MgSO_4$. The black oil was collected by filtration, washed with CH_2Cl_2 and was purified by repeated chromatography (silica, CH_2Cl_2, eluent: CH_2Cl_2/MeOH, 97:3; alumina, hexane/ether, 50:50, eluent: CH_2Cl_2/MeOH, 95:5; alumina, ether/EtOAc, 50:50, eluent: CH_2Cl_2/MeOH, 99:1) and recrystallised from ethyl acetate. A sand-brown powder was isolated (10.0 g, 0.035 mol) in 25% yield. Sand-brown powder (m.p. 138 °C). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 9.14 (dd, *J* = 4.18 and 1.48 Hz, 1 H, 9-H), 9.12 (d, *J* = 4.42 Hz, 1 H, 2-H), 8.26 (dd, *J* = 7.99 and 1.85 Hz, 1 H, 7-H), 7.75 (d, *J* = 9.10 Hz, 1 H, 5-H), 7.68 (d, *J* = 9.10 Hz, 1 H, 6-H), 7.64 (dd*J* = 7.99 and 4.31 Hz, 1 H, 8-H,), 7.55 (d, *J* = 4.66 Hz, 1 H, 3-H), 7.49 (d, *J* = 8.84 Hz, 2 H, H_o), 7.09, *J* = 8.86 Hz(d, 2 H, H_m), 3.90 (s, 3 H, Me) ppm. $C_{19}H_{14}N_{20}$: calcd. C 79.70, H 4.93, N 9.78; found C 78.74, H 5.05, N 8.23.

6,6′-Bis(γ-tetrahydropyranylpropyl)-2,2′-bipyridine (4): A 1.64 M *n*BuLi (14.0 mL, 23.0 mmol) solution was added dropwise to a solution of diisopropylamine (3.4 mL, 24.3 mmol) in THF (21 mL), under argon. A degassed solution of 6,6′-dmbp (2.0 g, 10.8 mmol) in anhydrous THF (20 mL) was cooled to − 78 °C and the freshly prepared LDA solution was added via a cannula. The solution turned from yellow to blue-purple and was stirred for a further 2 h at − 78 °C, after which the temperature was allowed to rise to 5 °C. The deep red solution was once again cooled to − 78 °C. Meanwhile, a solution of tetrahydropyrannyl-2-bromoethyl-ethyl (4.7 g, 24.0 mmol) in anhydrous THF (5 mL) was cooled to − 78 °C and degassed. This solution was then transferred, under argon, to the solution of 6,6′-dmbp at − 78 °C and the mixture turned deep green. The solution was then stirred for 16 h at room temperature. The clear orange-brown solution was hydrolysed with water (80 mL) and turned yellow. After the solvent was removed and the residue treated with CH_2Cl_2, the organic layers were washed with water, dried over $MgSO_4$, and the solvent was evaporated. The resulting orange oil was purified by column chromatography on alumina (eluent: hexane/diethyl ether, 50:50). The product was obtained in 63% yield (3.0 g, 6.8 mmol). Yellow oil. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 8.26 (dd, *J* = 7.87 Hz, 0.99 Hz, 2 H, 3,3′-H), 7.71 (t, *J* = 7.74 Hz, 2 H, 4,4′-H), 7.18 (dd, *J* = 7.60 and 0.99 Hz, 2 H, 5,5′-H), 4.57 (t, *J* = 3.44 Hz, 2 H, H_a), 3.80 (m, 4 H, H_e), 3.41 (m, 4 H, Hγ), 2.93 (t, *J* = 7.75 Hz, 4 H, H_α), 2.12 (m, 4 H, H_β), 1.59 (m, 12 H, $H_{b,c,d}$) ppm.

6,6′-Bis(γ-hydroxypropyl)-2,2′-bipyridine (5): The bipyridine derivative **4** (2.90 g, 6.61 mmol) was dissolved in 95% EtOH (45 mL) and heated to reflux. A spatula of *p*-toluenesulfonic acid (1.27 g, 6.54 mmol) was then added. The reaction was followed by TLC (SiO_2, eluent: CH_2Cl_2/5% MeOH) and the reflux was maintained for 4 h. Additional aliquots of acid (0.80 g, 4.12 mmol) were added and the solution was refluxed for a further 4 h. The ethanol was then removed and the residue was dissolved in a CH_2Cl_2/H_2O mixture. After neutralisation by an aqueous solution of K_2CO_3, the aqueous phase was extracted 3 times with CH_2Cl_2 and the organic layers were washed with water, dried over $MgSO_4$, filtered and the solvent evaporated. The crude mixture was purified by column chromatography on silica (eluent: CH_2Cl_2/MeOH, 94.5:5.5) to give the product (1.24 g, 4.55 mmol) in 69% yield. Yellow oil. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 8.09 (dd, *J* = 7.75 Hz, 0.61 Hz, 2 H, 3,3′-H), 7.75 (t, *J* = 7.74 Hz, 2 H, 4,4′-H), 7.21 (dd, *J* = 7.75 Hz, 0.87 Hz, 2 H, 5,5′-H), 3.90 (br. s, 2 H, OH), 3.68 (t, *J* = 5.91 Hz, 4 H, H_γ), 3.01 (t, *J* = 6.89 Hz, 4 H, H_α), 2.01 (m, 4 H, H_β) ppm.

Bis-THP Derivative of 2,2′-Bipyridine (6): A degassed solution of **5** (1.19 g, 4.36 mmol) in DME (25 mL) was added dropwise at 0 °C under argon to a suspension of NaH (0.60 g, 13.7 mmol) in DME (50 mL) for 40 min, upon which the mixture turned white. The ice bath was removed and at room temperature a degassed solution of 2-[2-(chloroethoxy)ethoxy)]ethoxy}tetrahydro-2*H*-pyran (3.64 g, 14.40 mmol) in DME (35 mL) was added dropwise to the mixture which was then heated at 50 °C for 3 h after which the temperature

was increased and the reaction heated at reflux for 14 h. The reaction was monitored by TLC (Alumina, eluent: CH_2Cl_2/5% MeOH). More NaH (0.21 g, 4.80 mmol) and a solution of tetrahydropyrannyl derivative (2.00 g, 7.91 mmol) in DME (20 mL) was added. The reaction mixture was maintained under reflux under argon for a further 34 h, then it was cooled to 0 °C. Excess NaH was neutralised by the gradual addition of EtOH until no further evolution of gas was observed (12 mL overall). The solvent was then evaporated and the residue was dissolved in a 1:1 H_2O/CH_2Cl_2 mixture. The organic layer was separated, and the aqueous layer was extracted 4 times with CH_2Cl_2. The organic layers were combined, washed with water, dried over $MgSO_4$ and filtered. Following evaporation of the solvent, the orange oil was purified twice by column chromatography on alumina eluting with a CH_2Cl_2/MeOH mixture (98.7:1.3; 99.9:0.1). Pure **6** was isolated (0.65 g, 0.92 mmol) along with a mixture of the starting material and of the monosubstituted product (1.30 g) which was treated as follows. This mixture was added to a suspension of DMSO (10 mL) containing KOH powder (3.16 g, 47.60 mmol). To this orange-brown solution, tetrahydropyrannyl derivative (4.81 g, 19.04 mmol) was added and the stirring was maintained for 3.5 h.. The mixture was then heated at 50 °C for 35 min. After cooling and addition of H_2O/CH_2Cl_2, the organic phase was separated and the aqueous phase was extracted with $CHCl_3$ (twice, 150 mL) and also CH_2Cl_2 (twice, 150 mL). The combined organic layers were washed, dried over $MgSO_4$, filtered and the solvents evaporated. The crude oil was purified four times by column chromatography on alumina (CH_2Cl_2/MeOH, 98:0.2; 99.6:0.4) to give pure **7** (0.99 g, 1.41 mmol). The overall yield of **7** (1.64 g, 2.33 mmol) from the two reactions was 53%. Colourless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.23 (d, *J* = 7.51 Hz, 2 H, 3,3′-H), 7.68 (t, *J* = 7.75 Hz, 2 H, 4,4′-H), 7.14 (d, *J* = 7.62 Hz, 2 H, 5,5′-H), 4.62 (t, *J* = 3.32 Hz, 2 H, H_a), 3.84 (m, 4 H, H_e), 3.64 (m, 24 H, 6 × $-CH_2-CH_2-$), 3.55 (t, 4 H, H_γ), 2.92 (t, *J* = 7.63 Hz, 4 H, H_α), 2.11 (tt, 4 H, H_β), 1.90−1.30 (m, 12 H, 4 H_b, 4 H_c, 4 H_d) ppm.

2,2'-Bipyridine 7: 6 (1.62 g, 2.30 mmol) was heated to reflux in 95% EtOH (16 mL) and then *p*-toluenesulfonic acid (0.45 g, 2.30 mmol) was added. The reaction was followed by TLC (SiO_2; eluent: CH_2Cl_2/5% MeOH) and reflux was maintained for 27 h. After evaporation of the solvent, the residue was dissolved in a CH_2Cl_2/H_2O mixture and neutralised with an aqueous solution of $NaHCO_3$. The aqueous phase was extracted 3 times with CH_2Cl_2 and the organic layers were combined, washed with water, dried over $MgSO_4$ and the solvent was evaporated. **6** was isolated (1.03 g, 1.92 mmol) in 84% yield and was used without further purification (purity > 95% by NMR). Colourless oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.23 (d, *J* = 7.25 Hz, 2 H, 3,3′-H), 7.69 (t, *J* = 7.75 Hz, 2 H, 4,4′-H), 7.15 (dd, *J* = 7.64 and 0.77 Hz, 2 H, 3,3′-H), 3.80−3.52 (m, 26 H, 2 × −OH, 6 × $-CH_2-CH_2-$), 3.56 (m, 4 H, H_γ), 2.92 (t, *J* = 7.63 Hz, 4 H, H_α), 2.12 (tt, 4 H, H_β) ppm.

3: In a degassed solution of **7** (1.03 g, 1.92 mmol) in DME (45 mL), NaH (0.93 g, 21.3 mmol) was added with a spatula and the mixture was heated to 50 °C. Allyl bromide (16 mL, 181.00 mmol) was then added via the cannula transfer technique. The reaction mixture was heated at reflux for 20 h and then monitored by TLC (Alumina; CH_2Cl_2/5% MeOH). The white solution was cooled to 0 °C and excess NaH was neutralised by adding small portions (3 mL) of absolute ethanol until there was no further evolution of gas. The solvent was then evaporated and the residue dissolved in a CH_2Cl_2/H_2O (1:1) mixture. The organic phase was separated and the aqueous phase was extracted 4 times with CH_2Cl_2. The organic phases were combined, washed with H_2O and dried over $MgSO_4$. After filtration of the solution and removal of the solvent, the oily residue was purified twice by column chromatography on alumina (eluent: CH_2Cl_2/MeOH, 99.5:0.5) to afford **3** (0.89 g, 1.44 mmol) in 75% yield. Pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.24 (d, *J* = 7.86 Hz, 2 H, 3,3′-H), 7.68 (t, *J* = 7.75 Hz, 2 H, 4,4′-H), 7.14 (dd, *J* = 7.62 and 0.98 Hz, 2 H, 5,5′-H), 5.91 (ddt, *J* = 17.22, 10.32 and 5.66 Hz, 2 H, H′), 5.26 (dtd, *J* = 17.10, 3.44 and 1.60 Hz, 2 H, H_t), 5.16 (m, *J* = 10.32, 1.72 and 1 Hz, 2 H_c), 4.01 (dt, *J* = 5.66 and 1.36 Hz, 4 H, H_g), 3.67−3.50 (m, 28 H, $H_{a,b,c,d,e,f}$, 4 H_γ), 2.92 (t, *J* = 7.50 Hz, 4 H, H_α), 2.11 (tt, *J* = 6.52 and 6.88 Hz, 4 H_β) ppm. FAB-MS for $C_{34}H_{52}N_2O_8$: *m*/*z* = 617.5 $[M + H]^+$, calcd. 617.4, 100%.

***cis*-[Ru(aphen)$_2$Cl$_2$]:** Following the complete dissolution of complex $[Ru(CH_3CN)_4Cl_2]$ (410.0 mg, 1.22 mmol) in a degassed solution of 1,2-dichloroethane (130 mL), the ligand aphen (684.0 mg, 2.39 mmol) was added and the orange-brown mixture was heated at reflux for 2 h. After evaporation of the solvent, the purple-brown residue was purified twice by flash chromatography on silica gel (Silica gel 60, 0.063−0.200 mm, Merck 7734) eluting with EtOH. The mixture of isomeric complexes *cis*-$[Ru(aphen)_2Cl_2]$ was obtained in 46% yield (412.5 mg, 0.55 mmol). The complexes obtained were purple in colour.

Separation of the Three Isomers of *cis*-[Ru(aphen)$_2$Cl$_2$]

The three isomers (460 mg, 0.620 mmol) were separated 13 times by flash chromatography on alumina (aluminium oxide 90, acidic, activity I, 0.063−0.200 mm, Merck 1078). The eluent was a mixture of CH_2Cl_2/MeOH (3%). The purple isomer **(*a*,*a*)**, which migrates as the first band, (100 mg, 0.134 mmol) was isolated as 87% of the theoretical yield (25%).

Isomer (*a*,*a*): ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 10.50 (d, *J* = 5.56 Hz, 2 H, 2-H), 8.23 (, *J* = 9.04 Hz d, 2 H, 5-H), 7.98 (d, *J* = 5.52 Hz, 2 H, 3-H), 7.97 (dd, *J* = 7.96 and 1.12 Hz, 2 H, 7-H), 7.93 (dd, *J* = 5.44 and 1.00 Hz, 2 H, 9-H), 7.88 (d, *J* = 9.28 Hz, 2 H, 6-H), 7.71 (d, *J* = 8.64 Hz, 4 H, H_o), 7.21 (d, *J* = 8.60 Hz, 4 H, H_m), 7.19 (m, 2 H, 8-H), 3.96 (s, 6 H, 2 Me) ppm. UV/Vis (CH_2Cl_2): λ = 553 (7400) nm. **Isomer (*a*,*e*):** ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 10.43 (m, 2 H, 2-H_a, 9-H_e), 8.43 (dd, *J* = 8.12 Hz, 1 H, 7-H_e), 8.23 (d, *J* = 9.10 Hz, 1 H, 5-H_a), 8.04 (dd, 2 H, 5-H_e, 6-H_e), 8.00−7.85 (m, 4 H, 3-H_a, 7-H_a, 9-H_a, 8-H_e), 7.86 (d, *J* = 9.10 Hz, 1 H, 6-H_a), 7.70 (d, *J* = 8.86 Hz, 2 H, $H_{o,a}$), 7.70 (m, 1 H, 2-H_e), 7.38 (d, *J* = 8.86 Hz, 2 H, $H_{o,e}$), 7.20 (d, *J* = 8.86 Hz, 2 H, $H_{m,a}$), 7.19 (m, 2 H, 8-H_a, 3-H_e), 7.04 (d, *J* = 8.86 Hz, 2 H, $H_{m,e}$), 3.95 (s, 3 H, Me a), 3.86 (s, 3 H, Me_e) ppm. UV/Vis (CH_2Cl_2): λ = 550 (9200) nm. **Isomer (*e*,*e*):** ^{1}H NMR (CD_2Cl_2, 400 MHz): δ = 10.48 (m, 2 × 9-H), 8.43 (d, *J* = 7.72 Hz, 2 H, 7-H), 8.06 (d,*J* = 8.80 Hz, 2 H, 6-H), 8.03 (, *J* = 9.16 Hz d, 2 H, 5-H), 8.01 (m, 2 H, 8-H), 7.71 (d, *J* = 8.80 Hz, 2 H, 2-H), 7.38 (dd, *J* = 8.44 Hz, 4 H, H_o), 7.20 (d, *J* = 8.80 Hz, 2 H, 3-H), 7.04 (d, *J* = 8.44 Hz, 4 H, H_m), 3.86 (s, 6 H, 2 Me) ppm. UV/Vis (CH_2Cl_2): λ = 547 (5800) nm.

***cis*-[(*a*,*a*)Ru(aphen)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$:** In a round bottomed flask, *cis*-[(*a*,*a*)Ru(aphen)$_2$Cl$_2$] (80 mg, 0.107 mmol) was heated at reflux under argon in a mixture of CH_3CN/H_2O 50:50 (12 mL) for 2.5 h. After cooling to room temperature, a saturated solution of aqueous KPF_6 (10 mL) and CH_3CN (5 mL) were added. The evaporation of the solvent caused a brown-orange solid to precipitate that was separated by filtration, washed with water and diethyl ether and then air-dried. *cis*-[(*a*,*a*)Ru(aphen)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$ was obtained in a yield of 45% (50 mg, 0.048 mmol). Brown-orange powder. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 9.76 (d, *J* = 5.40 Hz, 2 H, 2-H), 8.38 (d, *J* = 9.10 Hz, 2 H, 5-H), 8.35 (dd, *J* = 8.36 Hz, 1.24 Hz, 2

H, 7-H), 8.20 (d, J = 5.42 Hz, 2 H, 3-H), 8.04 (d, J = 9.10 Hz, 2 H, 6-H), 7.87 (dd, J = 5.41 and 1.23 Hz, 2 H, 9-H), 7.76 (d, J = 8.84 Hz, 4 H, H_o), 7.50 (dd, J = 5.29 and 8.25 Hz, 2 H, 8-H), 7.25 (d, J = 8.60 Hz, 4 H, H_m), 3.97 (s, 6 H, 2 Me) ppm.

Compound 8: A stoichiometric mixture of *cis*-$[Ru(phen)_2(CH_3CN)_2](PF_6)_2$ (69.7 mg, 0.084 mmol) and **3** (51.8 mg, 0.084 mmol) was heated at 140 °C in degassed ethylene glycol (6 mL) for 2 h. After cooling to room temperature, water (8 mL) and then a saturated solution of aqueous KPF_6 (6 mL) were added. The precipitate obtained was collected by filtration and washed with water and diethyl ether. The crude product was purified by chromatography on silica gel eluting with an acetone/water/aqueous saturated KNO_3 (100:4:2) mixture. The cation was precipitated from the eluent by addition of an aqueous solution of KPF_6 and the resultant solid was filtered off to give **8** (86.2 mg, 0.063 mmol) in 75% yield. Red compound. ^{1}H NMR ([D$_6$]acetone, 200 MHz): δ = 8.94 (dd, J = 8.15 and 1.10 Hz, 2 H, 4-H), 8.74 (dd, J = 5.17 and 1.22 Hz, 2 H, 2-H), 8.67 (dd, J = 8.35 and 1.22 Hz, 2 H, 7-H), 8.63 (d, J = 8.86 Hz, 2 H, 3,3′-H), 8.47 (d, J = 8.86 Hz, 2 H, 5-H), 8.38 (d, J = 8.86 Hz, 2 H, 6-H), 8.10 (dd, J = 7.86 and 7.88 Hz, 2 H, 4,4′-H), 8.10 (dd, J = 5.23 and 8.24 Hz, 2 H, 3-H), 7.97 (dd, J = 5.40 and 1.23 Hz, 2 H, 9-H), 7.62 (dd, J = 5.28 and 8.24 Hz, 2 H, 8-H), 7.44 (dd, J = 7.87 and 0.99 Hz, 2 H, 5,5′-H), 5.82 (, J = 17.34, 10.44 and 5.23 Hz ddt, 2 H, H′), 5.18 (m, 2 H, H_t), 5.04 (m, 2 H, H_c), 3.88 (dt, J = 5.42 and 1.54 Hz, 4 H, H_g), 3.60−3.20 (m, 24 H, $H_{a,b,c,d,e,f}$), 3.20−1.00 (12 H, $H_{\alpha,\beta,\gamma}$) ppm.

$[Ru(phen)_2(m\text{-}36)](PF_6)_2$ (1): To a degassed Schlenk containing **8** (117.0 mg, 0.086 mmol) and the catalyst (Grubbs ruthenium(II) carbene: [Ru], (Scheme 2), 4.9 mg, 7% mol), freshly distilled and degassed CH_2Cl_2 (8.5 mL) was added via a cannula to obtain a 0.01 M solution. This mixture was stirred at room temperature for 18 h during which a syringe needle was periodically inserted into the reaction vessel to allow the ethylene gas to escape. The reaction was monitored by ^{1}H NMR spectroscopy. A further 7 mol percent of the catalyst was added and further solvent was added in order to maintain the desired concentration of the reaction mixture. The stirring was continued for 5 days. The solvent was then evaporated and the crude product was purified by chromatography on silica gel (eluent: acetone/H_2O/KNO_3, 100:5:2). Pure **1** was isolated (77.2 mg, 0.058 mmol) in 67% yield. Red compound. ^{1}H NMR ([D$_6$]acetone, 200 MHz): δ = 8.94 (dd, J = 8.36 and 1.24 Hz, 2 H, 4-H), 8.76 (dd, J = 5.41 and 1.23 Hz, 2 H, 2-H), 8.68 (dd, J = 8.37 and 1.23 Hz, 2 H, 7-H), 8.62 (d, J = 7.38 Hz, 2 H, 3,3′-H), 8.47 (d, J = 8.86 Hz, 2 H, 5-H), 8.38 (d, J = 8.86 Hz, 2 H, 6-H), 8.09 (dd, J = 8.12 and 7.14 Hz, 2 H, 4,4′-H), 8.09 (dd, 2 H, 3-H), 7.92 (dd, J = 5.29 and 1.11 Hz, 2 H, 9-H), 7.67 (dd, J = 5.42 and 8.12 Hz, 2 H, 8-H), 7.43 (d, J = 7.88 Hz, 2 H, 5,5′-H), 5.39 (m, 2 H, $H_{cis,}$ 75%), 5.31 (m, 2 H, $H_{trans,}$ 25%), 3.90−1.50 (m, 40 H, H_g, $H_{a,b,c,d,e,f}$, $H_{\alpha,\beta,\gamma}$) ppm. FAB-MS for $RuC_{56}H_{64}N_6O_8P_2F_{12}$: m/z = 1195.3 $[M - PF_6]^+$, calcd. 1195.3, 8%; 1049.3 $[M - 2\ PF_6 + e^-]^+$, calcd. 1050.3, 11%; 462.0 $[M - 2\ PF_6 - m_{36} + e^-]^+$, calcd. 462.0, 32%. UV/Vis (CH_3CN): 450 nm (9200).

9: A stoichiometric mixture of *cis*-[(*a*,*a*)Ru(aphen)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$ (50.0 mg, 0.048 mmol) and **3** (29.5 mg, 0.084 mmol) was heated at 140 °C in degassed ethylene glycol (7 mL) for 2.5 h. After cooling to room temperature, water (5 mL) and then a saturated solution of aqueous KPF_6 (10 mL) were added. The precipitate obtained was collected by filtration and washed with water and diethyl ether. The crude product **9** was isolated (68.8 mg, 0.044 mmol) and was used without further purification. Red compound. FAB-MS for $RuC_{72}H_{80}N_6O_{10}P_2F_{12}$: m/z = 1435.3 $[M - PF_6]^+$, calcd. 1435.4, 5%, 1289.4 $[M - 2\ PF_6 + e^-]^+$, calcd. 1290.5, 6%; 674.1 $[M - 2\ PF_{6-}$**3** $+ e^-]^+$, calcd. 674.1, 46%.

$[Ru(aphen)_2(m\text{-}36)](PF_6)_2$ (2): To a degassed Schlenk containing **9** (68.8 mg, 0.044 mmol) and the catalyst [Ru], 3 mg, 8% mol), freshly distilled and degassed CH_2Cl_2 (5 mL) was added via a cannula to obtain a 0.01 M solution. This mixture was stirred at room temperature for one day during which a syringe needle was periodically inserted into the reaction vessel to allow the escape of ethylene gas. A further 9 mol percent of the catalyst (3.5 mg) was added and after 4 days further solvent added in order to maintain the desired concentration of the reaction mixture. Further catalyst (5 mg, 14% mol) was added. The stirring was continued for 1 day (overall duration of reaction: 6 days). The solvent was then evaporated and addition of water (3 mL) and a saturated solution of aqueous KPF_6 (5 mL) allowed the precipitation of a crude product which was collected by filtration, washed with water and diethyl ether and was purified by chromatography (silica, eluent: acetone/H_2O/KNO_3, 100:7:0.7; alumina, eluent: toluene/CH_3CN 35:65; alumina, eluent: toluene/CH_3CN, 40:60). **2,** not completely pure, was isolated (30.4 mg, 0.020 mmol) in 45% yield. Preparative chromatography on silica (eluent: $CH_3CN/H_2O/KPF_6$, 100:10:2), performed twice, afforded pure **2**. Red compound. ^{1}H NMR (CD_3CN, 500 MHz): δ = 8.45 (dd, J = 8.25 and 1.15 Hz, 2 H, 7-H), 8.42 (dd, J = 5.55 Hz, 2 H, 2-H), 8.36 (d, J = 9.55 Hz, 2 H, 3,3′-H), 8.34 (d, J = 9.10 Hz, 2 H, 5-H), 8.16 (d, J = 9.25 Hz, 2 H, 6-H), 7.97 (dd, J = 7.85 and 8.15 Hz, 2 H, 4,4′-H), 7.80 (d, J = 5.55 Hz, 2 H, 3-H), 7.74 (dd, J = 5.32 and 1.17 Hz, 2 H, 9-H), 7.67 (d, J = 8.75 Hz, 4 H, H_o), 7.46 (dd, J = 5.37 and 8.17 Hz, 2 H, 8-H), 7.29 (d, J = 7.85 Hz, 2 H, 5,5′-H), 7.23 (d, J = 8.95 Hz, 4 H, H_m), 5.34 (m, 2 H, H_c), 5.21 (m, 2 H, H_t), 3.92 (s, 6 H, 2 OMe), 4.30−0.08 (m, 40 H, $H_{a,b,c,d,e,f,g,\alpha,\beta,\gamma}$) ppm. FAB-MS for $RuC_{70}H_{76}N_6O_{10}P_2F_{12}$: m/z = 1407.2 $[M - PF_6]^+$, calcd. 1407.4, 8%; 1262.3 $[M - 2\ PF_6 + e^-]^+$, calcd. 1262.4, 9%; 674.0 $[M - 2\ PF_6$ − m-36 $+ e^-]^+$, calcd. 674.1, 78%. UV/Vis (CH_3CN): λ = 457 (9700) nm.

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