Cite this: Chem. Commun., 2011, 47, 11011-11013

www.rsc.org/chemcomm

## COMMUNICATION

## Efficient electron transfer through a triazole link in ruthenium(II) polypyridine type complexes<sup>†</sup>

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Received 20th June 2011, Accepted 30th August 2011 DOI: 10.1039/c1cc13683f

Spectroscopic, electrochemical and theoretical characterisations of photoactive systems readily assembled *via* click-chemistry show an efficient bi-directional charge shift through the triazole link.

The use of light energy to perform catalysis is a challenging task facing chemists. One particularly interesting application is related to conversion of solar energy into fuel, a process inspired by natural photosynthesis, where light energy is used to remove protons and electrons from water to fix carbon dioxide into energy-rich carbohydrates. The basic chemical modules needed to elaborate an artificial photosynthetic device are a photosensitiser and a catalytic unit. Ruthenium(II) trisbipyridine complexes are the most widely used photoactive chromophores in this field. Although ruthenium is not an abundant metal, derivatives of ruthenium(II)-polypyridine complexes have been implemented by Graetzel and his group in dye sensitised solar cells, which are currently proposed as cheaper alternatives for silicon based solar cells.<sup>1</sup>

Their unique photophysical and redox properties, high chemical stability and easy synthetic access are recognised assets.<sup>2</sup> However, chemically assembling a catalytic unit and the photoactive chromophore remains an important synthetic difficulty. The actual reaction schemes are long and tedious and therefore the development of efficient and versatile synthetic methodologies is needed. More importantly, the nature of the chemical link should not significantly alter the photophysical and redox properties of the modules, while it should allow charge shifts between the constitutive units under light excitation.

Copper-catalyzed Azide–Alkyne Cycloaddition (CuAAC),<sup>3,4</sup> a simple and efficient covalent ligation methodology known as *click chemistry*,<sup>5</sup> has actually found applications in almost every domain of synthetic chemistry, including coordination chemistry.<sup>6</sup> This synthetic tactic has been efficiently used in modular assemblies such as a copper(1)–rotaxane complex<sup>7</sup> and

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<sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures and characterisations for synthesis, as well as <sup>1</sup>H, <sup>13</sup>C, and 2D NMR spectra for compounds **1–7c**, DFT, emission and flash photolysis. See DOI: 10.1039/c1cc13683f

Ru–carbohydrate dendrimers.<sup>8</sup> Reports in the literature have presented the triazole as a "poor conduit for electrons" in polyoxometalate–porphyrin systems,<sup>9</sup> or as a photoluminescence quencher when incorporated directly into the coordination sphere of ruthenium ions.<sup>10</sup> Other studies, however, have shown the existence of photo-induced electron transfer in porphyrin–ferrocene conjugates,<sup>11</sup> and a pivotal role of triazoles as non-conjugating connectors favouring and stabilising charge separation has also been described in clicked push–pull systems.<sup>12</sup> We report here on the synthesis of bipyridine ligands which can be easily linked by means of *click chemistry* to organic fragments, acting either as electron donors or acceptors.

Our strategy is based on the introduction of a substituted triazole group onto the 4 position of a bipyridine ligand in the coordination sphere of a ruthenium trisbipyridine-type chromophore (Scheme 1).<sup>13</sup> The *azido* derivative (3) reacts efficiently with different arylacetylenes (4a–4c), in the presence of catalytic copper sulfate and sodium ascorbate in a methylene chloride/water biphasic medium.<sup>14</sup> After *N*-oxide reduction, the resulting modified bipyridines (6a–6c) were incorporated into ruthenium complexes by reaction with [Ru(bpy)<sub>2</sub>Cl<sub>2</sub>].<sup>15</sup> Complexes Ru–H, Ru–NMe<sub>2</sub>, Ru–NDI were isolated as the corresponding hexafluorophosphate salts (7a–7c), and characterised by electrochemical and spectroscopic techniques.

The electrochemical properties of the series of complexes were studied by cyclic voltammetry and show typical features of ruthenium complexes, namely, a reversible oxidation potential around +1.3 V vs SCE for the Ru(II) to Ru(III) process, and three quasi reversible reduction waves in the range of -1.20



Scheme 1 Reagents and conditions: (i) TFA,  $H_2O_2$  (88%);<sup>16</sup> (ii) HNO<sub>3</sub>,  $H_2SO_4$  (40%);<sup>17</sup> (iii) NaN<sub>3</sub>, DMF (91%); (iv) 4a-c, CuSO<sub>4</sub> (5 mol%), sodium ascorbate (10 mol%),  $CH_2Cl_2/H_2O$  1:1 (96–98%); (v) PCl<sub>3</sub>,  $CH_2Cl_2$  (64–87%);<sup>18</sup> (vi) Ru(bpy)<sub>2</sub>Cl<sub>2</sub>, AgNO<sub>3</sub>, MeOH; NH<sub>4</sub>PF<sub>6</sub> aq., MeOH (40–84%).

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Compound	$E_{1/2}$ (bipyridine)	$E_{1/2}$ (ligand)	$E_{1/2}$ (Ru <sup>III/II</sup> )
Ru–H Ru–NMe <sub>2</sub> Ru–NDI	$\begin{array}{c} -1.71, -1.48, -1.20 \\ -1.74, -1.50, -1.22 \\ -1.68^{b}, -1.44^{b}, -1.20^{b} \end{array}$		1.30 1.35 1.36

Values are reported vs SCE as  $E_{1/2} = (E_{pa} + E_{pc})/2$ .<sup>*a*</sup> Values obtained from the cathodic wave due to adsorption. <sup>*b*</sup> Values obtained from the anodic wave due to adsorption.

to -1.74 V attributed to the one electron reduction of each of the bipyridines in the coordination sphere. Additional redox features are observed for Ru-NMe2 and Ru-NDI derivatives. A quasi-reversible oxidation wave is noticed at +0.77 V for Ru-NMe<sub>2</sub> assigned to the tertiary amino group, while Ru-NDI presents two reversible reduction waves at -0.53 V and -0.88 V corresponding to single and double reduction of the NDI moiety (Table 1). It is noteworthy that no additional electrochemical process was observed for the reference compound **Ru-H**, indicating that the triazole group is electrochemically inert. Ground state absorption spectra (ESI<sup>+</sup>) of complexes Ru-H and Ru-NMe2 exhibit a MLCT band peaking at 460 nm and  $\pi - \pi^*$  (bipy) transitions at ~290 nm, while **Ru–NDI** also presents NDI  $\pi$ – $\pi$ \* transitions at ~340, 360 and 380 nm. For all the studied complexes, the emission (Table 2) is red-shifted by about 20 nm as compared to that of the  $[Ru(bpy)_3]^{2+}$  (ESI<sup>†</sup>), suggesting that functionalisation by a triazole group induces a slight ( $\sim 0.1$  V) decrease of the HOMO-LUMO energy gap.

The emission quantum yields  $(\Phi_{em})$  of complexes **Ru–H** and **Ru–NDI** are increased compared to  $[\text{Ru}(\text{bpy})_3]^{2^+}$ , whereas for **Ru–NMe**<sub>2</sub>  $\Phi_{em}$  is considerably reduced. The observed emission lifetimes were generally in good agreement with the steady state results except for **Ru–NMe**<sub>2</sub> where a fast component (<20 ns, out of detection range) is dominant. The emission data suggest that for **Ru–NMe**<sub>2</sub> the lowest excited state is not the usual emissive <sup>3</sup>MLCT. Transient absorption data (ESI†) confirm this result insomuch as the typical <sup>3</sup>MLCT bleaching at 450 nm was not observed for **Ru–NMe**<sub>2</sub> in contrast to both the **Ru–H** and **Ru–NDI** compounds. Interestingly, the emission for the **Ru–NMe**<sub>2</sub> complex was partially recovered in the presence of acid (*vide infra*).

In order to gain more insight into the electronic structures both in the ground and excited states, we have performed Density Functional Theory (DFT) calculations using B3LYP functional as we have previously shown to correctly describe experimental results on ruthenium based complexes.<sup>‡</sup> Our theoretical data confirm that in **Ru–H**, as in [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, the HOMO is a d<sub>π</sub> ruthenium orbital and the LUMO is a bipyridine-like π\* orbital. However, owing to the slight electron withdrawing

Table 2 Emission data for ruthenium complexes in MeCN

Compound	$\lambda_{max}/nm$	$\tau/ns$	$\Phi_{ m em}$
$[Ru(bpy)3]^{2+}$	608	900	0.059 <sup>a</sup>
Ru-H	632	750	0.097
Ru-NMe <sub>2</sub>	627	< 20	0.009
$Ru-NMe_{2}(H)^{b}$	633	860	0.027
Ru-NDI	635	750	0.140
Ru–NDI	635	750	0.140

<sup>*a*</sup> From ref. 19. <sup>*b*</sup> In the presence of formic acid.



Fig. 1 Spin density distribution for the lowest triplet state of Ru–H (left) and Ru–NMe<sub>2</sub> (right).

effect of the triazole ring, this LUMO is developed on the corresponding bipyridine and is partially delocalised on the triazole. The calculated lowest triplet state corroborates this finding. It can be described as a <sup>3</sup>MLCT state generated by transfer of electron density from the ruthenium to this LUMO, as evidenced by the spin density distribution map (Fig. 1a). For Ru-NMe<sub>2</sub>, DFT calculations show that the dimethylamino substituent exerts an important electron-donor effect on the phenyl ring and destabilises all the orbitals developed in this region. It results that the HOMO of the complex is no longer a  $d_{\pi}$  ruthenium orbital but a molecular orbital localised on the Me<sub>2</sub>N–C<sub>6</sub>H<sub>4</sub> fragment (ESI<sup> $\dagger$ </sup>). As a consequence, the computed lowest triplet state is now generated by electron transfer from the HOMO to the LUMO (similar to the LUMO of Ru-H) located on the extended ligand (see ESI<sup>†</sup>, Fig. S6). This <sup>3</sup>ILCT state is reminiscent of a triplet state of the corresponding ligand (ESI<sup>†</sup>) and, as evidenced on the spin density map, no longer involves the ruthenium centre (Fig. 1b). For this reason, this state is non-emissive and the emission of Ru-NMe2 is quenched, as already observed in previous examples.<sup>15,20</sup> In this context, protonation of the amino group readily explains the recovery of emission. These results indicate that the triazole link on the bipyridine ligand does not alter the intrinsic photophysical properties of the ruthenium(II) chromophore.

A crucial point to investigate concerns the feasibility of efficient electron transfer through the triazole in our synthetic systems holding either an electron donor or acceptor unit. Laser flash photolysis experiments with the reference compound **Ru–H** in the presence of methylviologen ( $MV^{2+}$ ) an electron acceptor) as well as ascorbate (an electron donor) showed behaviour similar to  $[Ru(bpy)_3]^{2+}$ . In the presence of 10 mM  $MV^{2+}$ , features associated with  $MV^{\bullet+}$  (peaks at 390 nm and 605 nm) are observed together with bleaching at (400-500) nm due to Ru(II) disappearance (Fig. 2a). The Ru(III) formed recombines with MV<sup>•+</sup> as indicated by the similar kinetics of the respective absorption decays. In the presence of 100 mM ascorbate (Fig. 2b), absorption bands at 510 nm, typical for Ru(I) formation, and at 360 nm, attributed to the oxidised form of ascorbate, are observed. Here again, kinetic measurements indicate the recombination of the geminate charges. It can be concluded that the triazole does not perturb the electron transfer properties of the excited state of the ruthenium chromophore.

In the case of **Ru–NMe<sub>2</sub>**, upon excitation in the presence of  $MV^{2+}$ , only weak and very short-lived bleaching of the 450 nm MLCT band of the Ru(II) was observed, although the  $MV^{\bullet+}$  radical was formed (Fig. 3a). These observations can be rationalised by a very fast decay of the <sup>3</sup>MLCT state to the lowest



**Fig. 2** Absorption changes upon laser flash excitation of **Ru–H** (a) in MeCN with 10 mM  $MV^{2+}$ . Inset: kinetics at 460 and 605 nm (b) in MeCN/H<sub>2</sub>O (50:50) with 100 mM ascorbate. Inset: kinetics at 360 and 510 nm. Spectra taken 1 µs after the laser flash.

<sup>3</sup>ILCT as described above, wherefrom charge transfer leads to the formation of the MV<sup>•+</sup> radical and the ammoniumyl radical cation.§ This fast intramolecular conversion (<sup>3</sup>MLCT  $\rightarrow$  <sup>3</sup>ILCT) is suppressed upon protonation of the amino group yielding, in the absence of  $MV^{2+}$ , transient absorption features similar to those of Ru-H (ESI<sup>†</sup>). Furthermore, in the presence of formic acid and MV<sup>2+</sup>, oxidation of the ligand occurs via formation of Ru(III) as shown by bleaching at around 450 nm observed at 100 ns and the decay kinetics of  $MV^{\bullet+}$  (605 nm) and of Ru(III) (460 nm) (ESI<sup>+</sup>). DFT calculations on the singly oxidised species clearly indicate a metal centred oxidised form in the case of  $[\mathbf{Ru}-\mathbf{H}]^+$  while in the case of  $[\mathbf{Ru}-\mathbf{NMe}_2]^+$ , the oxidation locus is situated on the aminophenyl group. Excitation of the Ru-NDI complex in the presence of ascorbate reveals appearance of NDI<sup>•-</sup> radical features<sup>21</sup> within *ca.* 30 ns (Fig. 3b). The fact that no spectral features of a Ru(I) intermediate were observed suggests a very fast (<20 ns) intramolecular electron transfer from Ru(I) to NDI. This reduced state lasts for few milliseconds.

In conclusion, we have used the mild synthetic procedure provided by *click chemistry* to covalently attach different functional groups on the 4 position of the 2,2'-bipyridine ligand. The corresponding heteroleptic ruthenium(II) complexes were isolated. We have found that the triazole on the 4 position on the bipyridine periphery alters neither the photophysical nor the electrochemical properties of the ruthenium chromophore in comparison with the parent Ru(II)–tris bipyridine complex. This is in sharp contrast to examples with the triazole in the ruthenium coordination sphere,



Fig. 3 Absorption changes upon laser flash excitation of (a)  $Ru-NMe_2$  with 10 mM  $MV^{2+}$  in MeCN, (b) Ru-NDI with 100 mM ascorbate in MeCN/H<sub>2</sub>O (50:50). Spectra taken 100 ns after the laser flash.

where photoluminescence was fully quenched at room temperature. Light driven electron transfer studies in the presence of a sacrificial electron acceptor or donor are in favour of efficient intramolecular electron transfer through the triazole link, either from the electron donating or to the electron accepting groups respectively. Further work to click putative catalytic units to the ruthenium chromophore is underway in our laboratories.

AB thanks the Life science division of the CEA for a postdoctoral fellowship. This work was partially supported by the ANR (projects ANR-05-JCJC-0199 and ANR 2010 BLAN 0926), the EU/Energy SOLAR-H2 project (FP7 contract 212508) and the Conseil Général de l'Essonne. Calculations were performed using HPC resources from GENCI-CINES/ IDRIS (Grant 2010-x2010085020).

## Notes and references

<sup>‡</sup> Geometry optimisations of the singlet ground state of the complexes were performed in the gas phase and followed by calculations in a PCM/H<sub>2</sub>O modelled medium to avoid computation artefacts.<sup>22</sup>

§ EPR measurements on the photolysed solution in the presence of a Co(III) salt as an electron acceptor were monitored by X-band EPR spectroscopy. The spectrum confirms the formation of photoreduced cobalt(II) species with g values around 4 while the generated ammoniumyl radical was observed at  $g \approx 2$ .

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