Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 7395

www.rsc.org/dalton

PAPER



# Ru-TAP complexes with btz and pytz ligands: novel candidates as photooxidizing agents†

**Alice Mattiuzzi,[a] Ivan Jabin,*[a] Cécile Moucheron*[b] and Andrée Kirsch-De Mesmaeker*[b]**

***Received 11th February 2011, Accepted 28th April 2011***
**DOI: 10.1039/c1dt10235d**

Two ligands containing 1,2,3-triazole moieties **1** and **3** were easily prepared by a $Cu^{I}$-catalysed "click reaction" between commercially available (trimethylsilyl)alkynes and benzyl azide. These ligands were used in the synthesis of Ru(II) complexes with TAP ligands, *i.e.* $[Ru(TAP)_2btz]^{2+}$ **2** and $[Ru(TAP)_2pytz]^{2+}$ **4**. The electrochemical and photophysical properties of these complexes were investigated. The data show that both complexes should behave as highly oxidizing agents under illumination. However, complex **4** displays more attractive photophysical properties than complex **2** and constitutes thus a Ru-TAP compound that can be easily derivatized for photodamaging biomolecules.

## Introduction

The photophysical and photochemical properties of the Ru(II) polypyridyl complexes continue to attract much attention particularly for the development of various applications such as the design of antenna systems for collecting light.[1] In addition, some Ru(II) polyazaaromatic complexes are characterized by a long-lived visible luminescence very sensitive to the microenvironment. Therefore they can be used as photoprobes of genetic material and considered as potential drugs in anti-cancer therapy.[2] In this context, it has been shown that Ru(II) complexes containing at least two highly π-deficient polyazaaromatic ligands such as 1,4,5,8-tetraazaphenanthrene (TAP) or 1,4,5,8,9,12-hexaazatriphenylene (HAT) are able to induce under illumination an electron transfer process from a guanine residue of DNA to the excited complex.[3] This photo-induced electron transfer can give rise to the formation of a covalent adduct between the Ru(II) complex and the guanine (G) base. These photo-adducts have been used for damaging DNA. In this way, they inhibit the activity of the enzymes interacting with DNA templates.[3f] Moreover, deoxyribonucleotides (ODN) derivatized *via* a phen ligand (phen = 1,10-phenanthroline) by a $[Ru(TAP)_2phen]^{2+}$ complex (Ru-ODN) can target their complementary sequence containing a G base. Thus, after hybridization and illumination, they irreversibly photo-crosslink to the DNA target.[2f,3f] Moreover if the target is not found during the illumination, these Ru-ODN form a photo-adduct with a G of their own sequence, in other words, they commit suicide.[2f] These Ru conjugates can thus lead to interesting applications in gene silencing. Despite these interesting photochemical properties, the high hydrophilicity of the Ru(II) complexes or Ru-ODN prevents their direct use in cellular biology. Indeed, the photoreactive TAP metallic complexes are unable to penetrate the cell in order to reach the cytoplasm or nucleus. Interestingly, Barton and co-workers recently showed that complexes based on more hydrophobic ligands such as the bathophenanthroline (diphenylphenanthroline) can easily penetrate the cell membranes.[4] Another strategy consists in functionalizing a ligand for tethering the resulting complex on a vector to allow the cellular uptake. In our previous work,[2f,2g] the grafting of the complex *via* the phen ligand was not straightforward. In our course of designing new Ru(II) complexes with a high oxidation power similar to that of $[Ru(TAP)_2phen]^{2+}$ for damaging biomolecules, we were interested in the development of a straightforward synthesis of bidentate N,N-ligands that can be readily functionalized and replace the derivatized phen ligand. For this, ligands containing 1,2,3-triazole moieties appeared as valuable candidates. Indeed, these ligands can be easily obtained through a Cu-catalyzed Huisgen 1,3-dipolar cycloaddition, the so-called "click reaction", between terminal alkyne and azide reactants.[5] Moreover, the coordination chemistry of 1,2,3-triazole ring systems constitutes a recent topic of great interest. These heterocycles were used in catalysis[6] (with Cu, Pd, Zn) and in radiolabelling of biomolecules[7] (with $^{99m}Tc$, Re, Mo). The tridentate ligand 2,6-bis(1,2,3-triazol-4-yl)pyridine forms stable Cu(I), Ru(II), Fe(II) and Eu(III) complexes.[6a,8] The bidentate ligand [1,2,3]triazolo[1,5-*a*]pyridine can lead to heteroleptic Ru(II) complexes,[9] while two other bidentate ligands 4,4′-bis(1,2,3-triazole)[10] (btz) and 2-(1,2,3-triazol-4-yl)pyridine[10b,11] (pytz) (Fig. 1) were used for the formation of heteroleptic or homoleptic Ru(II) complexes. From a synthetic point of view, all these 1,2,3-triazole based ligands are readily available. For example, Skoglund

[a]*Laboratoire de Chimie Organique, Université libre de Bruxelles (U.L.B.), Avenue F. D. Roosevelt 50, CP160/06, B-1050, Brussels, Belgium. E-mail: ijabin@ulb.ac.be; Fax: +32-2650-2798*
[b]*Service de Chimie Organique et Photochimie, Université libre de Bruxelles (U.L.B.), Avenue F. D. Roosevelt 50, CP160/08, B-1050, Brussels, Belgium. E-mail: akirsch@ulb.ac.be, cmouche@ulb.ac.be; Fax: +32-2650-3018*
† Electronic supplementary information (ESI) available: Fig. SI1–SI12. See DOI: 10.1039/c1dt10235d

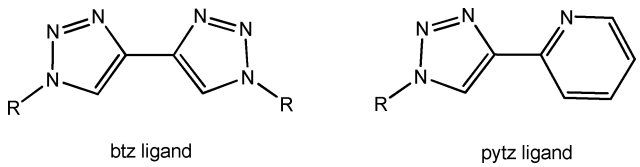



**Fig. 1** The btz and pytz ligands.

has recently described a multistep one-pot methodology based on click chemistry that leads to the btz and pytz ligands.[10b] In addition, thanks to the Cu-catalyzed Huisgen 1,3-dipolar cycloaddition, 1,2,3-triazole based ligands functionalized with a wide range of substituents are easily accessible. Thus, bidentate 1,2,3-triazole ring systems seem to be promising alternatives to 1,10-phenanthroline or 2,2′-bipyridine (bpy) for the design of readily functionalizable ligands devoted to the complexation of transition metal ions.

Nevertheless, although 1,2,3-triazole ring systems would be attractive for the tethering of Ru complexes, another condition which has to be fulfilled by the resulting complex formed from the $Ru(TAP)_2$ motif is the oxidation power of the excited state. This latter has to be higher than or equal to that of $[Ru(TAP)_2phen]^{2+}$ in order to damage the biomolecules as explained above. Therefore in this work, we report the synthesis of $[Ru(TAP)_2btz]^{2+}$ and $[Ru(TAP)_2pytz]^{2+}$ wherein btz = 1,1′-dibenzyl-4,4′-bi-1*H*-1,2,3-triazolyl and pytz = 2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine and the evaluation of their photochemical and electrochemical properties in view of their use with biological systems. Indeed in this context, although these two complexes contain two TAP ligands, it is difficult to predict whether a third ligand like btz or pytz would improve or decrease their photooxidation power as compared to a bpy or phen ligand.

## Results and discussion

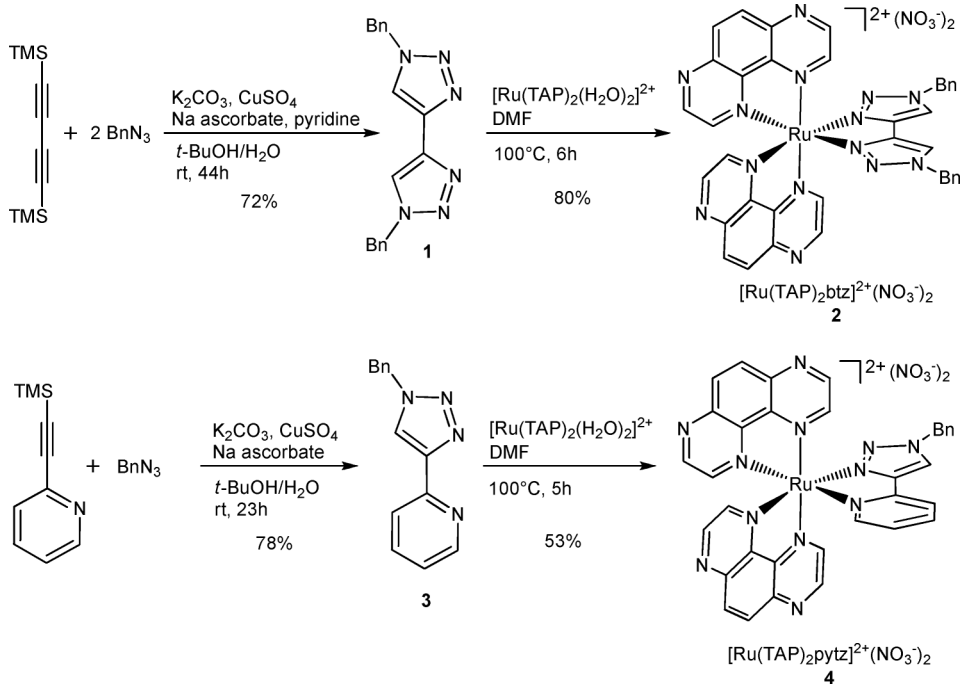
### Syntheses

The btz **1** and pytz **3** ligands were synthesized from commercially available (trimethylsilyl)alkynes and benzyl azide ($BnN_3$) through a one-pot tandem deprotection/click reaction (Scheme 1).[10b] For this, the protected alkynes were reacted with $BnN_3$ in $H_2O$/*t*-BuOH in presence of $K_2CO_3$ and a catalytic amount of $CuSO_4$. The presence of $K_2CO_3$ allows the *in situ* deprotection of the alkyne reactants. It is noteworthy that a washing of the crude residue with an aqueous $NH_4OH$ solution (5%) was necessary in order to remove the copper ion which was likely complexed to the obtained ligand. Pure btz and pytz ligands **1** and **3** were obtained after flash chromatography (FC) purification on silica gel in 72% and 78% yield respectively.

The subsequent reaction of these ligands with $[Ru(TAP)_2(H_2O)_2]^{2+}(NO_3^-)_2$ in anhydrous DMF yielded a dark-red solution which turned to brownish-orange. The complexes **2** and **4** were obtained in 80% and 53% yields respectively either after FC purification on silica gel (in the case of **2**) or chromatography on neutral alumina (in the case of **4**). Both complexes are orange solids, soluble in polar organic solvents and in water. The structure of **2** and **4** has been confirmed by NMR spectroscopy.[12]

### Electrochemical data

The electrochemical behaviour of **2** and **4** was examined by cyclic voltammetry in dry deoxygenated acetonitrile (for the reduction of **4** in MeCN, see Fig. 2). The data, along with those of some reference complexes,[10b,13,14] are collected in Table 1. Complexes **2** and **4** exhibit a reversible oxidation wave at +1.80 and +1.78 V *versus* SCE respectively that correspond to the oxidation of the Ru centre. In reduction, complexes **2** and **4** exhibit three reversible




**Scheme 1** Syntheses of $[Ru(TAP)_2btz]^{2+}(NO_3^-)_2$ **2** and $[Ru(TAP)_2pytz]^{2+}(NO_3^-)_2$ **4**.

**Table 1** Electrochemical data for complexes **2**, **4** and reference complexes

| Entry | Complex | Oxidation (V/SCE) | Reduction (V/SCE) | $E^*_{red}$[c] (V/SCE) | $\lambda_{max}$ (eV) |
|---|---|---|---|---|---|
| 1 | $[Ru(bpy)_3]^{2+}(PF_6^-)_2$[a,13] | +1.28 (r) | −1.35 (r, B), −1.54 (r, B), −1.79 (r, B) | +0.65 | +2.00 |
| 2 | $[Ru(TAP)_3]^{2+}(PF_6^-)_2$[a,13] | +1.94 (r) | −0.75 (r, T), −0.88 (r, T), −1.10 (r, T), −1.60 (r, T), −1.80 (r, T) | +1.30 | +2.05 |
| 3 | $[Ru(TAP)_2bpy]^{2+}(PF_6^-)_2$[a,13] | +1.70 (r) | −0.83 (r, T), −1.01 (r, T), −1.56 (r, B), −1.72 (r, T) | +1.10 | +1.93 |
| 4 | $[Ru(TAP)_2phen]^{2+}(Cl^-)_2$[a,14] | +1.73 (r) | −0.83 (r, T), −1.01 (r, T), −1.55 (r, P), −1.74 (r, T) | +1.15 | +1.98 |
| 5 | $[Ru(btzR_1)_3]^{2+}(Cl^-)_2$[b,10b] | +1.35 (r) | <−2.3 | — | — |
| 6 | $[Ru(pytzR_1)_3]^{2+}(Cl^-)_2$[b,10b] | +1.32 (r) | −1.82 | — | — |
| 7 | $[Ru(TAP)_2btzR_2]^{2+}(NO_3^-)_2$ **2**[a] | +1.80 (r) | −0.79 (r, T), −0.97 (r, T), −1.34 (r, T) | +1.24 | +2.03 |
| 8 | $[Ru(TAP)_2pytzR_2]^{2+}(NO_3^-)_2$ **4**[a] | +1.78 (r) | −0.78 (r, T), −0.97 (r, T), −1.50 (r, T), −1.75 (irr, T or pytz) | +1.23 | +2.01 |

[a] Redox potentials measured by cyclic voltammetry in MeCN, V *versus* SCE at room temperature, with 0.1 M $Bu_4N^+PF_6^-$[a] or with 0.1 M $TBA^+BF_4^-$[b] as supporting electrolyte and a Pt or a glassy carbon [b] working electrode. [c] The corresponding reduction potentials in the excited state (*vs.* SCE), as estimated from the reduction potential in the ground state and the energy of the emission maximum in MeCN ($E^*_{red} \approx E_{red} + \Delta E_{\lambda_{max}}$). The reversibility and attribution of the waves are given in parentheses. r = reversible; irr = irreversible; T = 1,4,5,8-tetraazaphenanthrene; B = 2,2′-bipyridine; P = 1,10-phenanthroline; $R_1$ = hexyl-; $R_2$ = benzyl-.

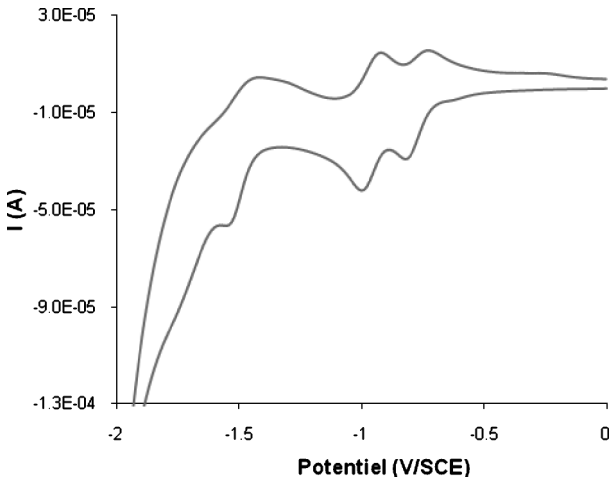



**Fig. 2** Reduction cyclic voltammogram of $[Ru(TAP)_2pytz]^{2+}(NO_3^-)_2$ **4** in MeCN, V *versus* SCE at room temperature, with 0.1 M $Bu_4N^+PF_6^-$ as supporting electrolyte and a Pt working electrode.

waves and a fourth irreversible one for complex **4**. The first two waves can be attributed to the two TAP ligands, in comparison with the reduction potentials of $[Ru(TAP)_3]^{2+}$, $[Ru(TAP)_2bpy]^{2+}$ and $[Ru(TAP)_2phen]^{2+}$ (Table 1, entries 2–4). The third reduction wave of complexes **2** and **4** can be assigned to a second reduction of a TAP ligand because the reduction potentials are not negative enough to account for the reduction of a btz or pytz ligand (around −2.3 V/SCE for $[Ru(btz)_3]^{2+}$ and −1.82 V/SCE for $[Ru(pytz)_3]^{2+}$, Table 1, entries 5 and 6).[10b,11c] The fourth reduction wave of complex **4** could be also assigned to a fourth reduction of a TAP ligand. However, such a fourth reduction wave should also be observed for complex **2**, which is not the case. Therefore, a fourth addition of an electron on the pytz ligand in complex **4**, although occurring at a potential less negative than for $[Ru(pytz)_3]^{2+}$, might not be totally excluded and could be due to the important electron withdrawing effect of the two TAP ligands. The reduction potentials of the excited $^3$MLCT state ($E^*_{red}$) have been estimated in the same way as for the other Ru complexes, *i.e.* from the reduction potential of the first reduction wave and the energy of the emission maximum (Table 1). These latter values being too small, it leads to oxidation powers of the excited state that are under-estimated. Nevertheless, the $E^*_{red}$ values for complex **2** (+1.24 V) and **4** (+1.23 V) are even slightly more positive than for $[Ru(TAP)_2phen]^{2+}$ (+1.15 V), *i.e.* the reference complex, which could be applied in gene silencing.[2f]

## Photophysical properties

The absorption data in acetonitrile and water for complexes **2**, **4** and reference complexes are given in Table 2.[12] The bands of complexes **2** and **4** at wavelengths shorter than 270 nm are similar to those of $[Ru(btzR_1)_3]^{2+}(Cl^-)_2$, $[Ru(btzR_2)_3]^{2+}$ and $[Ru(pytzR_1)_3]^{2+}(Cl^-)_2$ (Table 2, entries 4, 5, and 6). The most bathochromic absorption bands around 450–460 nm in both complexes **2** and **4** correspond most probably to MLCT transitions Ru→TAP as compared to $[Ru(TAP)_2bpy]^{2+}$ and $[Ru(TAP)_2phen]^{2+}$

**Table 2** Absorption data at 298 K in aerated solution for complexes **2**, **4** and reference complexes

| | | absorbance $\lambda_{max}$, nm ($\varepsilon/10^3$ $M^{-1}$ $cm^{-1}$) | |
|---|---|---|---|
| Entry | Complex | acetonitrile | water |
| 1 | $[Ru(TAP)_3]^{2+}(Cl^-)_2$[13] | 276, 408, 437 | 276, 408, 437 (13.0) |
| 2 | $[Ru(TAP)_2bpy]^{2+}(Cl^-)_2$[13] | 274, 412, 463 | 273, 412, 465 (12.8) |
| 3 | $[Ru(TAP)_2phen]^{2+}(Cl^-)_2$[14] | 272, 412, 458 | 230, 272, 410, 466 (14.5) |
| 4 | $[Ru(btzR_1)_3]^{2+}(Cl^-)_2$[a,10b] | 230, 301 | — |
| 5 | $[Ru(pytzR_1)_3]^{2+}(Cl^-)_2$[a,10b] | 237, 269, 382 | — |
| 6 | $[Ru(btzR_2)_3]^{2+}(Cl^-)_2$[10a] | 222, 302 | — |
| 7 | $[Ru(TAP)_2btzR_2]^{2+}(NO_3^-)_2$ **2** | 232, 275, 384, 452 (10.1) | 231, 278, 384, 455 (10.7) |
| 8 | $[Ru(TAP)_2pytzR_2]^{2+}(NO_3^-)_2$ **4** | 232, 273, 403, 456 (9.7) | 232, 274, 406, 459 (10.3) |

[a] Absorption data in MeOH; $R_1$ = hexyl-; $R_2$ = benzyl-.

**Table 3** Emission data for complexes **2**, **4** and reference complexes[a]

| | | acetonitrile | | | | | | water | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Entry | Complex | $\lambda_{max}$/ nm | $\tau_{air}$/ ns | $\tau_{Ar}$/ ns | $\Phi_{Ar}$/ $10^{-3}$ | $k_{r(Ar)}$/ $10^3$ $s^{-1}$ | $k_{nr(Ar)}$/ $10^5$ $s^{-1}$ | $\lambda_{max}$/ nm | $\tau_{air}$/ ns | $\tau_{Ar}$/ ns | $\Phi_{Ar}$/ $10^{-3}$ | $k_{r(Ar)}$/ $10^3$ $s^{-1}$ | $k_{nr(Ar)}$/ $10^5$ $s^{-1}$ |
| 1 | $[Ru(TAP)_3]^{2+}$ [18] | 604 | 53 | 55 | 7 | 103 | 146 | 602 | 210 | 223 | 14 | 63 | 44 |
| 2 | $[Ru(TAP)_2bpy]^{2+}$ [18] | 641 | 660 | 1965 | 174 | 83 | 4 | 649 | 605 | 778 | 40 | 51 | 12 |
| 3 | $[Ru(TAP)_2phen]^{2+}$ [14,15] | 626 | 760 | 1800 | — | — | — | 655 | 730 | 840 | — | — | — |
| 4 | $[Ru(TAP)_2btz]^{2+}$ **2** | 612 | 40 | 40 | 1 | 25 | 250 | 633 | 101 | 103 | 3 | 29 | 97 |
| 5 | $[Ru(TAP)_2pytz]^{2+}$ **4** | 616 | 385 | 536 | 19 | 35 | 18 | 640 | 715 | 940 | 27 | 29 | 10 |

[a] Temperature: 298 K. The luminescence decays corresponding to the excited state lifetimes ($\tau$) were measured by SPC or pulsed laser. Estimated experimental errors for the lifetimes: ~ 10%. The luminescence quantum yields $\Phi$ (approximate error <20%) were determined from the $\Phi$ values of $[Ru(bpy)_3]^{2+}$ as reference. $k_r = \Phi/\tau$; $k_{nr} = 1/\tau - k_r$.

(Table 2, entries 2 and 3) and on the basis of the reduction potential data. Thus, these data indicate that, in absorption, the novel complexes **2** and **4** behave similarly to $[Ru(TAP)_2bpy]^{2+}$ and $[Ru(TAP)_2phen]^{2+}$ in acetonitrile and water with the most bathochromic absorption corresponding to the transition dπ(Ru)–π*(TAP). Such bathochromic MLCT transitions are not present in $[Ru(btzR_1)_3]^{2+}$, $[Ru(btzR_2)_3]^{2+}$ or in $[Ru(pytzR_1)_3]^{2+}$since, in those complexes, the LUMO corresponds to that of $btzR_1$, $btzR_2$, and $pytzR_1$, much less stabilized than the LUMO of TAP according to the reduction potential values.

The emission data for complexes **2**, **4** and the reference complexes are collected in Table 3 (for the spectra in MeCN, see Fig. 3).[12]

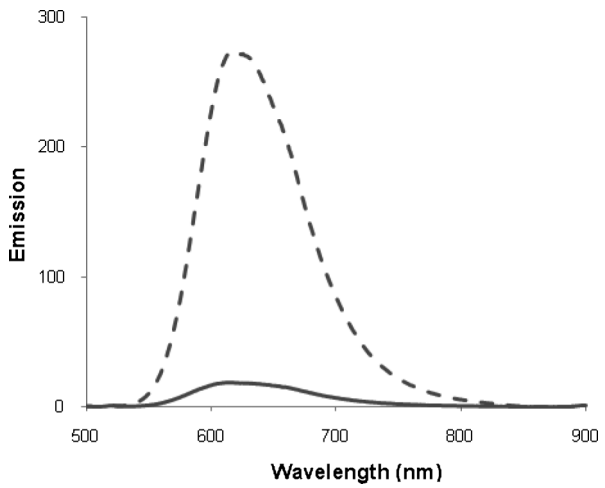



**Fig. 3** Emission spectra of $[Ru(TAP)_2btz]^{2+}(NO_3^-)_2$ **2** (—) and $[Ru(TAP)_2pytz]^{2+}(NO_3^-)_2$ **4** (– –) in MeCN under argon.

The emission maxima of $[Ru(TAP)_2btz]^{2+}$ **2** and $[Ru(TAP)_2pytz]^{2+}$ **4** are similar and can be assigned to the $^3$MLCT emission Ru-TAP as for $[Ru(TAP)_2bpy/phen]^{2+}$. As usually observed, there is a stabilization of the $^3$MLCT state in more polar solvents as indicated by the bathochromic shift of emission from acetonitrile to water (Table 3, entries 2–5).

The luminescence lifetimes and the corresponding radiative ($k_r$) and non radiative ($k_{nr}$) rate constants in acetonitrile and water as determined from the quantum yields of emission, are also given in Table 3. For both complexes **2** and **4**, the emission lifetimes (under air or argon) are longer in water than in acetonitrile. This contrasts with the case of numerous polypyridyl Ru complexes such as $[Ru(bpy)_3]^{2+}$ or $[Ru(TAP)_2(bpy/phen)]^{2+}$[13–15] (Table 3, entries 2 and 3) for which the excited state lifetime is usually shorter in water than in acetonitrile because of the efficient vibrational deactivation of the excited states by the O–H vibrators of water.[16] In the present case, a luminescence lifetime shorter in acetonitrile than in water is typical of a control of $\tau$ by another process than the radiationless deactivation of the $^3$MLCT to the ground state. Actually the emission lifetime behaviour of complexes **2** and **4** is similar to that of $[Ru(TAP)_3]^{2+}$ (Table 3, entry 1) for which it was clearly demonstrated[13] that the $^3$MLCT state is easily activated at room temperature to the $^3$MC state (Metal Centred), which does not emit and causes an emission lifetime shortening. As this crossing to the $^3$MC state is more efficient when the $^3$MLCT state is destabilized and thus closer to the $^3$MC state in less polar solvent, this explains the shortening of emission lifetime in acetonitrile in which the thermal activation from the $^3$MLCT to the $^3$MC state controls the lifetime. We should thus conclude that the new complexes **2** and **4** would present a photophysical mechanism similar to that of $[Ru(TAP)_3]^{2+}$. This would mean that the $k_{nr}$ (argon) value should include a term corresponding to this thermal activation to the $^3$MC state and should be important. This is certainly true for complex **2** ($k_{nr}$ = 250 $10^5$ $s^{-1}$) but for complex **4** the $k_{nr}$ value (18 $10^5$ $s^{-1}$) is not that important. There is also a striking feature for complex **2**, *i.e.* $k_{nr}$ not only in acetonitrile but also in water is very high. This could be attributed to the btz ligand itself. Indeed, because of the presence of two five-membered rings,[17] this ligand may not adopt a planar geometry.

Thus, some distortion to an octahedral geometry should result, increasing the radiationless deactivation in water. In order to test, as concluded from the above considerations, whether complexes **2** and **4** would exhibit a photophysical behaviour in acetonitrile, similar to that of $[Ru(TAP)_3]^{2+}$, *i.e.* would cross more or less easily to the $^3$MC state from the $^3$MLCT state, we examined the behaviour of the emission lifetime as a function of temperature (Fig. 4).

It is quite clear that the $^3$MLCT state of complex **2** behaves like $[Ru(TAP)_3]^{2+}$. Thus, from room temperature till *ca.* 260 K, the lifetimes remain very short and constant because they are controlled in this higher temperature domain, by the activation to the $^3$MC state. At *ca.* 250 K, the lifetimes start increasing because the $^3$MLCT state reaches less easily the $^3$MC state. However, even at *ca.* 230 K, the lifetime has not yet reached a maximum value. This contrasts with the behaviour of $[Ru(TAP)_2phen]^{2+}$ for which the emission lifetime does not increase much from room temperature

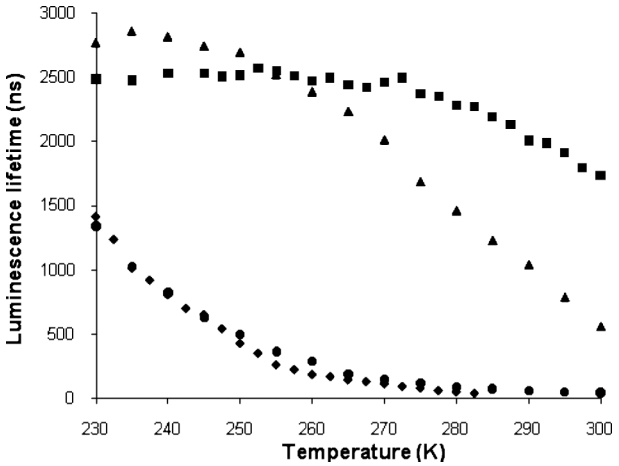



**Fig. 4** Luminescence lifetimes as a function of temperature. Diamonds: $[Ru(TAP)_2btz]^{2+}$ (**2**); circles: $[Ru(TAP)_3]^{2+}$; triangles: $[Ru(TAP)_2pytz]^2$ (**4**); squares: $[Ru(TAP)_2phen]^{2+}$.

till the plateau value at *ca.* 275 K, meaning that in that case, quasi for the whole temperature domain, the lifetime is not controlled by a participation of the $^3$MC state. For complex **4**, the data of Fig. 4 indicate that its behaviour is intermediate to the two previous cases: there is a more important increase of lifetime from room temperature till 255 K than for $[Ru(TAP)_2phen]^{2+}$ but a plateau value is reached from *ca.* 250 K. In conclusion, in acetonitrile the $^3$MLCT state of complex **4** can be activated to the $^3$MC state but much less efficiently than for complex **2**.

### Steady state illumination

As it is well known that photodechelation takes place from the $^3$MC state, we also examined the photodechelation of complexes **2** and **4** under steady state illumination as compared to that of $[Ru(TAP)_3]^{2+}$ and $[Ru(TAP)_2phen]^{2+}$ in the same experimental conditions (Fig. 5).

Fig. 5A indicates that complex **2** exhibits a little photodechelation even in water, as observed for $[Ru(TAP)_3]^{2+}$ in water (Fig. 5B). The products of dechelation correspond to the substitution of one bidentate ligand by two monodentate ligands ($Cl^-$ or $H_2O$) responsible for the bathochromic absorption around 500 nm. Thus the $^3$MLCT state of **2** and $[Ru(TAP)_3]^{2+}$ would indeed cross over the $^3$MC state in addition to an important deactivation to the ground state for **2**. For complex **4** in water, the absorption spectra do not change with the illumination time (Fig. 5C) as for $[Ru(TAP)_2phen]^{2+}$ (Fig. 5D) which is quite photostable. These observations correlate thus well with the data of Table 3 for water.

We also examined the photodechelation of the four complexes in acetonitrile (Fig. 6) in which the $^3$MLCT state is less stabilized, thus closer in energy to the $^3$MC state. Fig. 6A and 6B show that the photodechelation of both complexes, **2** and $[Ru(TAP)_3]^{2+}$, is important. This is in excellent agreement with the temperature dependence of their $^3$MLCT state lifetimes, as explained above. In this case, the bidentate ligand is substituted again by $Cl^-$ and/or MeCN. For complex **2** (Fig. 6A), the absence of isosbestic point indicates that more than one dechelation product is formed. Concerning complex **4** (Fig. 6C) and $[Ru(TAP)_2phen]^{2+}$ (Fig. 6D), it is clear that at room temperature, as concluded from the emission lifetimes dependence on temperature, complex **4**, in

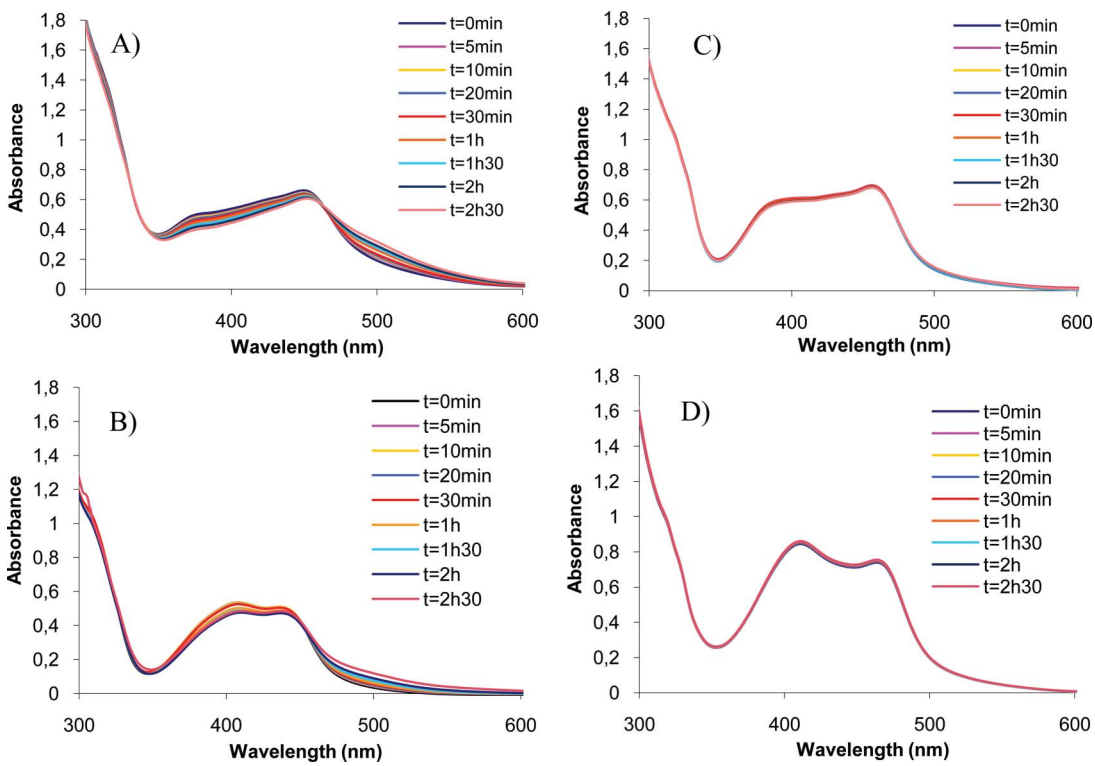



**Fig. 5** Absorption spectra as a function of the illumination time, for (A) $[Ru(TAP)_2btz]^{2+}(Cl^-)_2$ **2**, 6.2 $10^{-5}$M; (B) $[Ru(TAP)_3]^{2+}(Cl^-)_2$, 4.5 $10^{-5}$ M; (C) $[Ru(TAP)_2pytz]^{2+}(Cl^-)_2$ **4**, 6.6 $10^{-5}$ M; (D) $[Ru(TAP)_2phen]^{2+}(Cl^-)_2$, 4.6 $10^{-5}$ M, in $H_2O$, under argon.

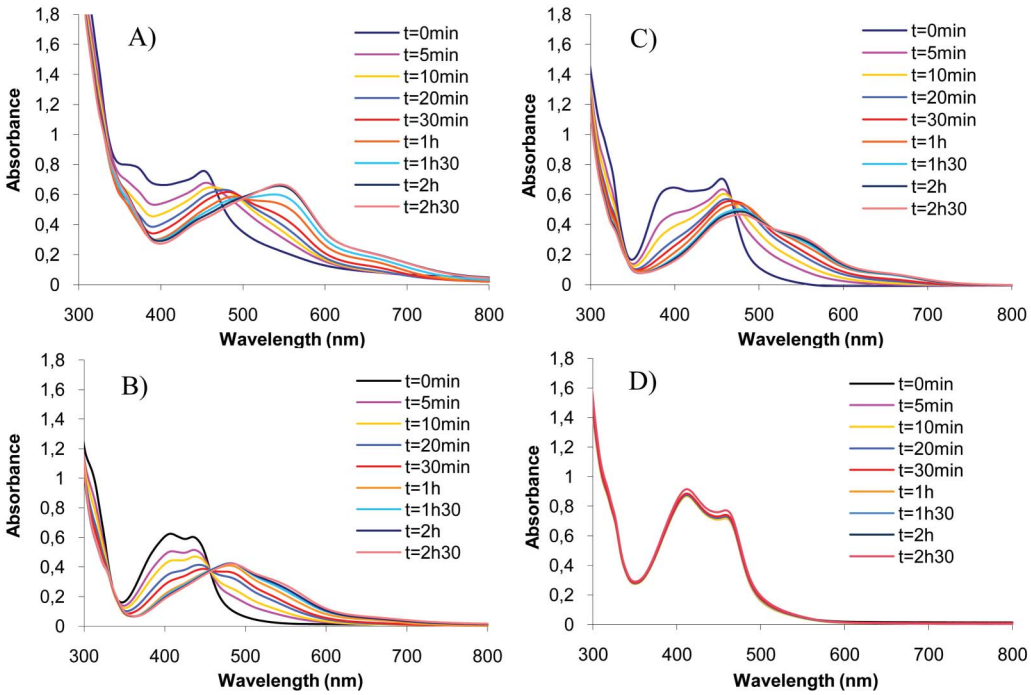



**Fig. 6** Absorption spectra as a function of the illumination time, for (A) $[Ru(TAP)_2btz]^{2+}(Cl^-)_2$ **2**, 7.5 $10^{-5}$M; (B) $[Ru(TAP)_3]^{2+}(Cl^-)_2$, 5.0 $10^{-5}$ M; (C) $[Ru(TAP)_2pytz]^{2+}(Cl^-)_2$ **4**, 7.2 $10^{-5}$ M; (D) $[Ru(TAP)_2phen]^{2+}(Cl^-)_2$, 5.1 $10^{-5}$ M, in MeCN, under argon.

contrast to $[Ru(TAP)_2phen]^{2+}$, undergoes the loss of a ligand with substitution; in this case again, several dechelation products are occurring.

## Conclusion

As explained in the introduction, we have chosen to synthesize and study $[Ru(TAP)_2btz]^{2+}$ **2** and $[Ru(TAP)_2pytz]^{2+}$ **4** especially because these complexes could fulfil two required conditions: (i) they should be sufficiently oxidizing in their $^3$MLCT state to extract an electron from components of biomolecules and give rise to photo-adducts. Therefore, they should contain at least two TAP ligands, provided that the third ligand does not change too much the oxidizing power, (ii) they should be readily functionalizable. The examination of their electrochemical and photophysical behaviour constitutes thus an important prerequisite for their use as conjugates or for tethering them on different vectors.

Interestingly, our results show that a simple change of a spectator ligand (*i.e.* the phen by a btz or a pytz ligand) influences greatly the resulting properties of the TAP-complex.

The electrochemical and emission data clearly show that both complexes should behave as excellent oxidizing agents in their $^3$MLCT states. Indeed, the oxidizing power under illumination is even slightly better than that of $[Ru(TAP)_2phen]^{2+}$. However, a more detailed examination of the photophysical parameters that characterize their luminescent excited states indicates that complex **4** with the pytz ligand should have the priority over compound **2** with the btz ligand. Indeed, the excited state lifetime of **4** is longer than that of **2**, which should favour the probability of quenching by a reducing biomolecular agent in water. Moreover **4** is more photostable than **2** at least in water. These advantages of complex **4** over **2** are due to the presence of the pytz ligand which probably adopts a less distorted octahedral geometry than **2** as indicated by the much smaller non radiative deactivation rate constant of **4**.

In conclusion, the combination of one functionalized pytz ligand with two TAP ligands in a ruthenium(II) complex makes the resulting metallic compound an attractive photoreagent for biomolecules and opens new horizons for applications with biological systems.

## Experimental section

### Instrumentation

The $^1$H NMR and $^{13}$C NMR spectra were recorded with a Bruker Avance-300 instrument and a Bruker Varian Unity-600. Chemical shifts are expressed in ppm. $CDCl_3$ was filtered over a short basic alumina column to remove traces of DCl. Most of the $^1$H NMR spectra signals were attributed through 2D NMR analyses (COSY, HSQC, HMBC). The electrospray mass spectra were recorded with a Water Q-TOF 2 spectrometer (at the University of Mons, Belgium). The emission spectra were recorded with a Shimadzu RF-5301PC and the absorption spectra with a Perkin-Elmer Lambda UV-Vis spectrophotometer. The determination of the molar absorption coefficients was performed by weight and absorption measurements. Cyclic voltammetry was carried out on a platinum disk working electrode (approximate area = 3 $mm^2$), in dried acetonitrile with tetrabutylammonium hexafluorophosphate (0.1 mol $L^{-1}$) as supporting electrolyte. The potential of the working electrode was controlled by an Autolab PGSTAT 100 (Eco Chemie B.V., Utrecht, The Netherlands) potentiostat through a PC interface with a scan rate of 100 mV $s^{-1}$ between –2 and +2 V *versus* SCE. The counter electrode was a platinum disk and the reference electrode a Saturated Calomel Electrode

(SCE). All measurements were performed in a single compartment cell. The emission lifetimes at room temperature were measured by using the single-photon counting technique (SPC) with an Edinburgh Instruments FL900 spectrometer (Edinburgh, U.K.) equipped with a nitrogen-filled discharge lamp and a peltier-cooled Hamamatsu R955s photomultiplier tube. The emission decays were analyzed with the Edinburgh Instruments software (version 3.0), based on nonlinear least-squares regressions using Marquardt algorithms. The emission lifetimes in acetonitrile as a function of temperature were measured by using the excitation source of a frequency-tripled (355 nm) Nd:YAG Q-switched laser (Continuum Inc.) coupled with an optical parametric oscillator (Continum Inc.) covering the wavelengths region 410–2300 nm with an average pulse energy of 15 mJ. The average pulse duration was 5 ns. The grating Czerny–Turner monochromator (Spectra Pro 2300i, Acton Research Corp.) was used for the spectral selection.

The steady state illuminations were performed with a Xe lamp (500 W) Thermo Oriel with a $KNO_2$ (0.2 M) and $H_2O$ filters.

## Chemicals

All the reactions were performed under an inert atmosphere. Anhydrous DMF was obtained from Alfa Aesar. All the solvents and reagents for the syntheses were at least reagent grade quality and were used without further purification. The reaction mixtures from the complexation with Ru(II) were protected from direct light during the synthesis to prevent photochemical degradation. Silica gel (230–400 mesh) was used for flash chromatography. Neutral aluminium oxide was used for chromatography. The solvents for photophysical measurements were of spectroscopic grade and water was purified with a Millipore Milli-Q system. $Ru(TAP)_2Cl_2$ and $[Ru(TAP)_2(H_2O)_2]^{2+}(NO_3^-)_2$ were prepared following the procedures described in the literature.[19] The syntheses of ligands **1** and **3** were already described in the literature but with different procedures than those given below.[10a,11a] For the steady state illumination experiments, $[Ru(TAP)_2btz]^{2+}(Cl^-)_2$ was obtained from complex **2** by anion exchange with a Dowex 1 × 8, 100–200 mesh. Besides, $[Ru(TAP)_2pytz]^{2+}(Cl^-)_2$ was obtained by purification of a small amount of complex **4** with a Sephadex SPC25.

**1,1′-dibenzyl-4,4′-bi-1*H*-1,2,3-triazolyl 1.** 1,4-bis(trimethylsilyl)-1,3-butadiyne (151 mg, 0.777 mmol) and benzyl azide (200 µL, 1.60 mmol) were dissolved in *t*-butanol (7 mL) and $H_2O$ (7 mL). $CuSO_4$ (48 mg, 0.301 mmol), sodium ascorbate (195 mg, 0.985 mmol), $K_2CO_3$ (211 mg, 1.53 mmol) and pyridine (600 µL, 7.46 mmol) were successively added and the mixture was stirred vigorously for 24 h at room temperature under inert atmosphere. $CH_2Cl_2$ (14 mL) and an aqueous $NH_4OH$ solution (5%, 15 mL) were added to the reaction mixture which was stirred for 30 min. The organic layer was washed with an aqueous $NH_4OH$ solution (5%, 2 × 15 mL). The combined aqueous layers were extracted with $CH_2Cl_2$ (2 × 20 mL) and the combined organic layers were washed with $H_2O$ (3 × 30 mL) until pH = 7 and then concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel ($CH_2Cl_2$/MeOH; 95 : 5) to yield the compound **1** as a white solid (178 mg, 0.563 mmol, 72%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K): $\delta_{(ppm)}$ = 5.56 (s, 4H, $NCH_2$), 7.28–7.38 (m, 10H, $H_{Bn}$), 7.94 (s, 2H, $H_{triazole}$).

**$[Ru(TAP)_2btz]^{2+}(NO_3^-)_2$ 2.** The bistriazole ligand **1** (21 mg, 0.0728 mmol) and $[Ru(TAP)_2(H_2O)_2]^{2+}(NO_3^-)_2$ (50 mg, 0.0801 mmol) were suspended in DMF (2 mL). The reaction mixture was heated for 6 h at 100 °C to yield a dark-red solution which turned to brownish-orange. The reaction mixture was concentrated under reduced pressure and the crude residue was purified by flash chromatography on silica gel ($CH_2Cl_2$/MeOH; 8 : 2) to yield the starting material (8 mg) and the Ru-complex **2** as an orange solid (32 mg, 0.0353 mmol, 80% given the 61% of conversion). m.p. 200 °C (dec.); IR (KBr): 3053, 1498, 1355, 871, 734; $^1$H NMR (300 MHz, $CD_3OD$, 298 K): $\delta_{(ppm)}$ = 5.49 (d, 2H, $^2J$ = 14.7 Hz, $NCH_2$), 5.56 (d, 2H, $^2J$ = 14.4 Hz, $NCH_2$), 7.12 (d, 4H, $^3J$ = 6.3 Hz, $H_{Bn}$), 7.28–7.35 (m, 6H, $H_{Bn}$), 8.56 (d, 2H, $^3J$ = 2.7 Hz, $H_{TAP}$), 8.59 (d, 2H, $^3J$ = 2.7 Hz, $H_{TAP}$), 8.64–8.66 (m, 6H, $H_{TAP}$ + $H_{triazole}$), 9.00 (d, 2H, $^3J$ = 2.7 Hz, $H_{TAP}$), 9.20 (d, 2H, $^3J$ = 2.7 Hz, $H_{TAP}$); $^{13}$C NMR (75 MHz, $d_6$-DMSO, 298 K): $\delta_{(ppm)}$ = 54.8, 124.6, 127.9, 128.7, 128.8, 132.3, 133.9, 139.9, 141.8, 142.3, 142.6, 144.0, 144.4, 148.9(8), 149.0(3), 149.9, 150.3; HRMS (ESI-TOF) calcd for $C_{38}H_{28}N_{14}Ru$ ($M^{2+}$) 391.0832, found 391.0829.

**2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)pyridine 3.** 2-(trimethylsilyl)ethynylpyridine (176 mg, 1.01 mmol) and benzyl azide (125 µL, 1.00 mmol) were dissolved in *t*-butanol (5 mL) and $H_2O$ (5 mL). $CuSO_4$ (34 mg, 0.213 mmol), sodium ascorbate (79 mg, 0.399 mmol) and $K_2CO_3$ (136 mg, 0.986 mmol) were successively added and the mixture was stirred vigorously for 24 h at room temperature under inert atmosphere. $CH_2Cl_2$ (10 mL) and an aqueous $NH_4OH$ solution (5%, 10 mL) were added to the reaction mixture which was stirred for 30 min. The organic layer was washed twice with an aqueous $NH_4OH$ solution (5%, 2 × 10 mL). The combined aqueous layers were extracted with $CH_2Cl_2$ (2 × 15 mL) and the combined organic layers were washed with $H_2O$ (3 × 20 mL) until pH = 7 and then concentrated under reduced pressure. The crude residue was purified by flash chromatography on silica gel ($CH_2Cl_2$/MeOH; 95 : 5) to yield the compound **3** as a white solid (187 mg, 0.793 mmol, 78%). $^1$H NMR (300 MHz, $CDCl_3$, 298 K): $\delta_{(ppm)}$ = 5.58 (s, 2H, $NCH_2$), 7.20 (td, 1H, $^4J$ = 1.5 Hz, $^3J$ = 5.5 Hz, $H_{py}$), 7.31–7.41 (m, 5H, $H_{Bn}$), 7.76 (td, 1H, $^4J$ = 1.8 Hz, $^3J$ = 7.8 Hz, $H_{py}$), 8.04 (s, 1H, $H_{triazole}$), 8.18 (d, 1H, $^3J$ = 8.1 Hz, $H_{py}$), 8.53 (d, 1H, $^3J$ = 4.8 Hz, $H_{py}$).

**$[Ru(TAP)_2pytz]^{2+}(NO_3^-)_2$ 4.** The triazole-pyridine ligand **3** (26 mg, 0.110 mmol) and $[Ru(TAP)_2(H_2O)_2]^{2+}(NO_3^-)_2$ (77 mg, 0.123 mmol) were suspended in DMF (2 mL). The reaction mixture was heated for 5 h at 100 °C to yield a dark-red solution which turned to brownish-orange. The reaction mixture was concentrated under reduced pressure and the crude residue was purified by chromatography on neutral alumina ($CH_2Cl_2$/MeOH; 8 : 2) to yield the Ru-complex **4** as an orange solid (47 mg, 0.0580 mmol, 53%). m.p. 197 °C (dec); IR (KBr): 3033, 1529, 1340, 866, 734; $^1$H NMR (600 MHz, $CD_3OD$, 298 K): $\delta_{(ppm)}$ = 5.55 (d, 1H, $^2J$ = 14.4 Hz, $NCH_2$), 5.60 (d, 1H, $^2J$ = 14.4 Hz, $NCH_2$), 7.19 (d, 2H, $^3J$ = 7.2 Hz, $H_{Bn}$), 7.32 (m, 3H, $H_{Bn}$), 7.35–7.38 (m, 1H, $H_{py}$), 7.79 (d, 1H, $^3J$ = 5.4 Hz, $H_{py}$), 8.11 (td, 1H, $^3J$ = 7.8 Hz, $^4J$ = 1.2 Hz, $H_{py}$), 8.32 (d, 1H, $^3J$ = 8.4 Hz, $H_{py}$), 8.36 (m, 1H, $H_{TAP}$), 8.53–8.55 (m, 2H, $H_{TAP}$), 8.59 (m, 1H, $H_{TAP}$), 8.61–8.70 (m, 4H, $H_{TAP}$), 8.94 (d, 1H, $^3J$ = 3.0 Hz, $H_{TAP}$), 9.04 (d, 1H, $^4J$ = 3.0 Hz, $H_{TAP}$), 9.10 (s, 1H, $H_{triazole}$), 9.19 (d, 1H, $^4J$ = 3.0 Hz, $H_{TAP}$), 9.22 (d, 1H, $^4J$ = 3.0 Hz, $H_{TAP}$); $^{13}$C NMR (150 MHz, $CD_3OD$, 298 K):

$\delta_{(ppm)}$ = 57.1, 124.6, 127.8, 127.9, 129.7, 130.2(6), 130.3(3), 133.9, 133.9(6), 134.0(5), 134.2, 134.6, 140.9, 143.7, 143.8, 144.3, 146.4, 146.7, 146.9, 147.0, 149.2, 149.6, 150.2, 150.4, 150.9, 151.8, 153.8; HRMS (ESI-TOF) calcd for $C_{34}H_{24}N_{12}Ru$ ($M^{2+}$) 351.0644, found 351.0651.

## Acknowledgements

The authors thank the Belgian Policy (Program IAP/PAI, P6/27) and the FRFC-FNRS Belgium (Fonds National pour la Recherche Scientifique) for financial support. A.M. is grateful to the FNRS for a PhD grant.

## Notes and references

1 (*a*) M. K. Nazeeruddin and M. Grätzel, Transition metal for photovoltaic and light emitting applications, *Struct. Bonding*, 2007, **123**, 113–175; (*b*) F. Puntoriero, F. Nastasi, M. Cavazzini, S. Quici and S. Campagna, *Coord. Chem. Rev.*, 2007, **251**, 536–545; (*c*) S. Rau, D. Walther and J. G. Vos, *Dalton Trans.*, 2007, 915–919; (*d*) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni and M. Venturi, *Sol. Energy Mater. Sol. Cells*, 1995, **38**, 159–173; (*e*) I. Ortmans, C. Moucheron and A. Kirsch-De Mesmaeker, *Coord. Chem. Rev.*, 1998, **168**, 233–271.

2 (*a*) K. K. W. Lo, *Struct. Bonding*, 2007, **123**, 205–245; (*b*) F. Pierard and A. Kirsch-De Mesmaeker, *Inorg. Chem. Commun.*, 2006, **9**, 111–126; (*c*) C. Metcalfe and J. A. Thomas, *Chem. Soc. Rev.*, 2003, **32**, 215–224; (*d*) K. E. Erkkila, D. T. Odom and J. K. Barton, *Chem. Rev.*, 1999, **99**, 2777–2795; (*e*) B. Nordén, P. Lincoln, B. Akerman and E. Tuite, *Met. Ions Biol. Syst.*, 1996, **33**, 177; (*f*) S. Le Gac, S. Rickling, P. Gerbaux, E. Defrancq, C. Moucheron and A. Kirsch-De Mesmaeker, *Angew. Chem., Int. Ed.*, 2009, **48**, 1122–1125; (*g*) C. Moucheron, *New J. Chem.*, 2009, **33**, 235–245.

3 (*a*) A. Kirsch-De Mesmaeker, J. P. Lecomte and J. M. Kelly, *Top. Curr. Chem.*, 1996, **177**, 25; (*b*) C. Moucheron, A. Kirsch-De Mesmaeker and J. M. Kelly, *J. Photochem. Photobiol., B*, 1997, **40**, 91; (*c*) C. Moucheron, A. Kirsch-De Mesmaeker and J. M. Kelly, *Struct. Bonding*, 1998, **92**, 163; (*d*) B. Elias and A. Kirsch-De Mesmaeker, *Coord. Chem. Rev.*, 2006, **250**, 1627; (*e*) L. Herman, S. Ghosh, E. Defrancq and A. Kirsch-De Mesmaeker, *J. Phys. Org. Chem.*, 2008, **21**, 670–681; (*f*) O. Lentzen, J. F. Constant, E. Defrancq, M. Prevost, S. Schumm, C. Moucheron, P. Dumy and A. Kirsch-De Mesmaeker, *ChemBioChem*, 2003, **4**, 195–202.

4 C. A. Puckett and J. K. Barton, *J. Am. Chem. Soc.*, 2007, **127**, 46–47.

5 (*a*) H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021; (*b*) C. W. Tornoe, C. Christensen and M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057–3064; (*c*) V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596–2599.

6 (*a*) T. R. Chan, R. Hilgraf, K. B. Sharpless and V. V. Fokin, *Org. Lett.*, 2004, **6**, 2853–2855; (*b*) B. Colasson, M. Save, P. Milko, D. Shröder and O. Reinaud, *Org. Lett.*, 2007, **9**, 4987–4990; (*c*) R. J. Detz, S. Arévalo Heras, R. de Gelder, P. W. N. M. van Leeuwen, H. Hiemstra, J. N. H. Reek and J. H. van Maarseven, *Org. Lett.*, 2006, **8**, 3227–3230.

7 (*a*) T. L. Mindt, H. Struthers, L. Brans, T. Anguelov, C. Schweinsberg, V. Maes, D. Tourwé and R. Schibli, *J. Am. Chem. Soc.*, 2006, **128**, 15096–15097; (*b*) H. Struthers, B. Spingler, T. L. Mindt and R. Schilbi, *Chem.–Eur. J.*, 2008, **14**, 6173–6183.

8 (*a*) R. M. Meudtner, M. Ostermeier, R. Goddard, C. Limberg and S. Hecht, *Chem.–Eur. J.*, 2007, **13**, 9834–9840; (*b*) Y. Li, J. C. Huffman and A. H. Flood, *Chem. Commun.*, 2007, 2692–2694.

9 C. M. Fitchett, F. R. Keene, C. Richardson and P. J. Steel, *Inorg. Chem. Commun.*, 2008, **11**, 595–598.

10 (*a*) U. Monkowius, S. Ritter, B. König, M. Zabel and H. Yersin, *Eur. J. Inorg. Chem.*, 2007, 4597–4606; (*b*) J. T. Fletcher, B. J. Bumgarner, N. D. Engels and D. A. Skoglund, *Organometallics*, 2008, **27**, 5430–5433.

11 (*a*) M. Obata, A. Kitamura, A. Mori, C. Kameyama, J. A. Czaplewska, R. Tanaka, I. Kinoshita, T. Kusumoto, H. Hashimoto, M. Harada, Y. Mikata, T. Funabiki and Y. Shigenobu, *Dalton Trans.*, 2008, 3292–3300; (*b*) M. Felici, P. Contreras-Carballada, Y. Vida, J. M. M. Smits, R. J. M. Nolte, L. De Cola, R. M. Williams and M. C. Feiters, *Chem.–Eur. J.*, 2009, **15**, 13124–13134; (*c*) B. Happ, C. Friebe, A. Winter, M. D. Hager, R. Hoogenboom and U. S. Schubert, *Chem.–Asian J.*, 2009, **4**, 154–163.

12 For the spectra, see the supporting information.

13 A. Masschelein, L. Jacquet, A. Kirsch-De Mesmaeker and J. Nasielski, *Inorg. Chem.*, 1990, **29**, 855–860.

14 I. Ortmans, B. Elias, J. M. Kelly, C. Moucheron and A. Kirsch-De Mesmaeker, *Dalton Trans.*, 2004, 668–676.

15 J. P. Lecomte, A. Kirsch-De Mesmaeker, M. Demeunynck and J. Lhomme, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3261–3263.

16 T. J. Meyer, *Pure Appl. Chem.*, 1986, **58**, 1193.

17 G. Orellana, M. L. Duiroga and A. M. Braun, *Helv. Chim. Acta*, 1987, **70**, 2073–2086.

18 (*a*) L. Jacquet and A. Kirsch-De Mesmaeker, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 2471–2480; (*b*) PhD thesis, ULB, L. Jacquet, 1992.

19 (*a*) B. P. Sullivan, D. J. Salmon and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334–3341; (*b*) I. P. Evans, A. Spencer and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1973, 204–209.