Photochemically Induced Isomerisation in Ruthenium Polypyridyl Complexes.

Stefano Fanni[a], Frances Weldon[a], Leif Hammarström,[b] Emad Mukhtar[b] Wesley R. Browne[a] Tia E. Keyes[c], and Johannes G. Vos*[a]

[a] National Centre for Sensor Research, School of Chemical Sciences, Dublin City University Dublin 9, Ireland. e-mail han.vos@dcu.ie

[b]Department of Physical Chemistry, University of Uppsala, Box 532, S-75121, Uppsala, Sweden, e-mail leif.hammarstrom@fki.uu.se

[c]School of Chemistry, Dublin Institute of Technology, Dublin 8, Ireland. e-mail tia.keyes@dit.ie

keywords; ruthenium, coordination modes, photochemistry

Abstract.

The synthesis and characterisation of a series of ruthenium polypyridyl complexes containing pyridyltriazole ligands in different coordination modes are described. The electrochemical and electronic properties of the compounds are reported and discussed with respect to the coordination mode of the pyridyltriazole ligand. Upon photolysis of the complex containing the 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole ligand irreversible ligand isomerisation is observed.

**** corresponding author***

Introduction.

During the last number of years we have been actively involved in the study of ruthenium and osmium polypyridyl complexes containing ligands with 1,2,4-triazole moieties such as pyridyl-[1] and pyrazyl-triazoles.[2] These studies have shown that for dinuclear compounds containing anionic triazolate bridges strong intercomponent interaction is observed[3] in addition mononuclear complexes containing negatively charged triazole rings were found to be photostable.[4] Of further interest in these studies is the inherent asymmetry of the ligands. The nitrogen atoms of the pyridine or pyrazine rings have significantly different electronic properties from the triazole-based nitrogens. In addition the N1 (or N2) and N4 atoms of the triazole ring are also inequivalent as is shown by differences between the acid-base properties of complexes containing N2 and N4 bound ligands.[1,2] With N-substituted triazole ligands either N2 or N4 coordination of the ligands is observed depending on the position of the substituent.[5] Furthermore, it has been shown that for complexes containing neutral pyridyltriazole ligands photochemically induced isomerisation of the pyridyltriazole ligand can occur.[4,6]

Recently we developed a new synthetic route to complexes containing N-substituted triazole ligands as shown in reaction 1.[7]

reaction 1

In this method the N2 isomer of a 3-(pyridin-2-yl)-1,2,4-triazole (L1) ruthenium polypyridyl precursor complex (**RuL1*N2***) is directly methylated yielding complexes then containing the ligands 1-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L2) and 4-methyl-3-(pyridin-2-yl)-1,2,4-triazole (L3). Surprisingly, the sterically least favoured complex, **RuL2*N2***, methylated at the N2 position is obtained as the main product, with a yield of about 90%, whereas in the reaction between L2 and $[Ru(bpy)_2Cl_2].2H_2O$ only the N4 isomer of the complex, **RuL2*N4,*** could be obtained in appreciable amounts. This new synthetic strategy provides us with the

first opportunity to compare their photophysical and photochemical properties and investigate the role steric hindrance. In this contribution we report on the photochemical and photophysical properties of ruthenium bis(bipyridyl) complexes with the N-substituted triazole ligands L2, L3 and 1,4-bis(1-methyl-3-(pyridin-2-yl)-1,2,4-triazol-5-yl)benzene (L4) (see Figure 1). In the latter ligand both the N2 and N4 site are sterically hindered, the effect of the presence of the benzene and the methyl groupings on the composition of the compounds and on their photophysical and photochemical properties are investigated. Emission lifetime, UV/VIS and NMR studies indicate that an irreversible photoisomerisation is obtained in which the sterically hindered N2 bound L2 complex is transformed into the N4 species. For the mono and dinuclear L4 complexes a less clear picture is obtained but photoinduced reactions are also observed. The results obtained are discussed with respect to the electronic properties of the compounds.

Results and Discussion.

General. An important issue to be addressed first is the coordination mode of the triazole rings in the products obtained, in particular in the L4 complexes. For L2 and L3 the coordination of the triazole ring is known from earlier studies. [1,7] From the reaction mixture of the mononuclear L4 complex, two isomers were isolated by semi-preparative HPLC. In the dinuclear complex coordination of the two metal units may occur via N2/N2', N4/N4' or N2/N4' of the triazole ring. HPLC analysis of the reaction mixture showed the presence of different isomers. One main isomer was isolated in a pure form by recrystallisation.

*^{1}H-NMR Spectroscopy***.** In the complexes obtained the position of the methyl resonances is diagnostic for the type of isomer obtained.(See Table 1) For L2 and L4 the resonance for the methyl substituent is expected at significantly higher field than for the free

ligand when the ligand is bound through the N2 atom, because of the steric interaction between the methyl group and a neighbouring bpy ligand. For the N4 isomer a smaller shift is expected since no interaction between the methyl group and the bpy ligands is possible.[1,5,8]. The methyl resonances recorded for the complexes fall clearly into two groups. The first set of signals at about 3.2 ppm is indicative of the presence of steric hindrance, since the values are shifted to higher field by about 0.7 ppm, with respect to the free ligand. Such a shift indicates N2 coordination for L2 and L4 complexes. The resonances found at about 4 ppm point to coordination modes where the methyl group does not interact with the neighbouring bpy ligands and indicative of N4 coordination for the L2 and L4 ligands and of N2 coordination in L3 complex. For the dinuclear L4 complex only one methyl signal is obtained at 3.23 ppm, clearly indicating that both centres are bound in the same manner, namely through N2.

*Redox Properties***.** All complexes show well-behaved electrochemistry (See Table 2). The redox processes are reversible, with peak to peak separations of 60-100 mV. **RuRuL4*N2N2'*** exhibits a single, 2 electron, metal based oxidation, without any sign of splitting indicating that the interaction between the metal centres is at best very weak. The N4-coordinated complexes exhibit somewhat lower $Ru^{II/III}$ potentials than the N2 compounds possibly indicating improved π-acceptor properties of ligands coordinated in the N2 mode. The similarity of the reduction potentials of the compounds reported in this work and those observed for $[Ru(bpy)_3]^{2+}$ suggests that the first reduction process is bpy based. This is further confirmed by the first reduction potential observed for $\mathbf{[Ru(L2}\boldsymbol{N4}\mathbf{)_3]^{2+}}$ (L2 coordinated via N4) of –1.75 V vs SCE, [9] about 400 mV more negative than observed for $[Ru(bpy)_3]^{2+}$. This value suggest that the lowest unoccupied molecular orbital (LUMO) in the L2 complex is about 3300 cm^{-1} higher than in the homoleptic bpy complex.

*Electronic Properties***.** The absorption spectra bands observed in the region 400-460 nm are associated with $d\pi$-π^* MLCT bands. The MLCT bands for complexes containing a N4 coordinated triazole ring are found at about the same energy as that of $[Ru(bpy)_3]^{2+}$. In agreement with the electrochemical data the N2-bound isomers have a MLCT band at higher energy suggesting that in this coordination mode the σ-donor properties of the L2 and L4 ligands are reduced.

All the compounds show emission at room temperature and at 77 K. The emission lifetimes of the complexes in acetonitrile, measured by time correlated single photon counting, are given in Table 3. For **RuL2*N4*** and **RuL4*N4*** the major decay component shows a lifetime of 9.0 ns and 35 ns, respectively. A minor, (< 5%) faster component has a lifetime of c.a. 1 ns. In contrast, for **RuL2*N2*** and **RuL4*N2*** the 1 ns component was dominating. In these samples, a second slower component was present, whose magnitude varied between 15% and 50% for different measurements. The lifetime of this component matched that of the corresponding N4 isomer. The dimeric **RuRuL4*N2N2'*** also has a dominating 1 ns component, with a minor slower (32 ns) component that matches the lifetime of **RuL4*N4***.

The results obtained from the lifetime measurements for the N2 isomers of L2 and L4 were at first hard to explain, since an impurity level as high as 50% would certainly have been detected by the other characterisation techniques. The formation of a photoproduct seems a more likely explanation for the behaviour observed. For the compounds under investigation the occurrence of photoinduced ligand processes is not unexpected. It is generally assumed that upon excitation of ruthenium polypyridyl complexes an electron is transferred from the metal based ground state to a singlet metal-to-ligand-charge-transfer (^{1}MLCT) state. From this singlet state the emitting ^{3}MLCT state is populated efficiently by intersystem crossing. Population of the nearby anti-bonding triplet metal centred state (^{3}MC) then explains the

photoinduced reactivity of the compounds and in the literature both ligand exchange and rearrangements have been reported .[4, 10,11]

To investigate this hypothesis further a photolysis was carried out in which ^{1}H NMR spectra were taken after various irradiation times. After irradiating for six hours in acetonitrile, analysis of the CH_3 resonance suggested that up to 70% of the complex underwent photoinduced isomerisation to the corresponding **RuL2*N4*** complex. Further irradiation (up to 12 h) resulted mainly in decomposition of the complex **RuL2*N2***. This decomposition probably occurs *via* the formation a photoinduced intermediate where the pyridyltriazole ligand is coordinated in a monodentate fashion. Such behaviour in strongly coordinating solvents has been reported before for other complexes containing neutral pyridyltriazole ligands.[6b] Under the same conditions, **RuL2*N4*** shows a remarkable photostability and decomposition become noticeable only after 24 h irradiation. The same experiment was carried out in a weakly coordinating solvent, namely acetone, in an effort to reduce the formation of secondary photoproducts (See Figure 2). Analysis of the methyl region of the spectrums shows that the resonance originally obtained for the N2 isomer at 3.54 ppm is replaced upon photolysis by a signal at 4.17 ppm. This is indicative for the formation of the N4 isomer and in acetone a 100% photoisomerisation of **RuL2*N2*** to **RuL2*N4*** was obtained after irradiation for 24 h. No evidence for the formation of a solvated metal complex was observed. No changes were observed in the ^{1}H-NMR spectra of **RuL2*N4*** after irradiating for 24 h. These results suggest that irreversible photoinduced isomerisation of **RuL2*N2*** to **RuL2*N4*** is taking place as shown in reaction 2.

reaction 2

This photoisomerisation process can also be observed using UV-Vis absorption spectroscopy. As can be seen in Figure 3, irradiation of **RuL2*N2*** in acetone causes a gradual decrease in intensity of the band at 415 nm and a concomitant growth of bands at 355 nm and 455 nm, which are associated with the **RuL2*N4*** complex (Table 3). The UV-Vis spectra

taken show isosbestic points at 448 nm and 372 nm, indicating that photoproducts are formed directly without the production of long-lived intermediates. Upon complete photolysis, no further changes in the absorption spectrum occur, which further indicates the photostability of **RuL2*N4***.

The conclusions drawn from the NMR and UV/VIS studies were further corroborated by emission lifetime measurements on **RuL2*N2*** in acetonitrile exposed to varying amounts of light. The results are shown in Figure 4. To minimise the light given to the sample during the lifetime measurements, these were continued for only 2-3 minutes (giving 1000 counts in the peak channel). In the first measurement, the contribution from the longer-lived N4 isomer emission was only 15%. However, after only a few minutes of subsequent irradiation with a 450W Xe lamp (using a water heat filter and a λ >385 nm cut off), this contribution had increased to 80%, indicating an almost complete conversion to the N4 isomer. When irradiation was continued, an instrument-response limited component (τ<150 ps) started growing in (not shown), and after 100 minutes of irradiation very little of the N4 isomer remained. We attribute the very short-lived component to the photolysed complex in which presumably the L2 ligand had been replaced by acetonitrile.

Since **RuL4*N2* and RuRuL4*N2N2'*** also showed a dual exponential emission decay, NMR experiments were also carried out for the L4 compounds. For all three complexes, irradiation in acetone resulted in a complex mixture of products, which could be attributable to partial isomerisation and decomposition of the starting material and products. The results obtained from these experiments were not further analysed.

Concluding remarks

The results obtained in this investigation demonstrate the importance of steric factors for the photochemical properties of ruthenium polypyridyl compounds. Earlier studies[4] have

shown that for the protonated L1 complexes a *reversible* N2/N4 photoinduced isomerisation is taking place. The results obtained for the L2 complex indicate that complexes that are sterically hindered (i.e. **RuL2*N2***), have the tendency to release the steric congestion upon photolysis by converting into the corresponding non-hindered isomer (i.e. **RuL2*N4***). The presence of a steric constraint in the compound leads therefore to an *irreversible* photoisomerisation.

Pyridyltriazoles are mainly σ-donor ligands and have only limited π-acceptor properties. It seems therefore likely that the small differences observed for the different isomers in the electronic spectra and in the $Ru^{II/III}$ redox potentials can be explained by a reduced σ-donor capability of the N2 isomer because of steric hindrance. This will lead to a lowering of the excited state ^{3}MC level for the N2 isomer in comparison with the N4 isomer and will facilitate photochemically induced isomerisation for the N2 isomer by a photochemically driven process.

When substituents are present on both the N1 and C5 position, (as in the three L4 complexes) neither of the possible isomers is sterically non-hindered. Hence, irradiation of these complexes results in a mixture of different isomers of similar stability (or, in other words, "photochemical instability").

Experimental Section

Materials**.** All synthetic reagents were of commercial grade and no further purification was employed, unless otherwise stated. All solvents employed in spectroscopic and electrochemical measurements were of HPLC or spectroscopic grade

Ligand synthesis.

Synthesis of 1,4-bis(1-methyl-3-(2-pyridyl)-1,2,4-triazol-5-yl)benzene (L4)

Step 1 *Synthesis of N2-methyl-2-pyridylamidrazone.* 2-cyanopyridine (36 g, 0.35 mol) and excess methylhydrazine (18.43 g, 0.40 mol) were mixed in a minimum amount of ethanol and allowed to stir overnight. The pale yellow crystalline product was filtered, washed with diethyl ether and air dried. Yield = 26.7 g (50%).mp 108-110 °C (lit. 109-110 °C)[12] ^{1}H-NMR [$CDCl_3$]: δ (ppm): 7.24 (1H, dd, pyridyl H_5), 7.67 (1H, dd, pyridyl H_4), 8.08 (1H, d, pyridyl H_3), 8.50 (1H, d, pyridyl H_6), 5.24 (2H, s, (broad) NH), 2.98 (3H, s, CH_3). ^{13}C-NMR [$CDCl_3$]: δ (ppm): 38.48, 119.60, 123.32, 136.02, 146.41, 147.77, 150.72.

Step 2. *Synthesis of N,N'-terephthaloyl-bis((N2-methyl-2-pyridyl)hydrazidine)* .

This intermediate was prepared by the drop wise addition of a THF solution (30 cm^3) of terephthaloyl dichoride (5.08 g, 0.025 mol) to a solution of N2-methyl-2-pyridylamidrazone (7.50 g, 0.05 mol) and triethylamine (10 cm^3) in THF while maintaining the reaction mixture at 0°C. The reaction mixture was then reduced to approximately 25 cm^3 and an equal volume of water added. The yellow product was filtered, washed with water, hot methanol and diethyl ether, dried under vacuum and then left in an oven at 60 °C for 24h. Yield = 7.00 g (65%) mp 178-180 °C. ^{1}H-NMR [$CDCl_3$]: δ (ppm): 8.15 (2H, s, phenyl), 8.10 (1H, d, pyridyl H_3), 7.65 (1H, dd, pyridyl H_4), 7.43 (1H, dd, pyridyl H_5), 8.60 (1H, d, pyridyl H_6), 10.30 (1H, s, (broad) NH), 4.11 (3H, s, CH_3). ^{13}C-NMR [$CDCl_3$]: δ (ppm): 38.50, 120.82, 124.67, 128.85, 129.10, 136.89, 148.24, 150.26, 153.79, 161.2.

Step 3. *Cyclization of N,N'-Terephthaloyl-bis((N2-methyl-2-pyridyl)hydrazidine) to form L3*. N,N'-terephthaloyl-bis((N2-methyl-2-pyridyl)hydrazidine) (7.00 g, 0.017 mol) was suspended in a minimum volume (~30 cm^3) of ethylene glycol and heated at reflux for 2 hours. A white crystalline precipitate was obtained upon cooling of the solution. Further precipitation of the product was induced by the addition of a small amount of water to the mother liquor. The ligand was recrystallised from boiling methanol, filtered and dried under

vacuum overnight. Yield 4.20 g (66%) mp 278-280 °C. ^{1}H-NMR [$CDCl_3$]: δ (ppm): 8.07 (2H, s, phenyl), 8.10 (1H, d, pyridyl H_3), 7.92 (1H, dd, pyridyl H_4), 7.45 (1H, dd, pyridyl H_5), 8.67 (1H, d, pyridyl H_6), 4.12 (3H, s, CH_3): δ (ppm): 37.65, 121.58, 124.15, 129.00, 129.13, 137.16, 149.45, 149.71, 154.26, 159.88. Mass Spectrum: m/z 395 (M+1). Calcd. for $C_{22}H_{18}N_8$ = C: 66.98; H: 4.60; N: 28.41 %. Anal. found: C: 66.69; H: 4.61; N: 27.95 %.

Synthesis of metal momplexes.

cis-[$Ru(bpy)_2Cl_2$].$2H_2O$ [13] was prepared as reported in the literature. **RuL2*N4*** and **RuL3*N2*** were prepared as reported before.[1] **RuL2*N2*** was prepared by direct methylation[7] of **RuL1*N2***.[1]

Synthesis of [$Ru(bpy)_2$L4]($PF_6)_2$. L4 (0.789 g, 2 mmol) was dissolved in hot methanol/water (2:1 v/v). To the solution was added *cis*-[$Ru(bpy)_2Cl_2$].$2H_2O$ (0.312 g, 0.6 mmol) and the mixture was heated at reflux for 6 hours. Following removal of most of the solvent by rotary evaporation and the addition of saturated aqueous NH_4PF_6 solution, the resulting precipitate was filtered and dried. HPLC analysis revealed the presence of two isomers in a 30:70 ratio (isomer 1:isomer 2). These were obtained in a pure form by semi-preparative HPLC using 80:20 acetonitrile/water containing 0.11 M KNO_3 as a mobile phase and a flow rate of 1.7 cm^3/min. Total yield after purification (isomer 1 + isomer 2): 0.20 g (30 %). Isomer 1, **RuL4*N4***: Calcd. for $C_{42}H_{34}F_{12}N_{12}P_2Ru.3H_2O$ = C: 45.78; H: 3.50; N; 14.58 %. Anal. Found: C: 45.24; H: 3.12; N: 14.14 %. Isomer 2, **RuL4*N2*** Calcd. for $C_{42}H_{34}F_{12}N_{12}P_2Ru.H_2O$ = C: 45.19; H: 3.23; N; 15.06 %. Anal. Found: C: 45.41; H: 3.15; N: 14.93 %.

Synthesis of [($Ru(bpy)_2)_2$L4]($PF_6)_4$.$3H_2O$ (**RuRuL4*N2N2'*)** *cis*-[$Ru(bpy)_2Cl_2$].$2H_2O$ (0.624 g, 1.2 mmol) and L4 (0.197 g, 0.5 mmol) were heated at reflux in ethanol/water (2:1 v/v) for 6

hours. Upon cooling of the reaction mixture, a few drops of a saturated ammonium hexafluorophosphate aqueous solution were added, whereupon a bright orange precipitate was obtained. This was filtered and recrystallised from acetone/water (2:1 v/v). HPLC analysis of the product showed the presence of only one isomer. Yield 0.30 g (33 %). Calcd. for $C_{62}H_{50}F_{24}N_{16}P_4Ru_2.3H_2O$ = C: 40.11; H: 3.04; N; 12.07 %. Anal. Found: C: 40.27; H: 3.08; N: 12.02 %.

Experimental Methods. ^{1}H-NMR spectra were recorded on a Bruker AC400 (400 MHz) instrument. For NMR scale photochemical experiments 5-10 mg of a given complex were dissolved in d_3-acetonitrile or d_6-acetone, 0.5 cm^3), placed in a borosilicate NMR tube and irradiated using a 150 W halogen lamp. NMR spectra were taken at regular intervals and the degree of isomerisation checked by integration of the CH_3 resonance signals. UV/Visible spectra (accuracy $\pm$ 2 nm) were obtained using a Shimadzu UV3100 UV-Vis-NIR spectrophotometer interfaced to an Elonex PC433 personal computer. The estimated error on extinction coefficients is 5 %. Emission spectra (accuracy $\pm$ 5 nm) were obtained on a Perkin-Elmer LS50B luminescence spectrometer equipped with a red sensitive Hamamatsu R928 detector, interfaced with an Elonex PC466 personal computer employing Perkin-Elmer FL WinLab custom built software. At room temperature, unless otherwise indicated, acetonitrile was the solvent used, and excitation and emission slit widths of 10 nm, were employed. At 77 K measurements were carried out in ethanol/methanol (4:1 v/v) using excitation and emission slit widths of 5 nm. The spectra were not corrected for the photomultiplier response. For electrochemical measurements HPLC grade acetonitrile, dried over molecular sieve, were employed. Potentials are $\pm$ 50 mV. The electrolyte used was 0.1 M tetraethylammonium perchlorate (TEAP). The electrochemical cell used was a conventional three-compartment cell with glass frits. The reference electrode used was a saturated calomel electrode. The working electrode was a 3 mm diameter teflon shrouded

glassy carbon electrode and a platinum gauze was employed as counter electrode. Prior to reduction measurements the solutions were degassed for 15 min. with nitrogen. Cyclic voltammetry (100 mVs^{-1}) was carried out using a CH instruments Model 660 electrochemical workstation interfaced to an Elonex 486 PC.

Analytical HPLC experiments were carried out using a Waters HPLC system, consisting of a model 501 pump, a 20µl injector loop, a Partisil SCX radial PAK cartridge mounted in a radial compression Z module and a Waters 990 photodiode array detector. A NEC APCIII computer controlled the system. The detection wavelength used was 280 nm and the flow rate was 2.0 cm^3/min. The mobile phase was 80:20 $CH_3CN:H_2O$ containing 0.1 M $LiClO_4$. Semi-preparative HPLC was carried out using an ACS pump, a 1 ml injection loop and a Waters Partisil SCX 10 µm cation exchange column (25 x 100 mm). The mobile phase used was 80:20 $CH_3CN:H_2O$ containing KNO_3 (0.12-0.20 M). The flow rate used varied between 1.50-2.0 cm^3/min.

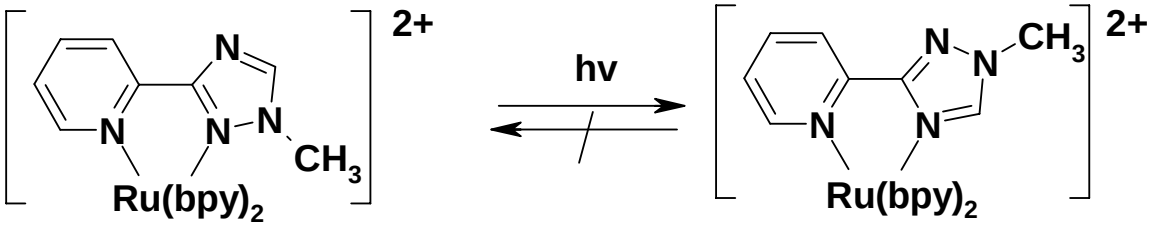
Single Photon Counting. Fluorescence lifetimes were determined using time correlated single photon counting. The excitation source has the tuneable output of a 200 kHz and a 120 femtosecond optical parametric amplifier (OPA, Coherent Radiation Inc). This device was pumped by a regenerative amplifier (700 µJ, 150 fs, 200 kHz) seeded by the 80 fs output of a Ti:Sapphire oscillator. The frequency-doubled fundamental generated in the OPA was used to excite the samples at 400 nm. A polariser was located before the sample to define the vertical polarisation of the excitation light and all fluorescence measurements were carried out with an analysing polariser before the detector oriented at the magic angle (54.7°), relative to the excitation polarisation, to remove anisotropy effects. Fluorescence was observed through an interference filter centred at 600 nm (Oriel, USA) with a full width at half maximum of 10 nm. A microchannel plate multiplier (Hamamatsu) was used for the detection. Instrumental response curves were measured by exchanging the 600 nm

interference filter after the sample with for a 400 nm filter and recording the scattering from a scatter solution. The instrumental response (FWHM) was c.a. 100 ps. The fluorescence decay data were analysed with a non-linear least-squares program using a modified Levenberg-Marquardt algorithm with iterative reconvolution. The reduced χ^2 and residual plots were used to judge the quality of the fits. The samples for emission lifetime measurements were dissolved in spectroscopic grade acetonitrile (Merck) to an optical density of c.a. 0.3 at the excitation wavelength. The solvents were not degassed since quenching by O_2 had negligible effect on the short lifetimes measured. Lifetimes are $\pm$ 10%

Acknowledgements.

The authors thank the EC TMR programme (Grant number CT96-0031) for financial assistance.

Graphical abstract



RuL2*N2* **RuL2*N4***

Table 1 *Chemical shifts (ppm) for methyl groupings. Measurements carried out in DMSO unless otherwise stated*

Compound		**CH_3**
RuL2*N2*		3.15 (3.54[a])
RuL2*N4*		3.97 (4.17[a])
RuL3*N4*		4.21
RuL4*N4*	(f)	4.07
	(b)	3.82
RuL4*N2*	(f)	4.10
	(b)	3.27
RuRuL4*N2N2*		3.23
(in CD_3CN)		3.17

[a] measured in acetone; (f) and (b) refer to the free and bound pyridyltriazole ring, respectively

Table 2 *Electrochemical data for the triazole complexes. All measurements carried out in acetonitrile with 0.1M TEAP.*

Complex	**Oxidation Potential (V *vs* S.C.E)**	**Reduction Potential (V *vs* S.C.E)**
RuL2*N2*	1.30	-1.36, -1.57
RuL2*N4*	1.20	-1.39, -1.61
RuL3*N2*	1.19	-1.39, -1.61
RuL4*N2*	1.31	-1.35, -1.56
RuL4*N4*	1.20	-1.35, -1.58
RuRuL4*N2N2'*	1.29	-1.38, -1.59
$[Ru(bpy)_3]^{2+}$	1.26	-1.35, -1.55, -1.80

All redox potentials measurements were performed using ferrocene as an internal reference[14].

Table 3 *UV-Vis absorption and emission data for the complexes. All measurements in acetonitrile unless otherwise stated.*

Complex	Absorption λ_{max}/nm ($\varepsilon/10^4 M^{-1}cm^{-1}$)	Emission λ_{max}/nm 300 K	77 K[a]	$\tau_{300\ K}$ (ns)
RuL2*N2*	435 (1.15)	615	566	1.0
RuL2*N4*	452 (1.07)[a]	600[a]	585	9.0
RuL3*N2*	440 (1.44)[a]	600[a]	584	14.0
RuL4*N2*	415 (1.33)	611	570	1
RuL4*N4*	453 (0.90)	614	584	35
RuRuL4*N2N2'*	414 (2.60)	603	573	1
$[Ru(bpy)_3]^{2+}$	452 (1.30)	615	582	950[b]

[a] measured in ethanol/methanol (4:1 v/v) [b] deaerated solution.

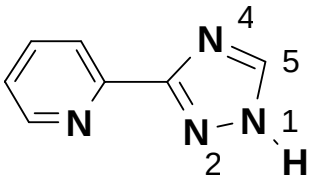
Figure Legends.

Figure 1 Ligand structures

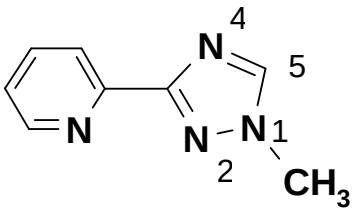
Figure 2. ^{1}H NMR spectra of methyl region taken during photolysis of **RuL2*N2*** in d_6 acetone.

Figure 3 UV-Vis absorption spectra of **RuL2*N2*** in acetone upon irradiation for (a) 0 min, (b) 2.5 min, (c) 5 min, (d) 10 min, (e) 17.5 min, (f) 27.5 min, (g) 120 min.

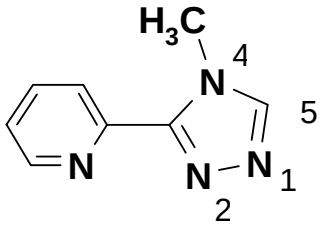
Figure 4. Emission decays for the same sample of **RuL2*N2*** in acetonitrile. Curve **A**: sample prepared in the dark; curve **B**: after 1.5 min. irradiation with a Xe lamp; curve **C**: after 6.5 min irradiation. The lines are double exponential fits to the data, with lifetimes of 1.0 ns and 9.0 ns. The contribution from the slower component increased from 15% in **A** to 40% in **B** and 80% in **C**.



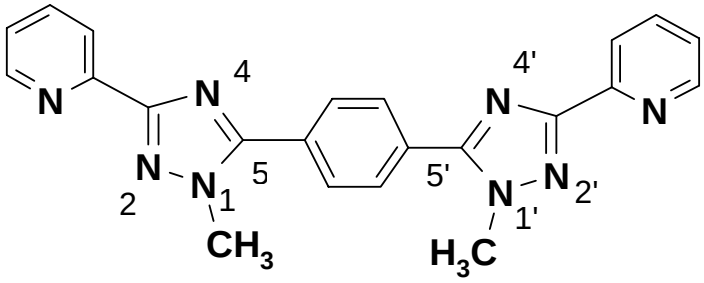
L1



L2



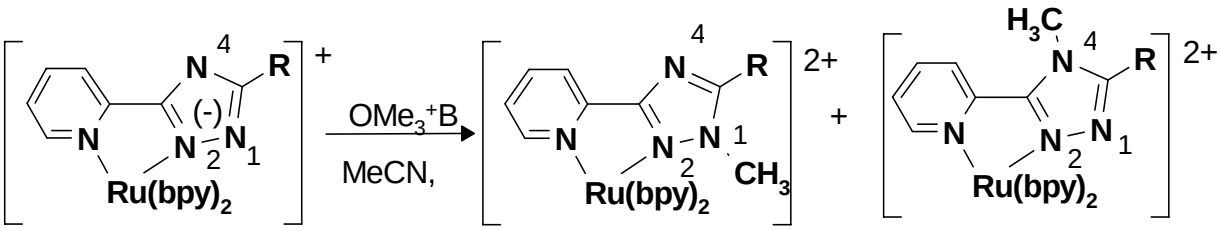
L3



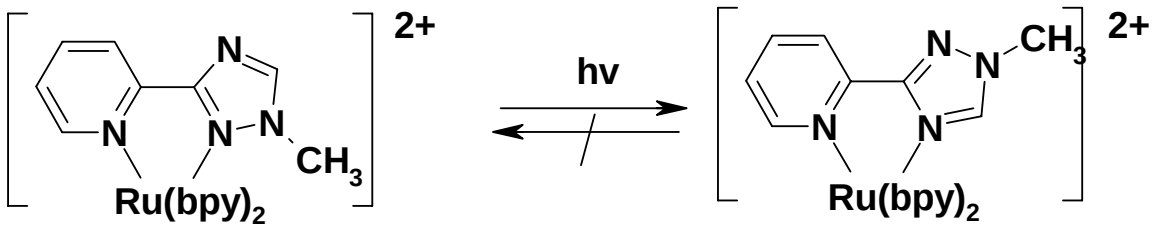
L4

Figure 1

Reaction 1



Reaction 2



RuL2*N2*

RuL2*N4*

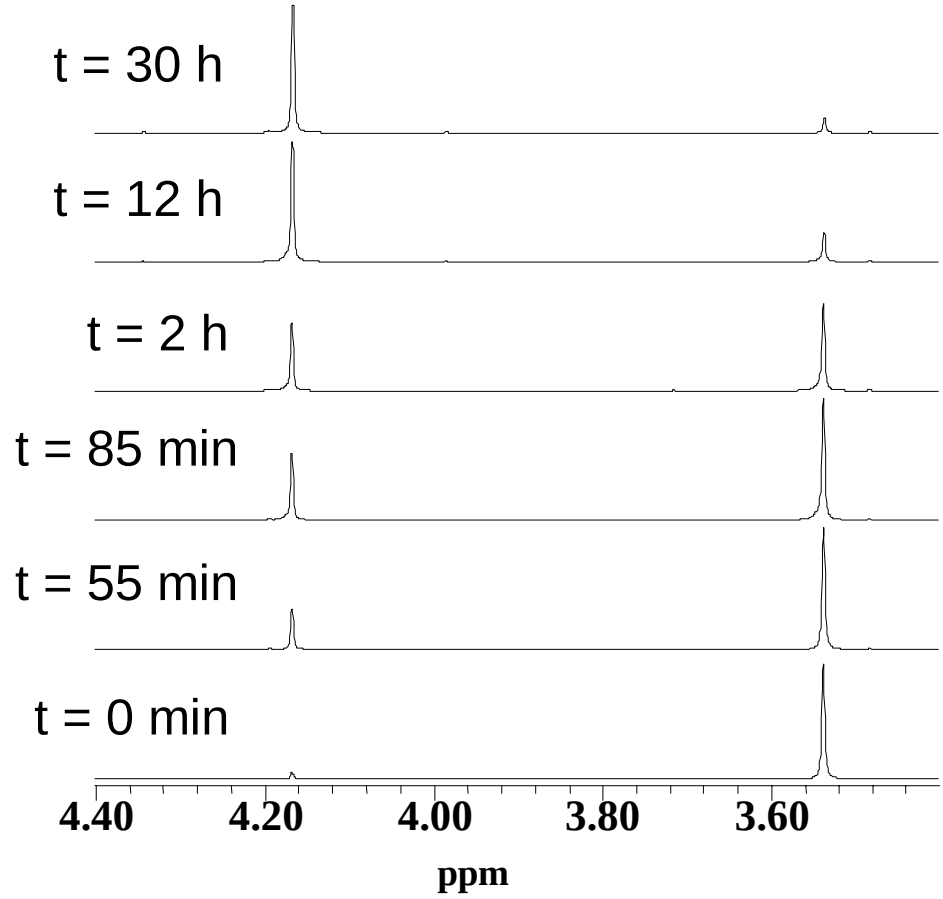


Figure 2.

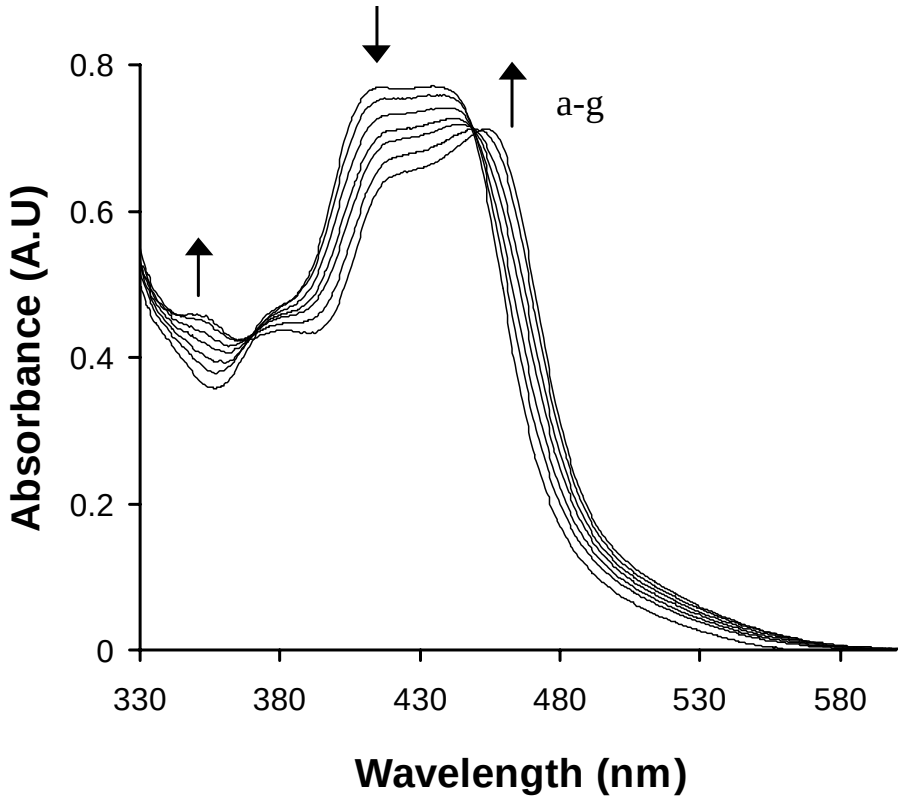

0.8
0.6
0.4
0.2
0
Absorbance (A.U)
330
380
430
480
530
580
Wavelength (nm)
a-g

Figure 3

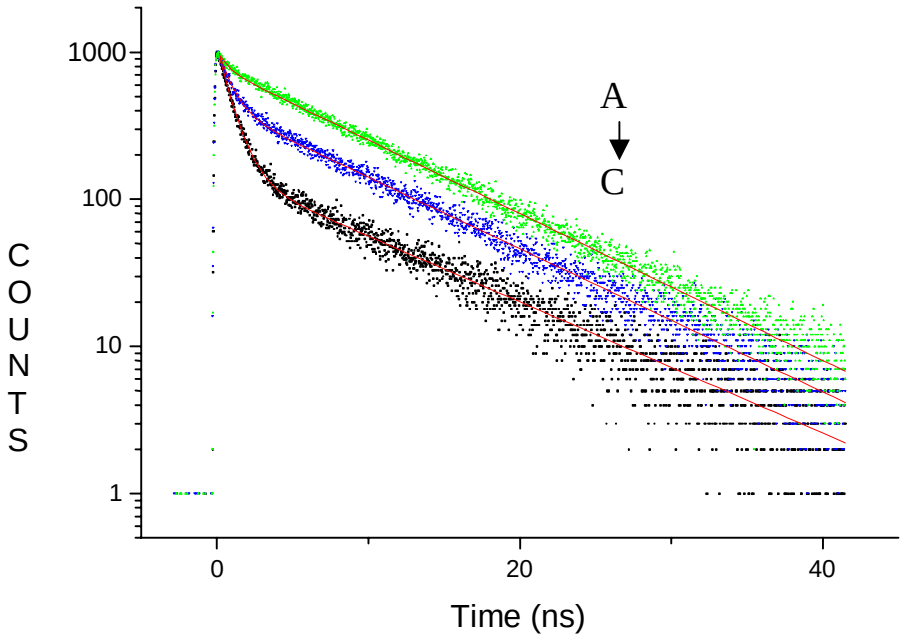


Figure 4

References.

1 a) R. Hage, R.. Prins, J.G. Haasnoot, J. Reedijk and J.G. Vos, *J. Chem. Soc. Dalton Trans*., 1987, 1381. b) B.E. Buchanan, J.G. Vos, M. Kaneko, W.J.M. van der Putten, J.M. Kelly, R. Hage, R.A.G. de Graaff, R. Prins, J.G. Haasnoot and J. Reedijk, *J. Chem. Soc., Dalton Trans*., **1990**, 2425.

2 R. Hage, J.G. Haasnoot, H.A. Nieuwenhuis, J. Reedijk, R. Wang and J.G.Vos, *J. Chem. Soc. Dalton Trans*., **1991**, 3271; b) H.A. Nieuwenhuis, J.G. Haasnoot, R. Hage, J. Reedijk, T.L. Snoeck, D.J. Stufkens, and J.G. Vos *Inorg. Chem*. **1991**, *30*, 48; c) T.E. Keyes, C.M. O'Connor , U. O'Dwyer, C.G. Coates , P. Callaghan, J.J. McGarvey and J.G. Vos, J. Phys.Chem A , **1999**, *103*, 8915.

3 R. Hage, J.G. Haasnoot, H.A. Nieuwenhuis, J. Reedijk, D.J.A. De Ridder and J.G. Vos. *J. Am. Chem. Soc.*, **1990**, *112*, 9245.

4 R. Wang; J.G.Vos.; R.H. Schmehl; R. Hage, *J. Am. Chem. Soc*., **1992**, *114*, 1964.

5 E.M. Ryan, R. Wang, J.G. Vos, R. Hage and J.G. Haasnoot, *Inorg. Chim. Acta*., **1993**, *208*, 49

6 a) B.E. Buchanan, H. Hughes, J.H. van Diemen, R. Hage, J.G. Haasnoot, J. Reedijk, and J.G. Vos *J. Chem. Soc, Chem Commun*. **1991**, 300 b) B.E. Buchanan, P. Degn, J.M. Pavon Velasco, H. Hughes, B.S. Creaven, C. Long, J.G. Vos, R. A. Howie, R. Hage, J.H. van Diemen, J.G. Haasnoot, and J. Reedijk. *J. Chem. Soc., Dalton Trans*. **1992**, 1177.

7 S. Fanni, S. Murphy, J. S. Killeen and J. G. Vos, *Inorg. Chem*. **2000**, *39*, 1320

8 P.J Steel, F. Lahousse, D. Lerner and C. Marzin, *Inorg. Chem*., **1983**, *22*, 1488.

9 R. Hage, Ph.D Thesis 1991, Leiden University.

10 a) S. Tachiyashiki, H. Ikezawa and K. Mizumachi, *Inorg. Chem*. 33 (1994) 623. b) R.Arakawa, S. Tachiyaskiki and T. Matsuo, *Anal. Chem*, 67 (1995) 4138

11 A. Juris, V. Balzani, F. Barigelletti S. Campagna, P. Belser and A. von Zelewsky *Coord Chem. Rev.*, 84, (1988), 85.

12 S. Kubota, M. Uda and T. Nakagawa, *J. Heterocyclic Chem*., **1975**, *12*, 855.

13 B.P. Sullivan, D.J. Salmon, T.J. Meyer, *Inorg. Chem*. **1978**, *17*, 3334