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Red-light-driven photocatalytic hydrogen evolution using a ruthenium quaterpyridine complex

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A high-temperature, microwave synthesis of [Ru(qpy)₃]²⁺ (qpy = 4,4':2',2'':4'',4'''-quaterpyridine) affords the photosensitiser in quantitative yield. The complex produces H₂ photocatalytically in a range extending from the UV region of the spectrum to the red with greater efficiency when compared to [Ru(bpy)₃]²⁺.

In the face of undeniable evidence of global warming, many researchers have focussed their research efforts on the development of sustainable energy sources.¹ In the context of energy transduction, converting solar energy into chemicals, e.g. hydrogen, is a challenge that has attracted considerable interest in the past decade.² Previous attempts focussed on building photocatalytic systems that mimic the most relevant steps found in natural photosynthesis.³ The molecular approach consists of covalently coupling a photosensitiser (PS), used to absorb incident light, to a catalyst, which insures efficient electron transfer to the substrate. The most studied PS remains the archetypical [Ru(bpy)₃]²⁺ model complex, (bpy = 2,2'-bipyridine). To improve the efficiency of PS/catalyst systems, researchers have focussed more recently on different metal couples, such as Re/Co⁴ or Ir/Co,⁵ albeit at a higher cost, as both PSs are more expensive than ruthenium. As half of the solar spectrum is composed of infrared radiation, osmium⁶ is also used in photocatalytic systems due to its red-shifted absorption in comparison to its ruthenium equivalent. However, osmium faces the same problem of high cost, and thus many Ru/Pt⁷ or Ru/Co⁸ systems are reported in the literature with the remaining challenge of designing ruthenium(II) complexes with red-shifted absorption and emission bands.⁹

One way to improve the properties of the Ru-based PSs is to modify its coordinating ligands, with a focus on appropriate design for extended supramolecular assemblies.¹⁰ Functionalisation of the bpy ligand in the [Ru(bpy)₃]²⁺ complex allows the fine-tuning of the photophysical properties of the

complex.¹¹ The aim of our work was to use the 4,4':2',2'':4'',4'''-quaterpyridine (qpy) as a ligand for Ru²⁺, thus extending π -conjugation of the bpy molecule. To the best of our knowledge, only one photocatalytic study uses the quaterpyridine ligand but with iridium.¹² Our results, in terms of hydrogen evolution with ruthenium(II), are presented herein.

The synthesis of [Ru(qpy)₃]²⁺ was conducted under microwave irradiation which generated a 97 % yield in just 15 minutes at 240 °C (See Supporting Information section *S.I.-2*), thus improving the yield and purification described in the literature.¹³ Furthermore, single crystals [Ru(qpy)₃]²⁺ were obtained and X-ray analysis of the PS was performed.

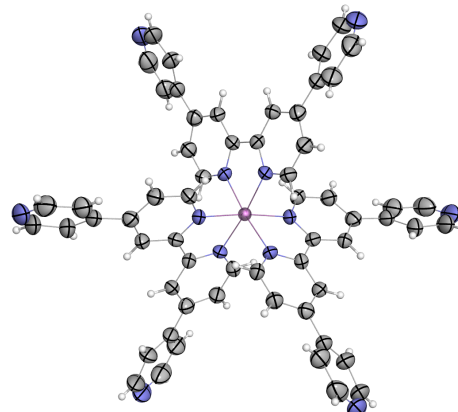


Figure 1: ORTEP representation of [Ru(qpy)₃]²⁺ at 50% probability. Hydrogen atoms, chloride counter ions, and co-crystallised solvent molecules have been omitted for clarity.

The [Ru(qpy)₃]²⁺ complex crystallised as both hexafluorophosphate (see *S.I.-3b*) and chloride salts (Figure 1) as determined by single crystal X-ray diffraction. When compared to [Ru(bpy)₃]²⁺, the global geometry of the molecule is not affected by the replacement of the *para* hydrogen of the

bpy ligand by a 4-pyridyl substituent. The average twist angle of the 4-pyridyl substituents to the bipyridine core is 30 degrees in the solid-state, which should allow inter-annular delocalisation in the ground state as exemplified by ground-state (Table 1) and excited-state data (Table 2). In the thermally-equilibrated ³MLCT state, one would expect that the extended π -system of fully planar 4-pyridyl groups gives rise to the superior photophysical properties of $[\text{Ru}(\text{qpy})_3]^{2+}$ as compared to $[\text{Ru}(\text{bpy})_3]^{2+}$ (Table 2).

The electrochemical data in acetonitrile are summarised in Table 1. The cyclic voltammogram presents a reversible oxidation process at +1.48 V corresponding to the Ru(II)/(III) oxidation which is more positive than that found for $[\text{Ru}(\text{bpy})_3]^{2+}$ (+1.29 V) because of the electron withdrawing nature of the 4-pyridyl group (Hammett parameter = 0.44)¹⁴. On the reduction side, the cyclic voltammogram displays six reversible reductions divided into two groups of three reductions corresponding to two successive reductions of each ligand. The first reduction potentials are at -0.99 V, -1.14 V and -1.34 V, thus indicating the much more facile reduction of the qpy ligand as compared to bpy.

Table 1: Redox data of the complexes $[\text{Ru}(\text{qpy})_3]^{2+}$ compared to $[\text{Ru}(\text{bpy})_3]^{2+}$ in acetonitrile.^a

	$E_{1/2}^{\text{Ox}}$	$E_{1/2}^{\text{Red 1}}$	$E_{1/2}^{\text{Red 2}}$	$E_{1/2}^{\text{Red 3}}$	Band Gap (V)
$[\text{Ru}(\text{qpy})_3]^{2+}$	+1.48 (77)	-0.99 (63)	-1.14 (66)	-1.34 (74)	2.47
$[\text{Ru}(\text{bpy})_3]^{2+}$	+1.29 ^b	-1.33 ^b	-	-	2.62

a) Potentials are in volts vs SCE for acetonitrile solutions, 0.1 M in TBAPF₆, at a sweep rate of 100 mV/s. The difference between cathodic and anodic peak potentials (millivolts) is given in parentheses. b) Reference 15.

To support this interpretation, the ground and vertical excited state electronic structures were investigated by the means of Density Functional Theory (DFT) and Time Dependent DFT (TD-DFT) using the hybrid functional PBE0 in conjunction with a double zeta valence basis set. Solvent (MeCN) was included by a continuum model. The computed HOMO and LUMO, centred on the metal and the ligand, respectively, are depicted in Figure 2 while further details on methods used and geometrical and electronic structure can be found in Supporting Information (Section S.I.-4).

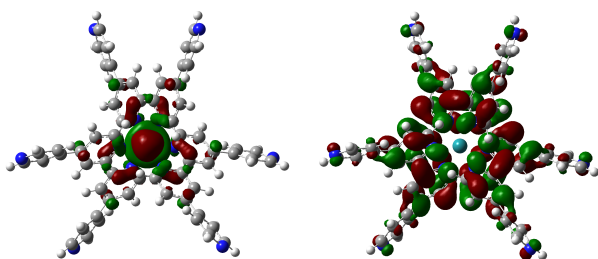


Figure 2: Representation of the molecular orbitals HOMO (left) and LUMO (right) of $[\text{Ru}(\text{qpy})_3]^{2+}$.

The absorption spectrum of $[\text{Ru}(\text{qpy})_3]^{2+}$ was measured in acetonitrile and presents four major bands (see Figure S8). The nature of the electronic transitions giving rise to these bands was disclosed by the means of TD-DFT. In particular, for $[\text{Ru}(\text{qpy})_3]^{2+}$, both the band at $\lambda = 473$ nm (and the shoulder around 448 nm) and the band at 356 nm are of MLCT nature. The latter band is actually absent in $[\text{Ru}(\text{bpy})_3]^{2+}$. On the other hand, the band at 307 nm is of a ligand-centred type (LC) while the band at 250 nm is again of MLCT character. Major orbital contributions to the most significant transitions are presented and discussed in Supporting Information (Table S6).

The emission spectrum was recorded in oxygen-free acetonitrile solution and the quantum yield was determined relative to $[\text{Ru}(\text{bpy})_3(\text{PF}_6)_2]$ in the same solvent.¹⁶ For both complexes, data are summarised in Table 2. The maximum emission wavelength of $[\text{Ru}(\text{qpy})_3(\text{PF}_6)_2]$ is red-shifted to 628 nm in comparison to the bipyridine complex at 608 nm. The quantum yield increases significantly from 9.5% to 23% as well as the excited state lifetime, which more than doubles to 1.78 μs .

Table 2: Emission data of $[\text{Ru}(\text{qpy})_3(\text{PF}_6)_2]$ and $[\text{Ru}(\text{bpy})_3(\text{PF}_6)_2]$ at room temperature in a degassed solution of acetonitrile.

	$\lambda_{\text{max abs. nm}}$ ($\epsilon \times 10^3$ (L.mol ⁻¹ .cm ⁻¹))	$\lambda_{\text{max em. (nm)}}$	Φ (%)	τ (ns)
$[\text{Ru}(\text{qpy})_3]^{2+}$	473 (29), 356 (27), 307 (93), 250 (129)	628	23	1780
$[\text{Ru}(\text{bpy})_3]^{2+a}$	450 (21), 287 (120), 244 (360)	608	9.5 ^b	870

a) Reference 15. b) Reference 16

With a high quantum yield and a long excited-state lifetime $[\text{Ru}(\text{qpy})_3]^{2+}$ is an excellent candidate to act as a photosensitizer in an artificial photosynthetic system. With an extended absorption over the visible region, $[\text{Ru}(\text{qpy})_3]^{2+}$ was tested as a PS for photocatalytic hydrogen evolution (experimental details are given in Supporting Information, section S.I.-5). The usual range of irradiation reported in the literature covers the whole visible region with wavelengths cut-off under 420 nm and over 780 nm. The observed behaviour is thus an average of the different pathways of decomposition depending on the wavelength of irradiation. To the best of our knowledge, the only study of the irradiation wavelength remains the work of Sakai and co-workers on a Ru/Pt system, by applying selected filters on their visible light source.^{7a} However, the longest wavelength light used was centred at 517 nm, and extended only as far as 600 nm. For that reason, our system was studied using narrow wavelength bands of light centred from blue (452 nm), green (525 nm), red (630 nm) and near-IR (733 nm). In order to compare the efficiency of the complex to a reported system¹⁷ $[\text{Ru}(\text{bpy})_3]^{2+}$ was run in parallel as a direct reference. For the same reason, we chose the classic $[\text{Co}(\text{dmgH})_2]$ complex as a catalyst, formed *in situ* as the tetrafluoroborate salt. To study only the half equation of hydrogen evolution reaction, triethanolamine was used as a sacrificial electron donor and aqueous tetrafluoroborate was the source of protons.

As depicted in figures 3 and 4, for green- and red-light respectively, the results demonstrate that the new PS is always more efficient than $[\text{Ru}(\text{bpy})_3]^{2+}$ and has an extended production of H_2 over the full visible spectrum. Longer wavelength irradiation in the near-IR (733 nm) demonstrates the limits of our system, with no measurable H_2 production beyond the tail of the MLCT absorption band for either complex.

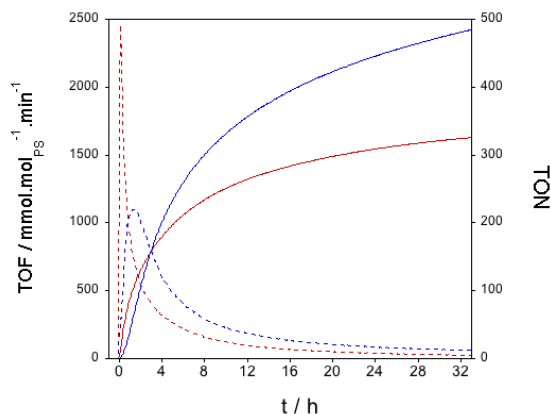


Figure 3 : Hydrogen evolution of $[\text{Ru}(\text{bpy})_3]^{2+}$ (red) and $[\text{Ru}(\text{qpy})_3]^{2+}$ (blue). Turn-over frequencies (TOF, dashed line) and Turn-over number (TON, plain line) are represented, measured under the same conditions using green-light irradiation (525 nm).

In the visible, under blue irradiation (452 nm) (see Figure S10), the production of H_2 starts after turning on the lamp, with no induction period observed. Using green light (525 nm), the system presents an inverted trend (Figure 3). After a ten-minute induction time the most efficient complex becomes the $[\text{Ru}(\text{bpy})_3]^{2+}$, with a turn-over frequency (TOF) of $2500 \text{ mmol.mol}_{\text{PS}}^{-1}.\text{min}^{-1}$, whereas $[\text{Ru}(\text{qpy})_3]^{2+}$ reaches only $1100 \text{ mmol.mol}_{\text{PS}}^{-1}.\text{min}^{-1}$. The $[\text{Ru}(\text{bpy})_3]^{2+}$ complex quickly degrades, presenting after 35 h a turnover number (TON) of 330 compared to the 495 for the studied complex (Figure 3).

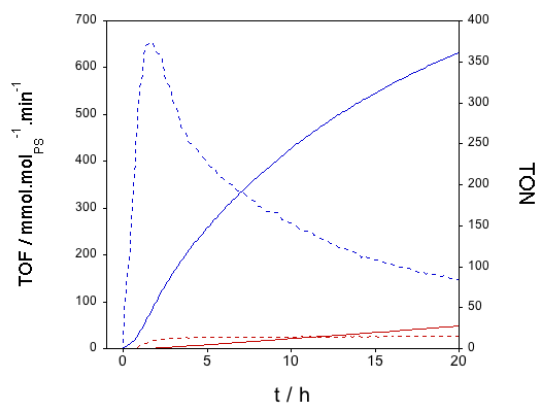


Figure 4 : Hydrogen evolution of $[\text{Ru}(\text{bpy})_3]^{2+}$ (red) and $[\text{Ru}(\text{qpy})_3]^{2+}$ (blue). Turn-over frequencies (TOF, dashed line) and Turn-over number (full line) are represented, measured under the same conditions using red light irradiation (630 nm).

A notable difference in efficiency is observed using red light (630 nm). The results shown in Figure 4 highlight the advantages of $[\text{Ru}(\text{qpy})_3]^{2+}$ versus $[\text{Ru}(\text{bpy})_3]^{2+}$. Indeed, a maximum turnover frequency TOF of almost $650 \text{ mmol.mol}_{\text{PS}}^{-1}.\text{min}^{-1}$ is observed for $[\text{Ru}(\text{qpy})_3]^{2+}$ whereas the TOF of the reference barely reaches $30 \text{ mmol.mol}_{\text{PS}}^{-1}.\text{min}^{-1}$. In the same way, the TON for $[\text{Ru}(\text{qpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$ are 375 and 30, respectively. The greater results obtained by the $[\text{Ru}(\text{qpy})_3]^{2+}$ might also be explained by possible spatial interactions with the catalyst through the nitrogen heteroatoms in the pendant pyridines when compared to the phenyl analogs.¹²

We report here an improved synthesis and first structural characterisation of $[\text{Ru}(\text{qpy})_3]^{2+}$. The complex presents enhanced photophysical properties as compared to its parent $[\text{Ru}(\text{bpy})_3]^{2+}$ complex, as well as an extended absorption in the visible range. The $[\text{Ru}(\text{qpy})_3]^{2+}$ complex was evaluated as a photosensitiser in a hydrogen evolution reactions, and was found to be much more efficient than the reference $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. The behaviour at different irradiation wavelengths was studied and the complex proved to be a better PS than the reference complex under red light irradiation by an order of magnitude. Therefore, $[\text{Ru}(\text{qpy})_3]^{2+}$ is an excellent PS for full visible light use in photocatalytic hydrogen production and may be promising as a building block in multimetallic architectures.¹⁸

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Notes and references

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‡ Crystal data for $[\text{Ru}(\text{qpy})_3]\text{Cl}_2$, ($\text{C}_{60}\text{H}_{42}\text{N}_{12}\text{Ru}_1$) $2(\text{Cl})$ $5(\text{H}_2\text{O})$, cubic, space group $P4_132$, $a = b = c = 21.1118(3) \text{ \AA}$, $\alpha = \beta = \gamma = 90.00^\circ$, $V = 9409.7(2) \text{ \AA}^3$, CCDC 104 6675

Crystal data for $[\text{Ru}(\text{qpy})_3][\text{PF}_6]_2$, ($\text{C}_{60}\text{H}_{42}\text{N}_{12}\text{Ru}_1$) $2(\text{PF}_6)$ $2(\text{CH}_3\text{Cl})$ ($\text{C}_4\text{H}_8\text{O}$), trigonal, space group $R-3$, $a = b = 17.6408(12) \text{ \AA}$, $c = 44.355(3) \text{ \AA}$, $\alpha = \beta = 90.00^\circ$, $\gamma = 120.00^\circ$, $V = 11954.0(19) \text{ \AA}^3$, CCDC 104 6674.

CCDC number 104 6675 for $[\text{Ru}(\text{ppy})_3]\text{Cl}_2$, and 104 6675 for $[\text{Ru}(\text{ppy})_3](\text{PF}_6)_2$. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electronic Supplementary Information (ESI) available: Instrumentation details, synthetic procedures, crystallographic data, computational details and additional information concerning hydrogen evolution experiments. See DOI: 10.1039/c000000x/

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